Aqueous-only exfoliation of pristine graphite to graphene : towards sustainable, multifunctional polymer nanocomposites

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**NANYANG
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SINGAPORE

**AQUEOUS-ONLY EXFOLIATION OF PRISTINE
GRAPHITE TO GRAPHENE: TOWARDS SUSTAINABLE,
MULTIFUNCTIONAL POLYMER NANOCOMPOSITES**

SEYED ISMAIL SEYED SHAHABADI

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

07 May 2019

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Date

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This thesis contains material from a paper published in the following peer-reviewed journal where I was the first author.

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- A/Prof Xuehong Lu provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Junhua Kong.
- I co-designed the study with A/Prof Xuehong Lu and performed all the laboratory work at the School of Materials Science and Engineering, Nanyang Technological University. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Shahrouz Amini assisted with the Raman spectroscopy. His assistance is acknowledged in this thesis and in the published paper.

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Abstract

The conventional, linear, take-make-waste economy which was a by-product of the industrial revolution is not a viable option anymore. Environmental concerns are driving the development of a new circular model in which reduce, reuse, and recycle are key. Since this circular model would keep materials in commerce for longer, safer product designs that would reduce the amount of hazardous materials are vital. In this work, the aim is to implement this design philosophy in producing polymer/graphene nanocomposites as a rapidly emerging class of materials. The design philosophy is based on two strategies: first, to substitute conventional, synthetic components by their naturally-occurring counterparts and, second, by eliminating chemicals by assigning their roles to other multifunctional components.

Graphene and, by extension, polymer/graphene nanocomposites have seen huge interest in academia and industry. Among different methods to produce graphene, liquid-phase exfoliation (LPE) is one of the most commonly used. LPE is a low cost, industrially-friendly, high-yield process in which graphite flakes are exfoliated into their 2D constituents, i.e., graphene, and stabilized in a liquid medium. Water is the most desirable medium for LPE but graphene needs stabilization with surfactants or stabilizers because of the huge mismatch between the surface energies of water and graphene. There have been a myriad of synthetic surfactants and stabilizers studied for this purpose, but natural surfactants have seen less attention. Here, lignin, an abundant, undervalued, byproduct of paper industry, will be used as a naturally-occurring stabilizer for graphene. Lignin-modified graphene (LMG) is non-covalently modified meaning its sp^2 structure, which is the reason for its amazing properties, is unperturbed.

Different polymer/graphene systems based on this sustainable design philosophy are produced. In the first work, LMG is added to waterborne polyurethane (WPU) to produce conductive films for antistatic coating applications. Since durability against environmental damage is an important factor for these coatings, functional properties such as self-healing and UV-resistance are required. However, instead of using self-healing agents and

synthetic UV blockers, LMG is tasked with enabling self-healability and improving UV stability. Thanks to its multifunctional properties, LMG can act as a photothermal converter creating heat after being illuminated by near-infrared (IR). This increases the rate of polymer diffusion at the site of damage which results in fast self-healing of the damage. Due to the anti-UV properties of LMG and lignin, these nanocomposite coatings show remarkable UV resistance as well. The combination of self-healing and UV-stability renders these films highly durable.

In the second work, graphene was used to produce multi-functional sensors. Commercially-available polyurethane (PU) sponges can become conductive by dip-coating in aqueous LMG suspensions. These sponges show electrical sensitivity to compression, and thanks to their high mechanical stability, they are able to accurately sense pressure with high accuracy over 5000 compression-release cycles. Since LMG acts as a negative temperature coefficient thermistor, these sensors can measure temperature with high sensitivity as well without the need for any temperature-sensitive component.

Finally, this design philosophy is taken to the next level by completely removing lignin in the third work. Here, WPU can be used as a stabilizer to produce WPU-modified graphene (PMG). In contrast to the WPU/LMG system, WPU/PMG nanocomposites have no external stabilizer. These highly conductive nanocomposites are electromechanically sensitive and show huge electromechanical responses to deformation. In addition to being the polymer matrix and stabilizer, WPU endowed the sensors with shape conformality too, which significantly increased the real-life sensitivity of the sensors in monitoring biomechanical deformations and reproducing blood-pressure waveforms. This innate shape-conformality obviated the need for an additional skin-conformal layer.

By adopting these strategies, organic liquid media and synthetic surfactants/stabilizers can be substituted by water and naturally-occurring lignin, or in case of the last study, lignin can be eliminated. Other functional additives such as self-healing agents, synthetic UV-stabilizers, or active materials are not required thanks to the multifunctional and multi-stimuli responsive nature of graphene.

Lay Summary

The conventional economical model which was a by-product of the industrial revolution is a linear route from extraction to landfill. This linear model will soon reach its dead-end since it fails to consider the impacts on ecosystem degradation, pollution, and resource depletion. As a result, a circular economy based on value retention by reducing extraction, reusing, and recycling is gaining popularity. Since products remain in service for longer in circular economy, a cleaner product design by reducing or removing hazardous chemicals is necessary. Therefore, the motivation for this study is to produce polymeric materials without synthetic chemicals by substitution with components found in nature or, if possible, elimination of those chemicals.

Graphene is a two-dimensional honeycomb sheet of carbon with many interesting properties, and it can be added to plastics to achieve desirable functionalities. There are different ways to produce graphene but one of the easiest and cheapest methods is to break the three-dimensional structure of graphite into two-dimensional graphene in a liquid medium. Water is an attractive choice, but graphene is not stable in water; therefore, certain materials such as surfactants or stabilizers should be added to produce stable graphene suspension in water. There have been many synthetic surfactants and stabilizers used for this purpose, but natural surfactants are more desirable. Here, lignin, an abundant, undervalued, byproduct of paper industry, was used as a natural stabilizer for graphene in water. Lignin does not damage the structure of graphene hence many of graphene's unique properties are unchanged.

Polymer/graphene nanocomposites were produced for different applications such as coating and sensing. Firstly, graphene was mixed with waterborne polyurethane to make conductive films. These films can be used as antistatic coatings to counter electrostatic discharge, which is hazardous to many applications such as electronics. Since durability against environmental damage is an important factor for coatings, they should be able to repair and heal environmental damage and resist UV irradiation. One way to enable healing is to add healing components that can be released in a controlled manner. Synthetic UV

blockers can also be used to improve UV stability. However, instead of using these compounds, graphene can be used to enable self-healability by Increasing temperature through converting near infrared (IR) light into heat and increase the rate of polymer diffusion at the damage which results in fast self-healing of the damage. Graphene can also absorb the damaging UV light and improve UV resistance remarkably.

Graphene can be used to produce sensors as well. Sensor is a device that can detect a change, such as pressure, strain, and temperature, in its environment. By submerging commercially-available polyurethane sponges in aqueous graphene suspensions and evaporating water they become conductive and their conductivity can change when they are pressed. The conductivity of graphene can also change with temperature which means that these sensors can measure temperature as well. Normally, this sensor would require separate pressure-sensitive and temperature-sensitive components, but graphene can serve both functions at the same time.

Finally, polymer/graphene nanocomposites can be produced without lignin as well, reducing the constituents to only two. Here, the polymer itself is used to stabilize graphene in water. These polymer/graphene nanocomposites are highly conductive and show changes in conductivity under deformation, so they can be used as strain sensors. In addition, the polymer that is used is very soft which allows it to conform to the shape of any substrate. Shape-conformality can improve sensor/substrate interface, enhance signal collection, and give rise to the sensitivity of the sensor, making these sensors very accurate in real-life applications such as monitoring bodily movements and blood pressure.

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Abbreviations

BST	Black Standard Temperature
CNT	Carbon Nanotubes
CVD	Chemical Vapor Deposition
DMA	Dynamic Mechanical Analysis
FESEM	Field Emission Scanning Electron Microscopy
GF	Gauge Factor
GNW	Graphene Nanowalls
GO	Graphene Oxide
IR	Infrared
LMG	Lignin-Modified Graphene
LOD	Limit Of Detection
LPE	Liquid-Phase Exfoliation
NTC	Negative-Temperature Coefficient
NTU	Nanyang Technological University
PDMS	Polydimethylsiloxane
PEDOT:PSS	Poly(3,4-Ethylenedioxythiophene) Polystyrene Sulfonate
PET	Polyethylene Terephthalate
PI	Polyimide
PMG	WPU-Modified Graphene
PTC	Positive-Temperature Coefficient
PTFE	Polytetrafluoroethylene
PU	Polyurethane
rGO	Reduced Graphene Oxide
ROS	Reactive Oxygen Species
RTD	Resistive Temperature Detector
TEM	Transmission Electron Microscopy
TMD	Transition Metal Dichalcogenides
TMO	Transition Metal Oxide
TPE	Thermoplastic Elastomer
UV	Ultraviolet
WPU	Waterborne Polyurethane

Chapter 1

Introduction

In this chapter, the rationale behind the need for designing sustainable products are presented. It is discussed that the linear take, make, waste business model is no longer a viable option, and a new circular economical model should be adopted instead. Green, sustainable materials design is an integral part of this new circular model which should be further developed. Polymer-based materials, which are present in almost all consumer products today, should be designed and produced based on new approaches that utilize this design. Polymer/graphene nanocomposites, in particular, have garnered huge interest in academia. Liquid-phase exfoliation (LPE) is perhaps the most industrially-viable option to produce graphene. The main objective of this study is to devise a sustainable, environmentally-friendly LPE of pristine graphite using water as exfoliation medium to produce non-covalently modified graphene with the aid of a proper stabilizer. This objective is furthered by substituting synthetic stabilizers with a naturally-occurring one, i.e., lignin, and reducing the number of components by assigning multifunctional roles to graphene, stabilizer, and polymer matrix. By exploiting multifunctionality, it is even possible to remove lignin and produce polymer/graphene nanocomposites with no external stabilizer, using only water. By adopting this strategy, sustainably-prepared polymer/graphene nanocomposites with similar or better performance compared to those of conventionally-prepared nanocomposites are produced.

1.1. Problem Statement and Design/Performance Target

1.1.1 From Linear Economy to Circular Economy

The last 150 years of industrial revolution has been about maximizing throughput across a linear approach following the model from extraction to landfill. Considering the estimates on global population put forth by the UN, i.e., 9 billion people by 2050¹, it is evident that this take-make-waste business model will soon reach its dead-end. Our current linear economical models usually fail to take into account the real cost of production in terms of ecosystem degradation, pollution, resource depletion, and toxification. Millennium ecosystem assessment estimates that more than 60% of global ecosystems have been severely degraded due to current and past economic activities resulting in serious resource depletion². Rate of environmental degradation can result in political instability and economical volatility. More significantly, it may even jeopardize life on Earth resulting in a mass extinction of species as humans are gobbling up our own life support system at an unprecedented rate³⁻⁴.

In the linear economical model, resources are extracted to produce products, and products are used until they are discarded and disposed. In this model, value is maximized by maximizing the volume of products produced and sold. In contrast, circular economy is based on the 3R approach, i.e., Reduce, Reuse, and Recycle. Here, as shown in Figure 1.1, value is created by value retention through reducing extraction by innovative approaches or by reusing parts. In the final step, after discarding a product, materials or parts are recycled. Current linear business models rarely consider recycling as part of the life cycle of a product. Therefore, not enough attention is paid to the chemistry of the materials that are put in products. As a result, current recycling approaches are seriously flawed as will be elaborated by two examples.

Nearly 300 million defunct tires get disposed in the United States annually. Tires contain a wide range of toxic metals and inorganic compounds with well-known health hazards. These tires are burnt as fuel or based on a seemingly brilliant idea are shredded to be spread

out over children's playgrounds. However, tires have never been designed with recycling applications in mind. Burning tires produces similar levels of emission as fossil fuels at best. In playgrounds, risk hazards involved with touching the tires by children or gas emission under the sunlight are blatantly overlooked. As another example, recycled foam padding, which is the remnants of used furniture and mattresses, are used below the carpet at homes. These paddings contain flame retardants to reduce the possibility of ignition. Despite the benefits these compounds offer, mounting evidence has associated these chemicals to adverse health effects such as endocrine and thyroid disruption, organ failure, cancer, reproductive toxicity, as well as adverse effects on immune system, fetal and child development, and neurologic function⁵. Sadly, these effects are more noticeable for children since it has been shown that they have higher contents of flame retardants in their bodies than adults⁶⁻⁸.

Figure 1.1 A simplified circular economical model

Unlike the linear business model, the circular business model is restorative by intention and design with a focus on keeping materials flowing in commerce longer. Here, at the design stage, products are envisioned for the ease of reuse, disassembly, repair, refurbishment, and then kept in closed loops, resulting in tremendous savings on energy,

air, and water missions. However, circular business model requires an essential pre-requisite: sustainable materials design.

1.1.2 Sustainable Materials Design

It was argued that a model for a better business, a more vibrant manufacturing, and a more prosperous world can be adopted by using circular economy. Since in this model, materials are kept in commerce longer, products should be designed to be safe for humans and the environment, since the chemistry of products cannot be changed after production. Nonetheless, the amount of hazardous materials allowed in consumer products nowadays is shocking.

One study in 2005 found 287 man-made chemicals in fetal umbilical cord blood from pesticides, flame retardants, and plasticizers, meaning humans are literally toxified before birth. Several studies have shown that the human breast milk is so contaminated that it cannot be sold on store shelves today. Therefore, we need to address product and material chemistry at the design stage in order to eliminate chemicals of concern for the betterment of humans' health and the environment. The challenge facing sustainable materials design is to achieve the desired functions and performance found in conventionally-produced products at similar or lower price points. Polymer-based products are one of the most vastly used consumer products today. In particular, polymer-graphene nanocomposites have attracted huge attention both in academia and industry due to the wide range of applications they offer. As a result, it is reasonable to validate the feasibility of this design philosophy in producing these materials.

Among different methods to produce graphene, liquid phase exfoliation (LPE) of graphene is the most promising thanks to its high yield, ease of use, low cost, and industrial upscalability. There is no arguing that water is the most desirable medium for LPE; nonetheless, due to a considerable mismatch between the surface energies of water and graphene, successful exfoliation of graphene in water is challenging. Oxidation of graphene has been a well-known approach to make exfoliation possible. Nevertheless, due to the loss

of sp^2 structure during oxygenation, the properties that make graphene unique are lost. Even reducing graphene oxide does not result in a satisfactory return of the sp^2 structure. Therefore, different stabilizers and surfactants have been used to make aqueous non-covalently modification of graphene possible to save its sp^2 structure. Polycyclic aromatic hydrocarbons, in particular, have shown their potential owing to their $\pi - \pi$ stacking interactions with graphene⁹⁻¹⁰. Pyrene derivatives are a group of PAHs that have been observed to adsorb onto graphene surface to stabilize graphene in water, yielding graphene concentrations as high as 0.8-1 mg.mL⁻¹ for applications in composites, solar cells, and electrochemical devices¹¹⁻¹³. Our review shows several other alternatives to PAHs, including but not limited to coronene tetracarboxylic acids¹⁴, hydrophilic dendrones based on pyrene¹⁵, bolaamphiphiles based on perylene¹⁶, sodium cholate¹⁷. Nonetheless, there is a dire need to substitute these surfactants and stabilizers with their sustainable, environmentally-friendly counterparts or even remove surfactants/stabilizers altogether if possible. Another approach to a more sustainable polymer/graphene nanocomposites preparation is to reduce the number of components by defining multifunctional roles for constituents. For example, a conventional production route for a self-healable, UV-resistant, conductive polymer nanocomposite would require self-healing pre-embedded agents, anti-UV components, electrically active material, and surfactants/stabilizers. However, by assigning multifunctional roles to graphene and lignin, the need for self-healing agents and anti-UV components can be obviated. As another example, using only graphene as a multi-stimuli responsive active material, multifunctional sensors can be produced that can detect different stimuli, instead of having different active materials each responsive to a specific stimulus.

1.2 Objectives and Scope

To address the problem stated earlier, three major objectives are set for this PhD study:

1. Sustainable production of multifunctional polymer/graphene nanocomposites with fewer components by assigning multifunctional roles to graphene and a naturally

- occurring stabilizer, i.e., lignin. These multiple functionalities should be synergistically in line with the potential applications of the final product.
2. Production of multifunctional sensors with only one multi-stimuli responsive active component instead of having different active components each sensitive to a specific stimulus.
 3. Complete removal of lignin and successful preparation of polymer/graphene nanocomposites using only water and no other chemicals.
 4. Elaborating the underlying mechanisms behind fast self-healing, high UV stability, and sensitive electromechanical sensing of polymer/graphene nanocomposites produced via our environmentally-friendly approach.

1.3 Dissertation Overview

Chapter 1 starts with describing the unsustainability issues with the current linear business model. It proposes a circular business model instead, a major component of which is sustainable design. The focus is on polymer-based products, specifically polymer/graphene nanocomposites. Chapter 1 advocates a design philosophy for polymer/graphene nanocomposites in which hazardous chemical components are substituted with sustainable, natural counterparts or eliminated completely. These polymer/graphene nanocomposites should deliver comparable, if not superior, performance compared to their conventional counterparts. The substitution/elimination of chemicals should render these nanocomposites more desirable economically and environmentally. In the end, the significant findings derived from this study are highlighted.

Chapter 2 starts with a brief background on polymer nanocomposites. Graphene, as a new-age material, will be introduced and its different production routes are described. Liquid-phase exfoliation, as one of the most popular production methods for graphene will

discussed in more detail and challenges accompanied with using water as an exfoliation medium, such as its huge surface energy mismatch with graphene, will be elaborated. In this chapter, lignin as a sustainable, natural stabilizer of graphene in water will be introduced. Some functional properties of polymer/graphene nanocomposites such as self-healing and electromechanical sensing properties will be discussed with background information in literature.

Chapter 3 elaborates on the materials and production methods, as well as the rationale behind these choices. It also thoroughly describes the experimental methods used to characterize polymer/graphene nanocomposites. Working principles and some basic theories are provided for the characterization techniques.

Chapter 4 reports on an aqueous-only production route for polymer/graphene nanocomposites using lignin as a sustainable, naturally-occurring stabilizer for graphene. Transmission electron microscopy (TEM), field-emission electron microscopy (FESEM), and Raman spectroscopy are used to show successful production of graphene. This aqueous solution of graphene is then mixed with waterborne polyurethane (WPU) to produce WPU/graphene nanocomposites. The morphology of these nanocomposites is observed using FESEM. The mechanical, self-healing, and UV-stability of these nanocomposites are investigated and mechanisms for the remarkable self-healing and UV-stability properties of these nanocomposites are presented.

Chapter 5 describes preparation of multi-stimuli responsive pressure sensors from graphene through a simple dip coating process using commercially available sponges. Thanks to the self-assembly of lignin-modified graphene (LMG) on their skeleton, these sponges can become conductive. Electromechanical measurements showed a decrease in resistance as these sponges were placed under pressure. FESEM was conducted to investigate the underlying mechanism for the electromechanical sensing behavior. The pressure sensors showed long-term stability over numerous pressure-release cycles. These multi-stimuli responsive sensors were able to measure changes in temperature. Moreover, they showed instant sensitivity to IR irradiation as well.

In Chapter 6, we take this approach to the next level by removing lignin and producing polymer/graphene nanocomposites without any foreign stabilizer or chemical other than water. These nanocomposites are then used to produce highly sensitive skin-conformal, electromechanical sensors. The morphology and electromechanical sensing properties of these sensors are investigated and the potential applications of these sensors for continuous health monitoring or biomechanical monitoring are discussed. One idea to further improve the sensitivity of the sensors is by improving their signal-to-noise ratio. This can be done by improving the surface conformality of the sensors through using a viscoelastic polymer base. This is particularly challenging since viscoelastic polymers can introduce time dependency of the signal which is not desirable.

In chapter 7, a thorough summary of the previous chapters is given. The objectives set forth in chapter 1 are reassessed to discover the extent to which they are met. The implications of these findings will be elaborated and opportunities and strategies for future work are explored. Some reconnaissance studies that were not presented in previous studies are also included. In the end, recommendations for future works are proposed.

1.4 Findings and Outcomes/Originality

This research resulted in several novel outcomes:

- 1) Multi-functional polymer/graphene nanocomposites were successfully produced by assigning multiple roles to graphene and lignin. Graphene improves the structural properties by acting as mechanical reinforcement, enables self-healability through its remarkable photothermal conversion, enhances durability by absorbing ultraviolet (UV) light, and makes the nanocomposite conductive thanks to its sp^2 structure, which is unperturbed by non-covalent modification with lignin. Lignin assumes multifunctional roles as well, by acting as a naturally-occurring stabilizer and UV absorber. These nanocomposites were successfully prepared via a sustainable, environmentally-friendly, aqueous-only route with no need for additional healing agents, reinforcement, synthetic UV blockers, or other chemicals. The synergy between

these functions allows for aqueous-only preparation of highly durable conductive nanocomposite coatings for antistatic applications.

- 2) For the first time, multifunctional sensors capable of sensing deformation, temperature, and irradiation were developed based on multi-stimuli responsiveness of LMG. These light, wearable, flexible sensors can be used as wearable electronics that can monitor bodily motions.
- 3) WPU nanocomposites were produced using only pristine graphite and water with no external stabilizer. WPU assumed a multifunctional role by acting as polymer matrix and a stabilizer for graphene. For the first time, using only pristine graphite, WPU, and water, highly sensitive electromechanical sensors were produced. This high sensitivity together with shape conformality of WPU made detecting minute soft-tissue biomechanical deformations possible. They also showed applications in monitoring blood pressure waveforms with marked accuracy so much so that even the effect of breathing on blood pressure was detected, which opens the door to many important biomedical applications.

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Chapter 2

Literature Review

In this chapter polymer nanocomposites with their significant potentials and countless applications along with graphene, one of the most important discoveries of the last decade, are introduced. Liquid-phase exfoliation (LPE), as a cheap, easy to implement, and versatile technique to produce graphene is discussed in more detail and methods to make LPE more environmentally friendly such as using naturally-occurring components are presented. Different applications of polymer/graphene nanocomposites with functional properties such as self-healability or electromechanical sensing ability are reviewed. This requires a brief review on self-healing materials and polymer/graphene nanocomposite sensors which are provided at the end of this chapter.

2.1 Polymer Nanocomposites

With technological advances during the past few decades, synthetic polymers have conquered our world. Their low price, low density, chemical resistivity, good insulation properties to heat and electricity, and etc. have made polymers irreplaceable materials. However, lower mechanical properties, thermal stability, biocompatibility, and several other properties have made it necessary to modify these materials. Combining reinforcement with polymers, i.e. polymer composites, is one way to improve on the shortcomings of polymers. Compared to traditional polymer composites based on conventional fillers such as magnesium, calcium carbonate, or glass fiber, polymer nanocomposites show significant improvement in physical, mechanical, and chemical properties.¹⁻² These nanocomposites therefore have superior mechanical properties³⁻⁵, high thermal stability⁶⁻⁸, excellent environmental stabilities, as well as many other functional properties such as electrical and thermal conductivities, self-healability, and electromagnetic shielding capability⁹⁻¹¹. Nanocomposites are produced from nanofillers with at least one dimension of reinforcement below 100 nm. The number of dimensions below 100 nm can be one, in case of nanoplatelets such as graphene and nanoclay, two, for nanowhiskers including carbon nanotubes (CNT), or three, for nanoparticles, e.g., Ag nanoparticles.

Polymer nanocomposites have replaced many of their traditional metal-based counterparts. This is because polymer nanocomposites can offer features which were not achievable in metal-based materials. In addition, cost reductions associated with easier production procedures of polymer nanocomposites have resulted in increased production efficiency¹². Categorically, there are two major groups of polymer nanocomposites based on their polymeric matrix: those based on polyester, phenolic, and epoxy, resins as well as rubbers form thermosetting nanocomposites, while those based on polypropylene, polyethylene are thermoplastic nanocomposites. There are many different types of nanosized reinforcement used in polymer nanocomposites and each would endow its host polymer with its own distinctive structural and functional properties. The set of functional properties that are of interest of this study limits the choice for the nanoadditive to graphene, a material that

exhibits unique optical and electronic properties, and has recently become a major focus point for researchers.

2.2 Graphene

Graphene has recently garnered enormous interest in academia and industry thanks to its extraordinary properties such as high charge carrier mobility which is higher than $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, measured at the electron density of $2 \times 10^{11} \text{ 1/cm}^2$ ¹³. It also has an exceptional Young's modulus value, more than 0.5 to 1 TPa, and huge spring constant, 1 to 5 N/m¹⁴. The enormous thermal conductivity of graphene, over 3000 Wm/K¹⁵; along with its full impermeability to gases¹⁶; and high surface area, predicted to be more than 2500 m²/g theoretically¹⁷ and measured to be 400-700 m²/g experimentally¹⁸ are among its other in-demand properties. As a result, graphene has found its applications in fields as diverse as biological labeling¹⁹, catalysis²⁰, gas and energy storage²¹, as well as possible high-tech applications such as flexible electronic devices and photonics²².

In theory, the idea of graphene had been around for more than sixty-five years²³ purely as a theoretical toy model to describe properties of different carbon-based materials. Although it was known that graphene is an integral part of 3D materials, it had been considered non-existent in the free state due to presumed thermodynamical instabilities of 2D crystals, first argued by Peierls, more than 75 years ago, and later developed by Mermin²⁴⁻²⁵. Simply put, the theory argues that the melting point of thin films, which sharply falls with decreasing film thickness, renders the film unstable at the thickness of about dozens of atomic layers²⁶. Therefore, 2D crystals had been considered only as building blocks of larger 3D entities. This notion, however, was challenged and changed by the discovery of graphene²⁷ and later other free-standing 2D crystals such as boron nitride²⁸. The existence of 2D crystals can be reconciled with the mentioned theory if one considers the crystals quenched in a metastable state due to strong interatomic bonds that guarantees that thermal fluctuations cannot result in the formation of dislocations or crystal defects, even at higher temperatures^{25,29}. Another factor in stabilizing the 2D structure is its crumbling in the third dimension^{21,30}, in the scale of about 10 nm³¹.

2.3 Graphene Production Methods

There are two major ways to produce graphene: bottom-up and top-down. The bottom-up method is based on producing graphene from its molecular building blocks through chemical reactions to link them covalently into a 2D block ³². This approach can be liquid- or substrate-based; however, the liquid-based approach suffers from two limitations as the size of the final product increases, since the resulting macromolecules become increasingly insoluble as they grow, and occurrence of side reactions becomes more likely. Because of these shortcomings, using a solid surface with catalytic activity as a substrate is preferred. In this method, graphene forms by building up from the molecular building blocks ³³, annealing silicon carbide substrate ³⁴, and chemical vapor deposition (CVD) ³⁵. Although this approach does not suffer from the limitations mentioned above and the resulting graphene is of high quality and defect free, there is a small thermodynamic window through which the production is possible which results in a low-yield production.

On the other hand, top-down approaches aim to produce graphene through exfoliating graphite. One major advantage of this approach is that it is not as thermodynamically constrained as the bottom-up methods, so various environmental conditions are possible. The exfoliation can be either mechanical, e.g., mechanical cleavage ²⁸ or ball-milling ³⁶, or in a liquid medium using ultrasound ³⁷. Although mechanical methods produce defect free sheets, the yield is low compared with liquid-phase exfoliation (LPE). As a result, LPE has become of increased interest because of its higher yield, more industrial viability, extreme versatility, potential up-scalability, and ease of use.

2.4 Liquid-phase Exfoliation of Graphene

Using LPE, graphene can be deposited on a variety of substrates in different environments not available via mechanical cleavage or growth methods. The extreme versatility of LPE method enables us with tuning of many physiochemical characteristics of the final material. As main components of numerous applications such as conductive transparent electrodes or thin-film electrodes, graphene-based composites or films can be produced by employing

LPE. Finally, LPE allows immediate utilization of exfoliated graphene sheets, suspended in solution, for spray painting, spin-coating, or other solution-based processes. Nonetheless, in terms of sheets quality, i.e., defects – which undermines mechanical and electrical properties, LPE is still not on par with bottom-up or mechanical cleavage approaches. Also, because of the trivial increase in entropy and considerable π - π attraction in 2D structures, dispersing graphene even in its good solvents, which are expensive, toxic, and not volatile, is still limited and fraught with challenges. Therefore, further research is required to improve the quality of produced graphene, as well as increase its yield. The graphene made by LPE is usually a mixture of single-, bi-, and multilayer (i.e., less than 10 layers) graphene. In general, the term graphene is reserved for single-layer graphene. For simplification purposes, however, the term graphene is used for a mixture of graphenes with different layer numbers throughout this thesis³⁸.

LPE can be either surfactant assisted or surfactant free, carried out in either aqueous or organic solutions. Although LPE of pristine graphite is possible, a greater number of studies have used graphite oxide as starting point. Graphite oxide is a bulk solid produced through oxidation processes that functionalizes its basal planes, resulting in an increase in interlayer spacing. The reason why it is so popular is due to greater scalability and ease of use of this material. It is also processable in basic and aqueous media ³⁹. There are many different functional groups available on GO such as, carboxyl groups, carbonyl, epoxy, and hydroxyl that can add functional groups to the 2D structure both covalently and non-covalently. So the physical and chemical properties of these materials can be greatly engineered ⁴⁰. In general, oxidation can be done by using a mixture of potassium chlorate (KClO_3) and nitric acid (HNO_3), as used by Brodie and Staudenmaier ⁴¹, or by using potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4), known as Hummers method ⁴².

However, there are some downsides to this process. First, oxides should be removed to reduce GO, which adds another step in the production procedure ⁴³. Moreover, because reduction cannot remove all the heteroatomic contamination and/or topographical defects resulted from the oxidation process some scholars refuse to consider reduced GO as

graphene⁴⁴⁻⁴⁵. These defects disrupt the band structure and result in poor electrical properties, which is the most important graphene characteristic⁴⁵.

In attempts to avoid oxidation, LPE of pristine graphite has been studied using ultrasonication. Ultrasonication creates pressure fluctuations which results in growth and collapse of micron-sized bubbles which in turn creates high pressure jets that induces shear forces and cavitation on graphene sheets, which are held within a π - π stacking distance of 3.35-3.4 Å, resulting in peeling of the sheets. The attractive van der Waals force, proportional to $1/r^6$, weakens profoundly as stacking distance increases beyond 5 Å. The solvent-graphene interactions are especially crucial after exfoliation to counter the attractive van der Waals forces between the sheets. Ideally, solvents should reduce the interfacial tension between themselves and graphene to decrease the work of cohesion between graphene sheets. This will result in the reduction in the energy per unit area that is necessary to separate graphene sheets and maximizes the area of the graphene surface that is in contact with solvent, increasing the dispersive London forces⁴⁶. This criteria limits us to solvents with the surface tension of 40 mJ/m²⁴⁷, e.g., ortho-dichlorobenzene (o-DCB, 37 mJ/m²)⁴⁸, N,N-dimethylformamide (DMF, 37.1 mJ/m²), and N-methyl-2-pyrrolidone (NMP, 40 mJ/m²)⁴⁷, Gamma-Butyrolactone (GBL, 46.5 mJ/m²), N,N-Dimethylacetamide (DMA, 36.7 mJ/m²), and Dimethylsulfoxide (DMSO, 42.9 mJ/m²) which in majority have several disadvantages such as toxicity⁴⁹. These solvents, moreover, have high boiling points, e.g., NMP, o-DCB, and THF, GBL, DMSO, boil at 203, 181, 154, 204, and 189 °C, respectively, which restricts their applications in electronics since without complete removal of solvents, the electrical performance of the device will be enormously affected. This is a major shortcoming in the production of graphene transparent conductors for field effect transistors⁵⁰, solar cells⁵¹, photodetectors⁵², and etc. Solvents presence in the samples also limits the application in organic electronics. NMP and DMF are very expensive and highly toxic. Long evaporation time may also lead to re-aggregation.

In contrast, most solvents with low boiling points like chloroform, ethanol, and water have surface tensions that are not appropriate for graphene exfoliation: 27.5, 22.1, and 72.8, mJ/m² for chloroform, ethanol, and water, respectively. Attempts have been devoted to

transfer graphene dispersions from good solvents such as NMP to low boiling temperature ones like ethanol using solvent exchange process ⁵³. However, direct exfoliation of graphene in a low boiling temperature solvent is more desirable because of the ease of use and simplicity of procedure. As a result, surfactants have been employed to make graphene exfoliation in these solvents possible. The exploration of organic solvents are mainly important when one aims to produce graphene for devices that can be negatively affected by residual water such as field-effect transistors, since water may enhance charge trapping phenomena and adversely affect the performance ⁵⁴.

Nonetheless, the idea of graphene exfoliation in water is highly attractive due to its cheap price and environmental friendliness. Research, however, has shown the challenging nature of exfoliating hydrophobic graphene sheets in water. One way to overcome this challenge is to use surfactants so as to reduce the high surface energy of water to obtain graphene suspension ⁵⁵⁻⁵⁸.

2.4.1 Lignin

Although there is a myriad of options for surfactants, as listed above, there have been a new trend to move towards more sustainable and more environmentally friendly surfactants and stabilizers. One naturally-occurring stabilizer which has been successful in LPE of graphene is lignin. Lignin, which accounts for 35 wt% of wood ⁵⁹, is an abundant natural polymer with annual production of $5\text{-}36 \times 10^8$ tons. It is a renewable resource which is produced through photosynthesis followed by aromatization and polymerization of carbohydrates ⁶⁰. Lignin is a cheap byproduct from pulp and paper industry with great potentials; however, being used mainly as fuel, lignin is considered underutilized by 5 to 10 times in terms of value even by conservative estimations ⁶¹⁻⁶³. The complex chemical structure of lignin is still obscure ⁶⁴. The main reason in identifying the chemical structure of lignin is that it is not still possible to isolate lignin from its natural state in fiber. However, most of the functional groups that make up this material have been identified (Figure 2.1) and structural models have been proposed by researchers, e.g., Alder (Figure 2.2) or Rouchi ⁶⁵.

Recently, the potentials for lignin in producing value-added materials is being realized in academia. For example, thanks to their interactions with biological systems, some compounds based on lignin have shown desirable results, such as antibiotic and anti-carcinogenic activities ⁶⁶, as well as antioxidant activity in physiological processes ⁶⁷⁻⁶⁸. Lignin has also shown to be biodegradable through depolymerization by certain wood-rotting fungi ⁶⁹ making it suitable to introduce biodegradability in polymeric materials. Lignin-based compounds can be used as photo- and UV-stabilizers, toughener for epoxies, and adsorbent for dyes and heavy metal ions. Lignin has also been added to polyurethanes, phenol-formaldehyde resin formulations ⁷⁰⁻⁷¹, polyethylene terephthalate, polyethylene oxide, polypropylene, polyvinyl alcohol ⁷², polystyrene ⁷³, polyethylene, and Polybutylene succinate ⁷⁴⁻⁷⁵.

Figure 2.1 Phenolic precursors that make up lignin ⁷⁶

Recently, Liu *et al.* reported a facile, economical, and environmentally-friendly method to exfoliate graphite into graphene using lignin aqueous solution. By investigating the effects of lignin concentration, initial graphite concentration, and sonication time they managed to produce high-quality graphene with high electrical conductivity. They argue that graphene stabilization in water happens due to the π - π interactions between graphene and aromatic rings present in lignin ⁷⁷.

Figure 2.2 Lignin structural model as proposed by Adler ⁷⁸.

2.4.2 Polymer-assisted Liquid-Phase Exfoliation

Colloidal stabilization of graphene can be achieved through direct growth of polymer brushes on exfoliated graphene surface acting as a macro-initiator, on which different polymers such as polystyrene, polybutylacrylate, or poly methylmethacrylate can be attached using atom transfer radical polymerization ⁷⁹. However, covalent attachment of polymer chains to the basal plane of graphene can perturb graphene's electronic structure, resulting in considerable change in property. Therefore, most polymer-exfoliated graphene suspensions are stabilized sterically with non-covalent interactions such as van der Waals forces ³⁷. This method, which had been used previously to exfoliate carbon nanotubes ⁸⁰⁻⁸¹, has shown similar results for graphene as well ⁸²⁻⁸⁴. In this method, polymer is added to the mixture of graphite and solvent and the resulting mixture goes through sonication. Due to the hydrophobic nature of graphene, organic solvents are much more compatible;

nonetheless, water is an irresistible option for up-scalability because of its non-toxicity and cheaper price.

Polymers can stabilize graphene through steric repulsion mechanism. In this method, polymer chains can attach to the surface of graphene and partially protrude into the solvent. When two graphene sheets with polymer chains attached to their surfaces come close, the protruding polymer chains cannot occupy the same space. This reduces the number of possible conformations for the chains and in turn increases the free energy of the system. This increase results in an effective repulsion that stabilizes graphene against aggregation. Using this technique, graphene has been exfoliated in liquids with the help of amphiphilic block copolymers⁸⁵, ethyl cellulose⁸⁶, polyvinylpyrrolidone⁸⁷, polybutadiene, polystyrene-*co*-butadiene, polycarbonate, polystyrene, polyvinylchloride, polymethyl methacrylate, polyvinylidenechloride, cellulose acetate, polyvinyl acetate⁸⁸.

2.5 Functional Polymer Nanocomposites

2.5.1 Polyurethane/Graphene Nanocomposites

Polymer-based nanocomposites with superior mechanical and thermal properties have been produced by exploiting the ease of processability and solubility of modified graphene. The significance of polymer/graphene nanocomposites has recently grown considerably due to their conventional and unique functional properties. Polymer/graphene nanocomposites have shown great application potentials for touch panel devices, gate dielectrics, electrochemical and electromechanical sensors, nanoelectronics and electroluminescent devices, energy storage, etc. These are an attractive group of materials since they are highly flexible, they offer electrical and thermal conductivity, and they can be processed at low temperatures through simple production techniques⁸⁹⁻⁹¹. In particular, electrical conductivity of graphene creates opportunities to produce vastly different types of sensor, as well as, antistatic, anticorrosive, microwave absorbent coatings, rechargeable batteries, supercapacitors⁹²⁻⁹⁴, and fuel cells. Nonetheless, like all nanocomposite materials, improving interfacial interactions between graphene and the polymer, which can

result in homogeneous dispersion of graphene in polymer is vital to obtaining desired results⁹⁵.

Among polymers, polyurethanes (PUs) are of huge interest since they are highly versatile engineering polymers. PUs are produced through a facile polyaddition reaction between isocyanate and polyol followed by the addition of a chain extender. These polymers have found multitude of applications in industry as elastomers, adhesives, coatings, foams and sealants finding their way in medical devices, primer, textile finish, and sports goods⁹⁶⁻⁹⁸. Graphenic materials have been added to PUs for a variety of applications such as films with improved gas impermeability⁹⁹, oil/water separation, and microwave shielding¹⁰⁰⁻¹⁰¹.

Like conventional solvent-borne PUs, waterborne PUs (WPU) are versatile polymers as well. These environmentally-friendly polymers are rapidly finding their applications as flexible substrates, adhesives, and coatings in rubber, paper, leather, automobiles, and wood industries¹⁰²⁻¹⁰⁶. Nevertheless, compared to conventional PUs, WPUs suffer from slower development of adhesion resulting from their poorer drying rates and have found limited applications. WPU/Graphene and WPU/GO nanocomposites have shown enhanced environmental friendliness¹⁰⁷, anticorrosive ability¹⁰⁸⁻¹¹², and improved mechanical properties¹¹³⁻¹¹⁴. Greater interest has recently been devoted to developing multi-functional properties in PU/graphene nanocomposites. Graphene can simultaneously act as a conductive network, UV stability, or introduce photothermal conversion. The combination of these properties can open the door to many exciting applications. Here, we discuss two major functional applications for graphene in PU.

2.5.2 Properties of Functional Polymer Nanocomposites

Unlike structural nanocomposites on which substantial research has been done, considerably fewer efforts have been spent on studying functional polymer nanocomposites. Here, we briefly mention some of the functional properties of polymer/graphene nanocomposites.

2.5.2.1 Self-Healing

Self-healing materials are a new class of materials capable of restoring their lost properties, mechanical or functional, after sustaining damage. Considering physical damage is inevitable, self-healability can prolong service life of these materials and as a result increase their reliability and ease environmental concerns by reducing waste ¹¹⁵⁻¹¹⁶. Therefore, self-healable materials have recently garnered huge interest. The original physical properties that are compromised after damage can be regained ¹¹⁶ either autonomously ¹¹⁷, or induced by an external stimulus such as heat ¹¹⁸ or pressure ¹¹⁹. Self-healability can be intrinsic which means that the polymer matrix itself is capable of self-healing using some potential functional groups that are capable of taking part in thermally-reversible, covalent or non-covalent bond-forming reactions ¹²⁰. Extrinsic healable polymeric systems, on the other hand, may be loaded with encapsulated or pipelined repair agents, i.g., monomers that can react with polymerization catalysts upon fracture ¹²¹, which are released when the damage breaks the containers. An advantage of intrinsic systems is that, unlike extrinsic systems whose self-healability is limited by their repair agent loading, they can heal many times thanks to their inherent self-healability. However, intrinsic systems are often non-autonomic and require an external stimulus. For example, in graphene nanocomposites with intrinsic self-healability, the role of graphene is to initiate or expedite self-healing by converting a stimulus such as radiation or electricity into heat and speeding up polymer chain diffusion. Figure 2.3 compares autonomous and non-autonomous self-healable systems.

Figure 2.3 Autonomous and non-autonomous self-healing systems ¹²²

2.5.2.2 Anti-UV Property

Traditionally, anti-UV compounds, broadly divided into absorbers, quenchers, and hindered amine light stabilizers, are added to polymers to improve UV stability. However, it has also been shown that graphene can have UV-stability properties as well ¹²³⁻¹²⁴. This will be useful for polymer/graphene nanocomposites with outdoor applications.

2.5.2.3 Electrical Conductivity

Compared to GO and rGO, non-covalently modified graphene has much higher conductance. Depending on the conductivity of polymer/graphene nanocomposites, different applications can be developed. Anti-static coatings, for instance, can eliminate static charges and prevent charge accumulation which may result in electrical discharge or other electrical events. With an increase in the conductivity of polymer/graphene nanocomposites, static dissipative materials can be produced which can decay charges at much faster rates. Polymer/graphene nanocomposites with even higher conductivities can be used for electromagnetic or radiofrequency interference shielding or sensing applications.

2.5.2.4 Electromechanical Sensors

Polymer/graphene nanocomposites are also being used in many electronic applications such as fuel cells, electromagnetic shielding, and sensors as witnessed by huge recognition given to these materials in these fields. By exploiting conventional properties of polymers combined with functional properties of graphene, a new class of polymer-based sensors have been produced that have higher selectivity and faster measurement capability compared to classical sensors. Traditionally, materials such as organic semiconductors, ionic membranes, solid electrolytes, semiconducting metal oxides, and semiconductors have been used as sensing devices. However, polymer nanocomposites are rapidly challenging these sensors for sensing applications such as gas, pH, humidity, temperature, strain, pressure, and etc in a variety of physical, chemical, and biological environments. Polymers have been used as both active and passive components in sensing devices: they either participate in conduction directly or contain conductive components in charge of sensing. One major factor that has significantly contributed to the use of graphene in sensors is its superior electrical conductivity. Current trends suggest exponential growth in the field of sensing applications. During the past decade research in this area has exploded with ever-increasing financial investments that has resulted in significant growth in the number of researchers and published literature.

2.5.2.4.1 Pressure Sensors and Their Applications

One particular booming research area for electromechanical sensors is developing sensitive and flexible pressure sensors that are cheap, compatible, easy to produce, and scalable. A pressure sensor is basically a transducer that converts the imposed pressure to an electrical signal ¹²⁵. These sensors that are able to monitor the position and strength of external pressure can be used in flexible and portable devices, artificial skin applications, healthcare monitoring equipment, or wearable electronics ¹²⁶⁻¹³¹. These sensors can also be used in integrated network structures for applications in robotics, human-machine interface, and artificial intelligence ¹³²⁻¹³⁵. It should be noted that this new class of polymer-based pressure sensors are not intended to replace conventional sensors based on silicon, which, despite being highly sensitive, have limited applications due to their rigidity. The new class of pressure sensors, on the other hand, offer a novel potential for niche applications for which flexibility, low price, and low weight are of higher significance ¹³⁶⁻¹³⁷.

The pressure range for different sensing devices can be divided into four different ranges. The first region is ultralow pressure which is less than 1 Pa. This pressure regime is rarely present in routine daily applications and include pressures close to a typical sound pressure with applications in hearing aids and microphones. Current polymer-based pressure sensors can hardly register this pressure regime ¹³⁸. Subtle pressure which is between 1 Pa to 1 kPa is a result of interactions with small objects and may have applications in developing ultrasensitive artificial skin with sensitivity higher than human skin, as well as ultrasensitive touch panels for mobile phones ^{136, 139}. The low-pressure region which is between 1 to 10 kPa is the most common range since it covers most pressures that are present in everyday interactions ¹⁴⁰. Most sensors that are developed are designed to perform in this region. Finally, medium-pressure sensors are designed to perform in the range of 10 to 100 kPa. This pressure range includes body weight plantar pressure and high-altitude atmospheric pressure. There has been increasing interest in developing medium pressure sensors for applications such as mobile blood and pulse-monitoring devices and wearable barometers ¹⁴¹⁻¹⁴².

Five key parameters are used to assess the performance of pressure sensors. The most important parameter in pressure sensors is sensitivity which can determine the efficacy and precision of the pressure sensing device. Sensitivity, usually denoted by S , is a change in output electrical signal divided by the change in the corresponding imposed pressure. Another important key parameter is limit of detection (LOD) or the threshold pressure which is the lowest pressure that produces a discernable signal. This parameter is more important in lower range of the pressure spectrum, for example in developing ultralow- to subtle-pressure sensors. Linearity specifies how well the relationship between the change in the value of the imposed pressure and the resulting change in output electrical signal follows a linear behavior. A more linear electrical response results in higher accuracy and reliability of the sensor; therefore, it is highly desirable to produce sensors with a broad linear region. The fourth important parameter in evaluating the performance of sensors is response time. Response time signifies the amount of time between imposing pressure and producing its corresponding electrical signal. This is particularly important in real-time monitoring of dynamic systems when a fast response is highly desired. Finally, the last important parameter is the required voltage under which the device operates. This parameter is vital to reduce the power consumption of the device.

There are different mechanisms under which sensors can transduce the imposed pressure into an electrical signal. Piezoresistivity, which is based on transducing the change in resistance of a sensor into an electrical signal, is one attractive mechanism for researchers since it is easy to exploit, and it can cover large ranges of pressure and strain. An increase in imposed pressure changes the structure of the conductive network and in turn results in a change in the resistance of the network. Sensors based on this mechanism have been found to have high sensitivity, relatively large strain ranges, and short response time, ease of production and signal collection, and low cost¹⁴³⁻¹⁴⁴. Initially, polymer-based piezoresistive sensors were based on conductive polymers or carbon black conductive networks¹⁴⁵⁻¹⁴⁶. These sensors, however, showed very low sensitivity, signal instability, and irreproducibility at low pressure regions resulting in limited applications. New strategies were, therefore, required to improve on the performance of these sensors and broaden their application. One interesting approach has been to base the conductive

network, e.g., carbon nanotubes (CNT), Ag nanowires, or graphene, on porous foams or sponges through solution dip-coating¹⁴⁷⁻¹⁴⁹.

2.5.2.4.2 Strain Sensors and Their Applications

The first report on electromechanical strain sensors goes back to 1856. Lord Kelvin showed that the resistance of metals changes as a result of mechanical strain. Ever since, strain sensors based on different metals and semiconductors have been widely used. In these sensors the resistance is defined as $R = \rho L/A$, where ρ is resistivity intrinsic to the material, L is length, and A is the average cross-sectional area of the conductor.

The cross-sectional area (A) of a solid is inversely related to the longitudinal strain through Poisson's ratio ν . This ratio ranges from 0.20 to 0.35 for most metals and from 0.06 to 0.36 for anisotropic silicon¹⁵⁰⁻¹⁵¹. Gauge factor (GF) is a measure of sensitivity of sensors and it is simply calculated using $GF = (\Delta R/R)/\epsilon$, where $\Delta R/R$ is resistance change ratio, and ϵ is strain. Resistance change ratio itself is dependent on both the geometry of the sensor and its resistivity as shown by $\Delta R/R = (1+2\nu)\epsilon + \Delta\rho/\rho$ ¹⁵². From the Poisson's ratios provided above GF of metal-based sensors can be approximated to be around 1.4 to 2.0. Therefore, it is apparent that these traditional sensors will be challenged by a new class of sensors based on polymers and conductive nanosized active components because of their low sensitivity. Silver nanowires, carbon nanotubes (CNTs), and graphene are some examples of these conductive components which have recently attracted considerable attention for electromechanical sensors. Compared to one-dimensional CNTs and silver nanowires, graphene offers a two-dimensional structure, thus production scalability via top-down approaches such as liquid-phase exfoliation. Electromechanical strain sensors have been produced using different techniques such as coating, filtration, micromolding, printing, and liquid-phase mixing¹⁵³⁻¹⁶⁴.

2.5.2.4.3 Mechanisms of Conductivity in Strain Sensors

2.5.2.4.3.1 In-Flake Resistance or Piezoresistive

Change in in-flake resistance is caused by the geometrical deformations in the conductive components. This effect can be purely geometrical as is the case for traditional metal-based sensors or related to the change in the bandgap as in the case of sensors based on semiconductors such as germanium and silicon¹⁶⁵⁻¹⁶⁶. In case of CNT nanowires, change in chirality can also contribute to the piezoresistive effect¹⁶⁷. Nonetheless, in case of polymeric nanocomposites, the contribution of the piezoresistive effect may not be noticeable as there is a huge mismatch between the elastic moduli of polymers and their conductive nanosized components which results in minuscule deformations for the nanomaterials¹⁶⁸⁻¹⁶⁹.

2.5.2.4.3.2 Direct Contact Resistance

Above percolation threshold, conduction can occur through passing of electrons through overlapping flakes. An increase in strain would result in the slippage of the flakes relative to each other and a fall in their common contact area. This in turn leads to a rise in contact resistance between flakes. This mechanism is shown in Figures 2.4 a-d.

Figure 2.4 Direct contact resistance as a function of overlap area between adjacent flakes¹⁷⁰

2.5.2.4.3.3 Tunneling Resistance

Although quantum tunneling, like many other observations of the quantum realm, is contrary to our everyday intuition, it is in fact responsible for many important physical and even biological phenomena such as alpha decay and DNA mutation¹⁷¹. Quantum tunneling allows elementary particles, atoms, or even small molecules to pass an energy barrier without having the required energy level. Quantum tunneling, which has no analogy in classical physics, is based on the fact that particles do not have a defined position until they are observed, and they are described by a probability function called the wave function. The probability of finding a particle, in this case an electron, at a certain location is defined as the squared of the amplitude of wave function at that location. Tunneling occurs because the value of the wave function does not immediately become zero at the barrier but rather it follows an exponential decay behavior. This means that if the barrier between two graphene flakes is short enough, the wave function can exit from the other side and therefore, there is a possibility that some electron may tunnel through the polymer matrix and end up on the other side of the barrier. The tunneling resistance which is basically the probability of electrons bouncing of the polymeric barrier is defined as:

$$R_{tunneling} = \frac{V}{AJ} = \frac{h^2 d}{Ae^2 \sqrt{2m\lambda}} \exp\left(\frac{4\pi d}{h} \sqrt{2m\lambda}\right)$$

Where J is tunneling current density, V is electrical potential difference, e is quantum of electricity, m is mass of electron, h is Planck's constant, d is distance, λ is height of barrier, and A is cross-sectional area of tunnel. This equation shows that unlike the direct contact resistance mechanism which is related to the change in contact area, tunneling resistance changes exponentially with distance and therefore it is more sensitive to the change between nanosheets, i.e., the strain.

2.5.2.4.3.4 Number of Pathways

If the distance between two graphene flakes exceeds a certain cut-off distance, the electrical current in between these flakes is halted. Cut-off distance depends on different factors such as type of barrier and conductive nanomaterials. The cut-off distance for polymer/graphene nanocomposites is reported to be between 2 and 3 nanometers. The increase in the number of cut-off pathways will contribute to the overall resistance in the conductive network.

2.5.2.4.4 Additional Sensing Applications

Graphenic conductive networks in polymer/graphene nanocomposites can be exploited to detect and measure other stimuli as well. For instance, chemical sensors ¹⁷², gas sensors ¹⁷³⁻¹⁷⁵, temperature sensors ¹⁷⁶, humidity sensors ¹⁷⁷⁻¹⁷⁹, etc. have been produced from different graphenic materials and polymers.

2.6 Concluding Remarks

Literature review shows that introduction of graphene in WPU can open the door to many potential applications. However, efforts should be made to exploit multifunctional properties of graphene, graphene stabilizer, or the polymer matrix. For instance, to develop antistatic coatings, graphene main role is electrical conductivity. However, graphene can have additional functions as well. For instance, it can improve the mechanical properties of the coating. Considering non-covalently modified graphene is an excellent photothermal converter, it can improve the durability of the coating by introducing self-healability to the material through photothermal conversion. Additionally, acting as a UV absorber, graphene can enhance UV resistance and prolong the lifetime of the coating. Similarly, lignin main role is to be a natural stabilizer for graphene. Since, it is shown that lignin also has anti-UV property, it can also improve UV stability of the coating even further as its secondary functionality.

The WPU polymer matrix can also have multifunctional properties. For instance, WPU can act as both a polymer stabilizer and polymer matrix paving the way to production of polymer nanocomposites with essentially no foreign stabilizer. The possibilities this approach can create in explored in chapter 6 in greater details.

In summary, it is the aim of the following chapters to demonstrate that sustainable production of polymer nanocomposites can be achieved through two approaches. Substituting conventional components with their naturally-occurring green alternatives. Reducing the number of required components by defining additional roles for the existing components.

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Chapter 3

Experimental Methodology

In this chapter, materials, sample preparation procedures, and characterization methods are described. The rationale behind choosing production procedures are presented and underlying working principles for characterization techniques are elaborated. Detailed sample preparations and specific operation procedures are not included in this chapter and are presented in Chapters 4,5, and 6.

3.1 Materials

3.1.1 Natural Graphite Flake

To produce graphene via liquid phase exfoliation, natural graphite flake (43319, 10 mesh, 99.9%) was obtained from Alfa Aesar (USA).

3.1.2 AL-Lignin

In order to produce stable graphene in aqueous media, surfactants or stabilizers should be used. Lignin has been shown to produce stable exfoliated graphene in water. Therefore, AL-lignin was purchased from TCI America (USA, TCI product number: L0082, softwood lignin) and used as received.

3.1.3 Waterborne Polyurethane

Waterborne polyurethane (WPU, Alberdingk ® U 3251), purchased from Alberdingk Boley Inc., USA, was an aqueous, anionic, solvent-free, low viscosity dispersion of an aliphatic polyester-polyurethane without free isocyanate groups. The average particle size by volume of WPU is 85 nm (Figure 3.1) and its Zeta potential is -40.4 mV at pH value of 7.0. WPU was used as polymer matrix for antistatic coatings as detailed in chapter 4. In chapter 6, WPU/graphene nanocomposites are produced without lignin. Therefore, WPU has multifunctional roles and it will be used as a stabilizer to produce graphene from graphite instead of lignin, as well as being a polymer matrix.

Figure 3.1 Particle size distribution of WPU particles

3.1.4 Polyurethane Sponge

To produce pressure sensors (Chapter 5), commercially available PU foams are used as elastic substrate on which graphene flakes are assembled. These foams show excellent elasticity and high durability. Upon dip coating, these foams become conductive and show resistance sensitivity to compression.

3.2 Materials and Sample Preparation Methods

3.2.1 Preparation of Lignin-Modified Graphene

Lignin-modified graphene (LMG) was produced by adding pristine graphite to lignin aqueous solution (0.5 mg/ml) followed by tip sonication for 8 h based on a method reported in our previous work ¹. After sonication, the suspension went through centrifugation for 1.5 h at 600 rpm. The top 30 mm of each tube (50 mm tubes) were added to a filtration unit to remove water. Excess water was added to rinse LMG and remove free lignin. The content of LMG trapped between graphene layers was measured to be 10wt% using TGA.

3.2.2. Preparation of WPU/LMG Nanocomposites

LMG was sonicated for 1.5 h in a bath sonicator to produce LMG aqueous dispersion. WPU/LMG nanocomposites were prepared by adding a desired amount of WPU to LMG aqueous solution and then casting it in petri dish in an oven at 50 °C. The films with a typical thickness of ~120 µm were carefully removed for further characterizations.

3.2.3 Preparation of WPU-Modified Graphene

In Chapter 5, WPU/graphene nanocomposites were produced without any “foreign” stabilizer. To achieve that stabilizer and polymer matrix should be the same. Therefore, WPU-modified graphene (PMG) was first prepared by adding graphite to 200 ml WPU aqueous solution in a 250-ml beaker, followed by sonication. The mixture was then poured in 50 ml tubes and centrifuged at 600 rpm for 1.5 h, after which the top 30 ml was used and the bottom 20 ml was discarded. Different factors were considered to optimize the process. To investigate the effect of WPU concentration, WPU solutions with varying WPU content ranging from 0.1 to 2 mg/ml were prepared. Then, 10 mg/ml of graphite was added to each solution and samples were sonicated for 4 h. To study the effect of initial graphite content, different amounts of graphite ranging from 10 to 80 mg/ml were added to 1.5 mg/ml WPU solutions and the mixtures were sonicated for 4 hours. Finally, to study the effects of sonication time, 10 mg/ml graphite was added to 1.5 mg/ml WPU aqueous solutions and sonicated for 2, 4, 6, and 8 hours.

3.2.4 Fabrication of WPU/PMG Sensors

PMG porous films were produced using a process consisting of filtration of PMG suspension through a 0.45 µm polytetrafluoroethylene (PTFE) membrane (Whatman®, Germany) for a few minutes, followed by turning off the vacuum pump to allow the suspension to precipitate slowly. Once a uniform porous PMG film was formed, excess suspension was removed meticulously, and the PMG film was dried. Afterwards, WPU was added onto the upper surface to infuse into the PMG films for reinforcement purpose. The

WPU/PMG films were then removed from PTFE membranes, and cut into desired dimensions. Electrodes were planted on the bottom surfaces of the films, which were later coated with a layer of WPU.

3.2.5 IR Lamp

To measure heat-driven self-healing in WPU/LMG nanocomposites a Philips InfraPhil lamp (PAR38E E27) was used to create localized heat. Figure 3.2 A shows radiation intensity distribution as a function of the distance from the axis of the lamp at 30 cm distance from the lamp. Figure 3.4 B shows irradiance distribution as a function of wavelength of light. This distribution shows a peak at about 1100 nm.

Figure 3.2 radiation intensity distribution as a function of the distance from the axis of the lamp at 30 cm distance from the lamp (A). irradiance distribution as a function of wavelength of light (B)

3.2.6 UV-Induced Degradation

To investigate the effect of LMG and lignin on UV stability of WPU/LMG nanocomposites an Atlas Suntest XXL+ UV lamp chamber was used to create UV-induced degradation.

This is a large xenon lamp weathering and lighfastness test chamber with an internal reflective Al layer to ensure equal UV exposure to all specimens. UV irradiation was conducted at black standard temperature of 55 °C with light intensity of 50 W/m² (300-400nm). Specimens were exposed to UV energy dosage of 180 Kj/m²h. This test is done to simulate aging which happens outdoors or indoors over long periods of time, e.g., months or years.

3.3. Characterization Techniques

3.3.1. UV-Vis Spectroscopy

Figure 3.3 shows a typical setup for a UV-vis spectrometer. The spectrometer consists of a source lamp like deuterium or Xenon Arc lamp. The next device in line is a monochromator which is made out of two slits separated by a prism. This is followed by a beam splitter which divides a beam of light into two equal parallel beams. Next is the sample compartment which contains cells for both reference and sample, and finally detectors which are devices that convert the impact of photons into electrical current that can be monitored by a computer. Upon turning on the source lamp light with a variety of wavelengths is created. This light passes through the first slit of the monochromator ensuring that all light photons are traveling along parallel pathways so that when they strike the prism they are refracted into a rainbow of colors. This means that each wavelength of light is moving to a different location in space and only one wavelength can go through the second slit in the monochromator and strike the beam splitter, becoming two beams of equal intensity. These two beams will then traverse the two cells, one for the reference and one for the sample cell. When a sample is illuminated by light, its electrons can absorb the energy and jump from bonding or non-bonding to empty anti-bonding orbitals. In the energy range of UV-vis spectroscopy, 200 to 800 nm wavelength, only a limited number of electron jumps are possible, the most important of which is from π bonding orbitals to π anti-bonding orbitals. Therefore, UV-vis spectroscopy can be used to study the concentration of graphene since it absorbs light in this range, due to containing π bonding electrons. As the beams exit these cells, they strike the detectors causing them to fire away

and create electrical currents, I_0 for the reference and I for the sample. The ratio of I over I_0 , i.e., transmittance, is a measure of the concentration of the sample. It is noted that transmittance does not change linearly with concentration of the sample; therefore, Beer-Lambert law is used to construct a linear relationship between a parameter called absorbance, which is $\log(I_0/I)$, and concentration.

Figure 3.3 A typical setup for UV-vis spectroscopy

In Chapter 3, UV-vis absorbance is used to determine the amount of LMG needed to produce WPU/LMG with varying LMG contents. LMG content can be measured directly by evaporating water and carefully weighing LMG content in the suspensions. However, this method is very time consuming, wasteful, and more prone to human errors. UV-vis spectroscopy on the other hand is a fast, straightforward method that requires a small amount of sample. However, UV-vis spectroscopy does not provide absolute values for concentration. As a result, a calibration curve of absorbance versus concentration should be constructed based on the results of a few samples with known concentrations, measured directly by evaporation and weighing. Upon constructing this calibration curve, LMG content in LMG aqueous suspensions can be calculated and the necessary amount of LMG aqueous suspension can be added to WPU to produce WPU/LMG nanocomposites. In Chapter 5, UV-vis spectrometer is used to determine the optimum set of conditions that produces the highest PMG yield. PMG yield, i.e., concentration, can be compared with comparing their absorbance values at a certain wavelength. UV-vis spectroscopy was performed on a UV-2501PC (Shimadzu Corporation).

3.3.2 Field emission scanning electron microscopy

To discover the relationships between structure, properties, and functionalities in polymer nanocomposites, electron microscopy is required. In this work, field emission scanning electron microscopy (FESEM) is used for different purposes such as qualifying the dispersion state of LMG in WPU, visualizing and analyzing the microstructure of nanocomposites under different conditions, investigating the conduction mechanism in the pressure sensors, and showing graphene orientation in the strain sensors. No other equipment can perform these investigations like FESEM. FESEM is also popular since it is easy to operate and does not need any sophisticated sample preparation.

In scanning electron microscopy, a cathode is used to emit electrons which later accelerate towards anode by a voltage ranging from 0.5 to 30 kV. The emitted electron beam has a cross section of 10 to 50 μm near the anode which is still too large to form a sharp-enough image. As a result, a system of lenses including several condenser lenses along with one objective lens are used to reduce the beam cross section size and focus it on the surface of the sample. This will reduce the size of the cross section to about 5 to 10 nm, at probe current of 10^{-12} to 10^{-10} A, in most SEMs. Increasing the probe current improves signal to noise ratio but gives rise to probe spot size as well. The distance from the sample to the lower pole piece ranges from 5 to 30 mm which allows for various signals that are produced through the interactions between the electron beam and the sample to be collected by detectors. Beam deflection coils that are placed in front of the objective lens scan the emitted electron probe line by line over the area of interest. The selected signal is then amplified by the operator. The image is formed by variation in the signal which is a result of the interaction between the sample and the electron beam. The interaction is dependent on different factors such as the composition of the sample or its topography. Higher magnification micrographs can be obtained through reducing the deflection coil current, while the image size is kept constant on the monitor. Figure 3.4 shows different types of signals that are generated from electron beam interaction with the sample. A significant upside of using SEM, among many, is its profound depth of focus. At comparable

magnifications to those of light microscopes, 1000x for example, SEMs can have a depth of focus that is 100 times greater².

Figure 3.4 Schematic representation of signals produced from the interactions between the emitted electrons and the sample. E_0 , E , E_{AE} , and $h\nu$ denote the energies of beam electrons, signal electrons, Auger electrons, and radiation. ΔE denotes energy loss of inelastically scattered electrons².

3.3.3 Transmission electron microscopy

Transmission electron microscopy, performed on a Libra® 120 Transmission Electron Microscope (Carl Zeiss, Germany), is used to analyze LMG layers. TEM can be a complimentary microscopy tool to FESEM and provide observations at much higher magnifications with considerably more details which cannot be obtained from FESEM. Unlike FESEM, in which the surface of the specimens is observed, in TEM, a thin cross-section of the specimens can be observed. TEM operates through electron beam irradiation of a thin sample with uniform current density.

In terms of voltage, TEM can be categorized in three groups: low, medium, and high voltage that work in the ranges of 100-200 kV, 200-500 kV, 0.5-3 MV. Increasing the voltage improves the transmission and resolution of TEM. Similar to FESSEM, a

thermionic, schottky, or field emission gun can be used to emit electrons. The beam goes through several condenser-lens systems, which are positively charged, in order to adjust illumination aperture and area ³.

In TEM, electrons have very high energy. While going through the sample, three situations may occur. The electrons can go through the matter without any interaction, i.e., unscattered electrons, which consequently contain no information about the sample. The second type of electrons can bounce off the nucleus and bend and as a result convey important information about the structure of the sample. This type of electrons is called elastically scattered electrons, since they do not have a change in energy and speed and merely have a change in direction. There is also another scattering process which is not desired. In this case, the emitted electrons interact with the electrons in the sample and lose some of their energy by passing it to the sample, i.e., inelastically scattered electrons. These electrons only contribute to the noise in the image while at the same time they might damage the sample as well. In order to reduce the adverse contribution of inelastically scattered electrons, a typical thickness of below 100 nm is required for the sample. After transmission of electrons through the sample, the electrons that now carry information about the structure of the sample go through a different set of lenses, i.e., projection lenses, to amplify the signal. There are two types of contrast that can be achieved from elastically scattered electrons. The first type is called amplitude contrast that is used to visualize the cross section of the sample. These electrons are trapped by an aperture that allows the unscattered electrons to go through but blocks the scattered ones. In this way, regions in which a lot of scattering happened remain dark while regions with less scattering remain bright. This imaging, which utilizes the particle quality of electrons, falls short when it comes to acquiring high resolution images. Therefore, we need the phase contrast image, which is formed using the wave quality of electrons, by utilizing the objective aperture to make the elastically scattered and unscattered electrons interfere. One important source of limitation in TEM is the manufacturing defects in lenses. These defects cause the lens to be imperfect, i.e., to have no rotational symmetry, resulting in an aberration which should be compensated. Among these aberrations, the spherical aberration, denoted by C_s , is the most significant one which affects the objective lens. Each objective lens has a certain

value of aberration which can be decreased by using an objective aperture or omitted by using C_s correctors that are composed of several magnetic lenses. TEMs also use energy filters which act similar to how a prism filters light depending on the wavelength, i.e., energy. Energy filters can filter out the inelastically scattered electrons that only contribute to the noise. This is particularly useful for thick samples in which case the signal is low and the noise is high. These energy filters can be placed outside or, in case of modern TEMs, inside the column, Figure 3.3. The signal in the end is projected on the imaging plate or a digital camera. The state of the art TEMs are capable of reaching $0.8 \text{ \AA}$ as long as the sample is not radiation sensitive.

For TEM sample preparation, firstly, LMG dispersion was diluted with water to produce an almost-colorless suspension. Then a drop of this suspension was placed on a Cu grid. The grid was placed in an oven to evaporate the water.

Figure 3.5 A conventional TEM with energy filter outside the column (A), a newer TEM with energy filter inside the column (B) ³.

3.3.4 Raman spectrometry

Raman spectroscopy is a non-contact, non-destructive, vibrational spectroscopy. It provides thorough analysis of both organic and inorganic substances through a simple procedure since it requires no sample preparation. This technique can provide information on crystal structure and molecular vibrations in the sample. Thanks to these advantages, Raman spectroscopy has been an integral part in a variety of industries and academic fields such as pharmaceuticals, batteries, polymers, semiconductors, and life sciences.

Raman spectroscopy is based on a phenomenon called Raman effect. After a laser light source irradiates a sample with monochromatic light, a minute portion of the light get scattered in all directions. If the scattered light has the same frequency as the incident light, the scattering is called Rayleigh or Elastic Scattering. However, if the frequency of the scattering and incident lights differ, the scattering is called Raman or Inelastic Scattering. This infinitesimal amount of inelastic scattered light was first observed by C.V. Raman in 1928. This finding is important since every molecule returns a unique Raman response.

Since TEM can provide only local observation of graphene layers, a more comprehensive tool is required to characterize graphene. Raman spectroscopy has become a benchmark test to characterize graphenic materials, in particular layer thickness. Although the differences in Raman spectra of graphite and graphene such as band positions, band shapes, and relative intensities may be subtle, when analyzed more closely these differences can provide important information on the structure of graphene. The G band located at ~ 1584 $1/\text{cm}$ is extremely sensitive to graphene number of layers and its intensity changes linearly with the thickness of few-layer graphene. The position of the G band can also be related to the number of layers; however, since the position can be affected by other factors as well, caution should be taken when using position to characterize graphene. The 2D band is another strong band whose shape and position can be used to characterize graphene.

Raman spectroscopy was performed on a confocal Raman microscope (alpha300, WITec, Ulm, Germany) equipped with a 488-nm laser source and a 20X Nikon objective lens. Each Raman spectrum was acquired for 60s using 0.5s integration time.

3.3.5 Dynamic Mechanical Analysis

One of the most useful techniques to study and analyze mechanical properties of polymers is dynamic mechanical analysis (DMA). DMA can be used to measure a variety of parameters such as elastic and loss moduli as a function of strain, frequency, temperature, and so on. These parameters can be used to assess the effect of graphene on the mechanical reinforcement of the polymer host, quantify self-healing, and quantitatively compare the

effect of UV irradiation on different specimens. In addition, coupled with Autolab, DMA can be used to put samples under controlled deformations in order to measure their electrical response to that deformation. For example, in case of electromechanical sensors, DMA can be used to put sensors under strain or pressure while Autolab records changes in their electrical resistance. Other mechanical testing devices such as Instron can also be used instead of DMA, but since the polymer/graphene specimens were soft and small, DMA had advantages in terms of precision and ease of use. Instron, for example, required special components necessary to study soft polymers which were not available in our labs.

Basic principles of DMA can differ depending on the variety of modes it can be used in. It can perform static deformation-strain measurements where specimen is put under deformation and the corresponding stress is recorded or vice versa. It can also perform dynamic measurements in which case a sinusoidal deformation at a certain amplitude is applied and its mechanical responses such as stiffness, damping, loss modulus, elastic modulus, etc. are recorded. When coupled with Autolab, DMA can also put samples under static or dynamic deformations in order to measure their electrical response to these deformations. Different DMA modes such as stress-strain, amplitude sweep, frequency sweep, and single frequency cyclic tests were conducted. DMA was used extensively to calculate elastic modulus, quantify self-healability and UV resistance, measure electrical sensitivity, and determine cyclic durability of different specimens.

DMA was carried out on a DMA Q800 (TA Instruments, USA). The frequency sweep data were recorded in the range of 1 to 10 1/s at an amplitude of 1% to remain in the viscoelastic region.

3.3.6 Four-Probe Resistivity Measurement

The electrical conductance of graphene films was measured on a resistivity/sheet resistance measurement station (Advanced Instrument Technology, Model: CMT-SR2000N). The instrument consists of four equidistant metal tips made from tungsten supported by springs to minimize sample damage. Measurement is done by passing the current through two outer

probes and inducing a voltage in the two inner ones. All four probes are placed on a stage which can move around and probe the surface of the sample.

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Chapter 4

An Aqueous-Only, Green Route to Self-Healable, UV Resistant, and Electrically Conductive Polyurethane/Graphene/Lignin Nanocomposite Coating

In this chapter, lignin-modified graphene (LMG) was added to waterborne polyurethane (WPU) to produce WPU/LMG nanocomposites. Unlike unloaded WPU, WPU/LMG nanocomposites show complete self-healing after only 150s of IR irradiation because of entropic and enthalpic contributions of LMG to self-healing. Furthermore, WPU/LMG nanocomposites exhibit substantial improvement in UV stability owing to LMG's preventive antioxidant activities such as UV absorption and gas impermeability, its radical scavenging properties, as well as the synergy between lignin and LMG. LMG and lignin both show multifunctional properties. LMG improves the mechanical properties of the films, acts as a photothermal converter contributing to self-healing, and improves UV stability. Lignin, also, acts as a sustainable stabilizer for graphene in water and contributes to UV stability of the final nanocomposite films. Finally, WPU/LMG shows decent conductance, up to 0.276 S/m, which means that these self-healable, UV-resistant films can find applications as durable antistatic coatings.

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4.1 Introduction

As discussed in chapter 2, since the discovery of graphene, polymer/graphene nanocomposites have attracted enormous attention. Incorporation of graphene into polymers can result in significant mechanical reinforcement owing to the exceptionally high aspect ratio and intrinsic strength of graphene. Its two-dimensional sp^2 hybridized structure can also lead to emergence of thermal and electrical conductivities, IR absorption properties, gas impermeability, and improvement in UV resistance of the nanocomposites.¹⁻²

Owing to growing environmental concerns on emission of organic volatiles, waterborne polyurethane (WPU) has become an attractive material for paint, adhesive, and coating applications.³ This incentivizes more efforts to study graphene-based WPU nanocomposites. Using graphene oxide (GO) had been the first approach to producing graphene-based nanocomposites, because of great scalability, versatility, and ease of use.⁴ Nonetheless, most of graphene's amazing properties result from its sp^2 network structure, which is lost after oxygenation.⁵ Therefore, attempts have been made to reduce GO to recover its sp^2 network structure. However, reduced GO (rGO) still suffers from permanent partial loss of its sp^2 structure and poor dispersibility, frequently requiring a secondary surface modification.

Another approach is covalent modification of pristine graphene,⁶⁻⁷ which produces a strong interface between polymer and graphene sheets, resulting in a significant rise in mechanical properties due to efficient load transfer.⁸⁻⁹ The sp^2 network, however, can be perturbed by covalent modification, which may have serious repercussions on functional properties such as IR and UV absorptions, EMI shielding, and electrical conductivity. Non-covalent modification, on the other hand, avoids perturbing the sp^2 structure. Liquid-phase exfoliation (LPE) is a desirable approach to exfoliate graphite into graphene mainly because it is straightforward, easy to implement, and scalable with significant versatility that allows for fine-tuning of many physical and chemical properties.¹⁰ In LPE, solvent-graphene interactions need to counter the attractive forces between the sheets. There are

some solvents that satisfy this requirement; however, these solvents come with high boiling points, toxicity, and high prices. To reduce cost, broaden applications, and increase environmental friendliness and sustainability, water is a tempting choice as an exfoliation medium, especially for WPU/graphene nanocomposites. However, graphene's hydrophobicity should be countered through modification, preferably using sustainable non-covalent modifiers.

In case of polyurethane (PU)/graphene nanocomposites, other than reinforcement effects and functional properties such as conductivities and UV stability brought about by graphene, another interesting property that has caught researchers' attention is their self-healability. Li *et al.*¹¹ studied the self-healing property of PU/GO nanocomposites. Damaged specimens placed in an oven for 4 h at 150 °C followed by 24 h at 65 °C showed a 98% healing efficiency for unloaded PU, which dropped to 69% after GO was introduced because of molecular motion being disturbed by the presence of GO. Despite high healing efficiency, placing specimens in an oven is not suitable for some real-world applications. A more realistic approach is to use a form of irradiation to trigger self-healing, preferably at shorter healing times. Using near IR irradiation for instance, Kim *et al.*¹² triggered self-healing in PU/GO. However, after irradiations as long as 2 h only a slight rise in healing efficiency was observed, 17% for unloaded PU and 39% for a PU with 0.75wt% GO. Above this GO content, they even witnessed a fall in healing efficiency which again was attributed to GO disturbing chain diffusion. Lu *et al.*¹³ have reported very high healing efficiency, 99%, for pristine few-layer graphene/thermoplastic PU nanocomposites, for which the graphene was prepared by a modified arc-discharge method and incorporated into the PU through solvent blending. Obviously, to develop sustainable self-healing WPU/graphene nanocomposites, an alternative approach is needed. An in-depth study is also required to reveal the detailed mechanism for self-healing.

In this chapter, to address some of the ever-growing environmental concerns, for the first time, an aqueous-only route for producing graphene-based WPU nanocomposites from pristine graphite is presented. In a previous publication,¹⁴ it was demonstrated that lignin, an abundant natural polymer produced as a byproduct from paper manufacturing industry,

could be used as a sustainable surfactant to produce lignin-modified graphene (LMG) aqueous dispersion, which could then be re-dispersed in solvents to make epoxy/LMG nanocomposites. In this work, LMG was directly mixed with WPU for film casting. To the best of our knowledge, this is the first polymer/graphene nanocomposite system with pristine graphite as the starting point prepared using no solvent/chemical other than water throughout the whole composite production processes. In addition, although polymer nanocomposites based on graphene with unperturbed sp^2 structure had been previously produced using organic solvents such as THF, DMF, NMP,¹⁵⁻¹⁶ UV-stability of these systems has not yet been studied. Our multifunctional WPU/LMG nanocomposites show impressive UV stability and fast self-healing due to unperturbed sp^2 structure of graphene as a result of non-covalent modification by lignin; they also exhibit a decent rise in storage modulus and a modest electrical conductivity. As such, our sustainable production route can produce highly durable multifunctional nanocomposites that can be potentially used as antistatic coatings. A detailed mechanism will be proposed to explain the observed two-dimensional healing process in which the healing progresses uniaxially at each phase.

4.2 EXPERIMENTAL SECTION

4.2.1 Materials

Natural graphite flake (43319, 10 mesh, 99.9%) was obtained from Alfa Aesar (USA). AL-lignin was purchased from TCI America (USA, TCI product number: L0082, softwood lignin) and used as received. Polyurethane (Alberdingk ® U 3251), purchased from Alberdingk Boley Inc., USA, was an aqueous, anionic, solvent-free, low viscosity dispersion of an aliphatic polyester-polyurethane without free isocyanate groups. The average particle size by volume of WPU is 85 nm and its Zeta potential is -40.4 mV at pH value of 7.0.

4.2.2 Preparation of LMG

LMG was produced by adding pristine graphite to lignin aqueous solution (0.5 mg/ml) followed by tip sonication for 8 h based on a method reported in our previous work.¹⁴ The content of LMG trapped between graphene layers was measured to be 10wt% using TGA.

4.2.3 Preparation of WPU/LMG Nanocomposites

WPU/LMG nanocomposites were prepared by adding a desired amount of WPU to LMG aqueous solution, bath sonication for 1.5 h, and then casting in petri dish in an oven at 50 °C. The films with a typical thickness of ~120 μm were carefully removed for further characterizations.

4.2.4 Characterization

UV-vis spectroscopy was performed on a UV-2501PC (Shimadzu Corporation). Field emission scanning electron microscopy of graphene was carried out on a JEOL JSM-6340F Field Emission Scanning Electron Microscope. The top-view micrographs of graphene belong to samples obtained from drying graphene solution on a conductive substrate. The cross-sectional micrographs of WPU/LMG nanocomposites were obtained using a JSM-7600F Schottky Field Emission Scanning Electron Microscope. The cross-sectional micrographs of WPU/LMG nanocomposites belong to cryogenically fractured samples that were coated with Au for 30 seconds. Raman spectrometry was acquired with a confocal Raman microscope (alpha300, WITec, Ulm, Germany) equipped with a 488-nm laser source and a 20X Nikon objective lens. Each Raman spectrum was acquired for 60s using 0.5s integration time. Dynamic mechanical analysis was carried out on a DMA Q800 (TA Instruments, USA). The frequency sweep data were recorded in the range of 1 to 10 1/s at an amplitude of 1% to remain in the viscoelastic region. The width of the specimens was ~6.3 mm and the lengths were between ~15-20 mm. A Philips InfraPhil lamp (PAR38E E27) with a wavelength spectrum showing a pronounced peak at about 1100 nm was used to induce self-healing. UV-induced degradation was done in an Atlas Suntest XXL+ UV

lamp chamber, with an internal reflective Al layer to ensure equal UV exposure to all specimens. UV irradiation was conducted at black standard temperature (BST) of 55 °C with light intensity of 50 W/m² (300-400nm). Specimens were exposed to UV energy dosage of 180 Kj/m²h. The electrical conductance of graphene films was measured on a resistivity/sheet resistance measurement station (Advanced Instrument Technology, Model: CMT-SR2000N) using the four-probe method.

4.3 Results and Discussions

4.3.1 Aqueous-only Route to WPU/Graphene Nanocomposites

As mentioned in the introduction, in this work, a small amount of lignin was used as surfactant to exfoliate graphite and stabilize graphene aqueous suspension¹⁴ because it satisfies three conditions: it is water-soluble, it is from a sustainable source, and it can potentially add secondary functionalities in addition to stabilizing graphene suspension. The FESEM image in Figure 4.1A shows the lateral size of LMG flakes after freeze drying. Figure 4.1B shows a curled-up bi-layer LMG with a flake size of several microns, as observed by TEM. LMG aqueous dispersions can be stable for months (Figure 4.1C). The cast films produced by LMG are macroscopically uniform at first glance (Figure 4.1C inset). Figure 4.1D shows the Raman spectra of graphite and LMG, both of which mainly dominated by the G band located at ~1584 1/cm, attributed to sp² carbons. Nevertheless, LMG shows a noticeable D band at ~1352 1/cm, and a broader 2D band at ~2700 1/cm (Figure 4.1E) both of which indicating the presence of structural disorder caused by edge and/or plane defects, as shown in Figures 4.1F and 1G respectively.¹⁷ After a large number of TEM observations, only sporadic planar defects were observed and the majority of LMG sheets had intact planes. We, therefore, attribute the rise in disorder to edge defects mainly, which, unlike planar defects, do not disrupt the functional properties of graphene. LMG produced using this method has a single-layer yield of about 13% with 70-75% of flakes having numbers of layers less than four. In terms of length, about 60% of the measured flakes have lengths between 0.5-2 μm.

Figure 4.1. top-view FESEM micrograph of LMG showing typical flake size (A), TEM observation of an isolated bi-layer LMG with a flake size of several microns (B), LMG dispersion showing little precipitation after two months of storage, the inset shows a WPU/LMG film after solution-casting (C), Raman spectra of graphite and LMG (D), detailed 2D band for graphite and LMG (E), TEM micrographs showing defects caused by ultrasonication on edge (F) and plane (G) of LMG.

Figures 4.2A-C show low-magnification FESEM micrographs of WPU/LMG nanocomposites containing 1wt% (2A), 3wt% (2B), and 5wt% (2C) LMG. The low-magnification FESEM micrograph of unloaded WPU is similar to that of WPU/LMG 1wt% and hence is not included. Figure 4.2A shows a smooth fracture surface for WPU/LMG 1wt% with sporadic features. Since LMG cannot be seen on the fractured surface, it is safe to assume that the level of LMG dispersion is very high. In case of WPU/LMG 3wt% (Figure 4.2B), a more feature-rich fracture surface can be seen that is mainly due to protruding agglomerated LMG stacks. For WPU/LMG 5wt% (Figure 4.2C), the fracture surface has considerably more protruding LMG agglomerations. Figures 4.2D and 4.2E show a comparison between the states of LMG agglomeration for 3 and 5wt% WPU/LMG nanocomposites. As can be seen, the prevalence of agglomerations, i.e., boxed areas, is significantly higher in case of 5wt% WPU/LMG nanocomposite film. This suggests a

deterioration in LMG dispersion at higher LMG content, which is attributed to increased spatial hindrance imposed on LMG sheets.

Figure 4.2. Low magnification FESEM micrographs of the fractured surfaces of WPU/LMG nanocomposites containing 1wt% (A), 3wt% (B), and 5wt% (C) LMG. A comparison of the states of agglomeration, boxed areas, in WPU/LMG nanocomposites containing 3wt% (D) and 5wt% (E) LMG.

4.3.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis was conducted to determine the elastic modulus of the films, since it is more sensitive to the structural changes than viscose modulus. Figure 4.3A shows the elastic moduli of the samples in the frequency range of 1-10 1/s. Figure 4.3B shows the elastic moduli of the films at the frequency of 5.4 1/s for WPU and WPU/LMG films. Adding 1, 3, and 5wt% LMG increased the elastic modulus by about 40, 50, and 171%, respectively. The rise in elastic modulus is a result of restrictions imposed on polymer chains movement by LMG sheets. Restricted chains cannot easily conform to induced strain and relax external stress.

Figure 4.3. Elastic modulus of unloaded WPU and WPU/LMG nanocomposite films versus frequency (A). Elastic modulus of unloaded WPU and WPU/LMG nanocomposite films at the frequency of 5.4 1/s (B).

4.3.3 Self-Healability

Inevitability of sustaining damage makes self-healing one of the most important properties of coating materials, since self-healable materials can remove the effects of damage and prolong their service life. Our first qualitative assessment using a light microscope show that a 90s period of IR irradiation can heal a macro damage in a WPU/LMG 1wt% (Figures 4.4A). For comparison, an unloaded WPU film was cut (Figure 4.4B) and left under identical conditions to heal. it can be observed that unloaded WPU does not respond to IR and hence does not self-heal. In case of WPU/LMG 1wt%, a minor scar after 90s of irradiation can still be observed. By increasing irradiation time to 150 s, however, no scar was observed in all three loaded samples (Figures 4.4C-4.4E). A more quantitative measure of self-healability can be done by defining a recovery ratio, using any physio-mechanical property. Here, the recovery ratio is defined as the ratio of elastic modulus after placing a cut to its corresponding value of the virgin state. The cuts were placed by a razor blade on the middle of the films, parallel to the widths of the specimens, with ~ 3 mm lengths. Over the frequency range studied, the results, depicted in Figure 4.5A-D, show almost no increase in recovery ratio for unloaded WPU but a marked rise in recovery ratios for all the loaded samples, after 150s of IR irradiation. As shown in Figure 4.5E, the recovery ratios after 150s of IR irradiation seem to be independent of LMG contents.

In this system, self-healing is governed by polymer chains diffusion and subsequent re-entanglement. Chain diffusion is not Fickian in that it is not driven by concentration gradient but rather by number of available conformations gradient. Ergo, chains diffuse from the bulk with lower number of available conformations to the interface created by damage with higher number of available conformations, which is due to higher free volume at the interface. Because entropy changes for polymer chains are considerably small due to confinement by surroundings, chain flexibility, indicated by T_g , becomes very important. Enthalpy change, contributed by introducing stimuli-responsive components, can also affect self-healability. Therefore, upon introduction to WPU, LMG sheets can act as nanoheaters throughout WPU and provide ultrafast heat transfer to surroundings.¹⁸⁻¹⁹ Theoretically, the effect of temperature on diffusion can be described through reptation diffusion coefficient $D_c \sim T e^{-\frac{Q_d}{kT}}$ where T , Q_d , and k are temperature, activation energy of diffusion, and Boltzmann constant. Considering the rise of temperature can also temporarily reduce crosslink density, resulting in a decrease in the activation energy for diffusion (Q_d), an increase in temperature can contribute to an increase in diffusion coefficient.

Figure 4.4. Self-healing of WPU/LMG 1wt% nanocomposite (A) and unloaded WPU (B) after IR irradiation for 90s. Self-healing of WPU/LMG 1wt% (C), 3wt% (D), and 5wt% (E) nanocomposites after IR irradiation for 150s.

Figure 4.5. Recovery ratios for Unloaded WPU (A), WPU/LMG 1wt% (B), WPU/LMG 3wt% (C), and WPU/LMG 5wt% (D) in the frequency range of 1 to 10 1/s, after 150s of IR irradiation. Effect of 150s of IR exposure on the recovery ratios at the frequency of 5 1/s for loaded and unloaded samples (E).

Observing the evolution of self-healing for WPU/LMG indicates that for a macroscale cut, self-healing is a two-dimensional process, but it only progresses along one axis at each point in time. It means that the healing process does not take place along both the cut axis, denoted by x , and the axis perpendicular to it, denoted by z , simultaneously (Figure 4.6); but rather, healing first proceeds along the x -axis, at the base of the cut, and only after complete healing at the base, healing progresses along the z -axis and reaches the top of the cut.

We propose the following mechanism to explain this self-healing behavior: while placing the cut, the blade forces the created surfaces away from each other. A portion of the stress created in this process is stored in the bulk due to the viscoelastic nature of the polymer. After the removal of the blade, the stored stress is released resulting in the two surfaces coming back together and forming an intimate contact interface (stage 1 in Figure 4.6A). This response to damage is called viscoelastic recovery response and it has been observed in different systems (Figure 4.7).²⁰ Concurrently, due to surface-tension-driven viscoelastic restoration (Figure 4.8), the surfaces at the base of the cut start to approach each other while the ones at the top of the cut move away from each other.²¹ Upon IR irradiation, diffusion rate significantly increases along y -axis at the tip of the cut and healing progresses along the x -axis, but initially only at the base of the cut because surface-tension-driven viscoelastic restoration aids and expedites diffusion at the bottom of the cut. Since the same

phenomenon pulls the surfaces at the top away from each other, self-healing along z-axis is not dominant in this phase. After the whole cut is healed at its base along x-axis, i.e., end of phase one, self-healing proceeds along z-axis, i.e., start of phase two. Figure 4.6B shows a schematic representation of this moment, at which the whole cut is “zipped up” at the bottom along x-axis and the “zipping up” along z-axis starts, i.e., transition from phase one to phase two. Diffusion-driven self-healing is a multi-stage process, consisting of approach, wetting, diffusion, and randomization (Figure 4.9A and 9B). Approach can happen by the help of viscoelastic recovery response at the tip of the cut or surface tension driven viscoelastic restoration at the base of the cut. In the second stage, i.e., wetting, hypothetical spheres enveloping each chain come in contact with each other forming a point on the interface plane, akin to nucleation step in crystallization of spherulites. Afterwards, the inter-diffusion of these two chains results in the growth of the healed area around the nucleus, similar to the growth of spherulites. The growth continues until both chains reach an equilibrium state of inter-diffusion. This inter-diffusion brings other polymer chain pairs together. Figure 4.9 C-H show how the continuation of this process can result in the healing of the two interfaces through nucleation, growth, impingement, and finally coalescence of healed areas. The inter-diffusion mechanism has strong resemblance to the theory put forth by Avrami, Johnson, and Mehl to describe polymer crystallization. However, it should be mentioned that this is just a figurative analogy to better conceptualize the self-healing process and no actual nucleation takes place. The last step of self-healing is randomization in which the history of the interface is forgotten, and the properties of the specimen is restored to its pre-cut stage, in an ideal scenario. A rise in temperature affects all these stages of self-healing. For example, it can affect wetting stage by influencing both nucleation density and growth rate of wetted areas.

Figure 4.6 Evolution of self-healing can be divided into two distinct phases: healing of the cut along x-axis, stages 1-4, and healing of the scar along z-axis, stages 5-8 (A). Schematic 3D representation of transition from phase one to phase two when self-healing has “zipped up” the cut along x-axis and proceeds with “zipping-up” along z-axis (B).

Figure 4.7 Schematic view of viscoelastic recovery response.

Figure 4.8 Surface-tension-driven viscoelastic restoration pushes the surfaces at the top away from each other while the surfaces at the bottom of the film approach each other.

Using GO to produce self-healable films results in both enthalpic and entropic penalties. First, oxygenation disrupts the aromatic, conjugated character of graphene sheets, resulting in lower IR absorption. In addition, due to interactions between GO functional groups and polymer chains, T_g can increase as well.²²⁻²⁵ Reduction can restore some of IR absorbance

of graphene²⁶⁻²⁷ and reduce the number and diversity of functional groups, hence decrease the amount of constraining interactions with polymer chains. However, at least 20% of sp³-hybridized carbon cannot be removed by reduction.²⁸ Moreover, rGO solutions are unstable without a secondary surface modification.²⁹⁻³⁰ In comparison to GO and rGO, our LMG can be produced through a simple one-step aqueous process and can have higher photothermal conversion efficiency due to intact sp² structure. What is more, as evidenced by DSC, data not included, LMG does not noticeably increase the T_g of WPU, hence no entropic penalty. The improvement in self-healing can be linked to the difference between healing temperature and T_g. Above T_g, any increase in this temperature difference is beneficial to self-healing. An empirical theory of self-healing provided by wool³¹ states the relationship between recovery ratio (R) and healing time such that:

$$R \simeq 1 - \frac{1 - R_0}{(1 + Kt_h)^\alpha}$$

In which R₀, K, and α are constants and t_h is healing time. The effect of temperature can be added to this equation by using empirical models such as William-Landel-Ferry or Arrhenius equation³²⁻³³. However, since both equations predict an increase in diffusion as temperature increases and determining the exact form of temperature dependence of self-healing is outside the scope of this study, Arrhenius equation will be used for its simplicity to describe the constant K such that:

$$K = K_0 e^{-\frac{E_a}{kT}}$$

In this equation, K₀, E_a, and k are exponentiation coefficient, activation energy, and Boltzmann constant, respectively. Based on this equation, an increase in temperature directly results in a fall in K. Also, since rising temperature results in the dissociation of physical crosslinks, and reduces E_a, it also further reduces K indirectly. A reduction in the value of K results in a rise in the recovery ratio or a fall in healing time.

Figure 4.9 Four stages of diffusion, from top to bottom: approach, wetting, inter-diffusion, and diffusion to equilibrium (A). Cross-sectional view of inter-diffusion as seen on the interface plane, from top to bottom: nucleation, growth, and growth to equilibrium. Nucleation and growth of chain pairs (C-E). impingement (F) coalescence (G) and total healing of the interfaces (H).

4.3.4 UV Stability

UV stability is an important property of coating materials. UV irradiation can generate reactive oxygen species (ROS) by partial reduction of molecular oxygen which can then degrade polymers and reduce their molecular weight by chain scission. This results in considerable fall in mechanical properties and eventually renders the material useless. For this reason, understanding how a certain material responds under UV exposure and attempting to alleviate the adverse effects of UV irradiation are critical. UV-induced degradation can be quantified by defining a retention ratio, which can be a ratio of any physio-mechanical property, e.g., storage modulus, after UV exposure to its corresponding value before UV exposure. After exposing unloaded WPU and WPU/LMG films to UV for a week, it was discovered that only nanocomposites have enough structural integrity for retention ratio measurements. Unloaded WPU loses its dimensional stability after three days so its retention ratio was recorded after only two days of exposure.

LMG contains about 10wt% lignin which means that WPU/LMG 1wt%, WPU/LMG 3wt%, and WPU/LMG 5wt% have about 0.1, 0.3, and 0.5wt% lignin. Since lignin has been shown to improve UV stability by exhibiting antioxidant properties,³⁴ efforts should be made to de-convolute the contributions to UV stability from lignin and graphene. So, the effect of lignin on UV stability was studied by producing WPU/lignin films with varying lignin contents. It was discovered that WPU/lignin films with lignin contents below 4.5wt% could not retain their dimensional stability after a week of UV exposure. Figure 4.10A shows the retention ratios in the frequency range of 1-5 1/s for WPU/LMG nanocomposites and WPU/lignin film with 4.5wt% lignin after one week of UV exposure. The results for unloaded WPU, which were recorded after only 2 days of exposure, are also included. To get a better perspective, retention ratios at the frequency of 5 1/s are plotted against exposure time in days (Figure 4.10B). The results from Figure 4.10B are also listed in Table 4.1. It can be seen that adding 4.5wt% lignin noticeably improves UV stability of the film. Discoloration in WPU/lignin films was observed after a week of exposure to UV, suggesting lignin consumption in the film (Figure 4.11). It can be observed that although adding 4.5wt% lignin significantly improves UV stability of WPU, this improvement falls

considerably short when compared to WPU/LMG 1wt%, which contains only 0.1wt% lignin. Therefore, this significant rise in UV stability of WPU/LMG films cannot be attributed to lignin but rather to graphene and/or a synergy between graphene and lignin.

Figure 4.10 Retention ratios in the frequency range of 1 to 5 1/s after a week of UV exposure for WPU/LMG nanocomposites and WPU/lignin film, and after two days of exposure for unload WPU film (A). Retention ratios, at the frequency of 5 1/s, vs exposure time for unloaded WPU, WPU/LMG, and WPU/lignin with 4.5wt% lignin (B). The inset compares the retention ratios of WPU/LMGs with different LMG contents and that of WPU/lignin film with 4.5wt% lignin.

Table 4.1 Retention ratios after 2 and 7 days for unloaded WPU, WPU/lignin with 4.5 wt% lignin, WPU/LMG 1wt%, WPU/LMG 3wt%, and WPU/LMG 5wt%.

Content	Retention Ratio after	
	2 days	7 days
Unloaded WPU	0.50	NA
WPU/Lignin 4.5wt%	0.83	0.35
WPU/LMG1wt%	0.90	0.62
WPU/LMG 3wt%	0.94	0.71
WPU/LMG 5wt%	0.96	0.78

Antioxidant properties of graphene seem to result from a combination of preventative and radical scavenging activities. For instance, graphene-based materials' excellent gas barrier property³⁵⁻³⁶ can improve antioxidant property by reducing the diffusion of oxygen inside the bulk of the polymer.³⁷ These materials can also prevent degradation by absorbing some of the harmful UV irradiation and converting it into heat.³⁸ This heat, however, may result in thermal degradation of WPU. Fortunately, the most common route to WPU degradation is the breakage of urethane link into initial reagents, i.e., isocyanate and alcohol, mainly

because this route takes place at a lower temperature and a higher rate.³⁹ Because of excellent impermeability of LMG, initial reagents cannot easily escape the bulk of the polymer, and some of them may reversibly link to form urethane bond after the external heat source is removed. This process dissipates some of UV irradiation and prevents it from permanently degrading WPU.

Figure 4.11 Discoloration of WPU/lignin film with 4.5wt% lignin after a week of UV exposure on a white PTFE sheet.

Graphene-based materials have radical scavenging properties as well. For example, rGO has shown a pronounced radical scavenging activity, higher than GO, suggesting that sp^2 carbon network is far more effective at radical scavenging than functional groups on GO.⁴⁰⁻⁴² Nonetheless, in addition to complications associated with reducing GO and re-dispersing rGO, rGO suffers from partial loss of sp^2 carbon. As a result, rGO has shown lower antioxidant activity than pristine or non-covalently modified graphene.³⁸ One can also entertain the possibility of synergistic relationships between the antioxidative properties of lignin and graphene through two different routes. First, one should note that the effect of lignin on improving LMG dispersion is reciprocal, i.e., at the same time graphene is dispersing lignin on a molecular level as well. This improvement in dispersion of lignin may give an additional boost to its antioxidative property.³⁴ Second, Wang *et al.*⁴³ have proposed that graphene, by acting as a substrate for free radicals, can make hydrogen atom and electron transfers between free radicals and antioxidant easier, which may further increase the antioxidative property of lignin.

4.3.5 Electrical Conductance

The conductance for filtrated LMG film on membrane was measured to be 3673 S/m. WPU/LMG 1wt%, WPU/LMG 3wt%, and WPU/LMG 5wt% show conductance values of $4.44\text{E-}4$, $8.13\text{E-}3$, and 0.276 S/m, respectively. This shows that conductance rose by about an order of magnitude each time LMG content increased by about 2-3wt%, as shown in Figure 4.12. These electrically conductive coatings are potentially useful for many applications,⁴⁴ e.g., corrosion prevention by passivation⁴⁵ and antistatic coatings.⁴⁶

Figure 4.12 Conductance of WPU/LMG nanocomposite films.

Figure 4.13 A, B, and C compare the conductivity of these coating materials with similar graphene-based nanocomposites with about 1, 3, and 5wt% loadings. Figure 4.13 D compares all the results from this study and similar results in literature in one graph. The results expand over 10 orders of magnitude. The Figure shows that the conductance of the films at 1 and 3wt% are decent. It can also be seen that at 5wt%, these coatings have the highest reported conductance compared to similar nanocomposite systems.

Figure 4.13 conductance of similar graphene-based nanocomposites for 1wt% (A), 3wt% (B), and 5wt% (C). All results are redrawn for more comprehensive comparison (D) ^{9, 47-58}

4.4 Conclusions

WPU/LMG nanocomposites were prepared using a facile, green, aqueous-only production route from pristine graphite. Because of the non-covalent nature of modification by lignin, the sp^2 structure of our LMG is unperturbed. Dynamic mechanical analysis shows a positive correlation between LMG content and storage modulus of the nanocomposite films. A 171% rise in storage modulus is achieved in case of WPU/LMG 5wt%. Self-healability measurements show a fast recovery from damage for all nanocomposite films. Unloaded WPU, however, does not show any IR-responsiveness. Moreover, LMG does not noticeably increase the T_g of WPU, and hence results in no entropic penalty for self-healing. The intact sp^2 structure of LMG also preserves its high photothermal conversion efficiency and, therefore, improves enthalpic contribution to self-healing. In addition, although the nanocomposite coatings display a two-dimensional healing behavior, at each phase the healing progresses uniaxially. The observation can be explained in terms of viscoelastic recovery response, surface-tension-driven viscoelastic restoration, and

polymer diffusion. What is more, WPU/LMG nanocomposites exhibit significant rise in UV stability, which can be attributed to LMG's preventive antioxidant activities such as UV absorption and gas impermeability, its radical scavenging properties, as well as the synergy between lignin and LMG. Finally, WPU/LMG nanocomposite films show decent conductance, as high as 0.276 S/m. Our self-healable and UV-resistant nanocomposites may, therefore, find applications as antistatic coatings.

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Chapter 5

An aqueous-only route to wearable, flexible, multi-stimuli responsive sensors based on lignin-modified graphene

A sustainable aqueous-only dip-coating approach is used to produce wearable sensors with sensitivity to multiple stimuli. The sensing mechanism is based on the change in the resistivity of the percolated graphene network placed on the skeleton of commercially-available PU sponges through dip-coating. Electron microscopy shows that under pressure, the number conduction pathways increase while the length of electron conduction decreases which result in a fall in resistivity. Electromechanical investigations show that these highly sensitive pressure sensors can detect compression up to -60% (equivalent to ~7MPa pressure) with sensitivity reaching as high as $S = 0.25 \text{ kPa}^{-1}$. In addition, the graphene network is sensitive to the change in temperature as well, which makes these sensors multi-stimuli responsive. The temperature sensitivity of these sensors reaches as high as $4.3\% \text{ C}^{-1}$. These sensors can have applications in smart clothing such as smart shoes and smart gloves.

5.1 Introduction

In the previous chapter, WPU/LMG nanocomposites were produced through a simple water-only production route. LMG played multiple roles such as being a photothermal convertor, forming an electrically conductive network, acting as a UV stabilizer, and improving mechanical reinforcement. The combination of these functions allowed the production of conductive nanocomposite coatings with high durability due to self-healing and UV resistance. These nanocomposite coatings can have antistatic coating applications. In this chapter, using a simple approach, sensitive multi-stimuli responsive sensors will be produced that are able to respond to pressure and temperature.

Pressure sensors are a subgroup of electromechanical sensors that transduce pressure into an electrical signal¹. These sensors have attracted huge attention in recent years and have potential applications in artificial intelligence, wearable electronics, and mobile biomonitoring devices²⁻³. In general, pressure sensors utilize different strategies to transduce pressure into an electrical signal. In optical pressure sensors, the intensity or wavelength of light which is guided through the pressure sensor is affected by pressure⁴⁻⁵. The second group of sensors use capacitance to measure pressure. Capacitance is the ability of a material to store electrical charge. The capacitance of a dielectric material is related to its geometry, which can change under deformation and therefore be linked to applied pressure⁶⁻⁷. Sensors based on piezoelectricity exploit the generation of an electrical potential that is created when certain crystals undergo deformation. The electric charge created is proportional to the applied pressure that has generated it⁸⁻⁹. Finally, piezoresistive sensors work based on the piezoresistive effect. This effect is observed when the resistance of a conductive material changes under deformation. Piezoresistive nanocomposite sensors have been thoroughly studied because of their low cost of fabrication, low energy consumption, ease of fabrication, production scalability, wide range of pressure detection, and easy signal readout. Thanks to their pliability, chemical stability, and flexibility, these sensors show great promise in a variety of applications such as health monitoring¹⁰⁻¹¹, E-skin¹²⁻¹³, and human-machine interface^{3, 14}. In general, piezoresistive sensors utilize different structures such as cracked structure, low-percolation

threshold conductive networks, and hierarchical nano-micro structures to transduce pressure into resistance change.

Graphene has recently seen a huge rise in pressure sensing applications. Recent advances in graphene-based materials have brought about major breakthroughs in production methods of flexible pressure sensors that are cheaper and upscalable with many potential attractive applications. There are different ways to fabricate graphene-based interconnected 3D structures including in-situ unzipping of carbon nanotubes ¹⁵, chemical vapor deposition ¹⁶, freeze-drying ¹⁷⁻²⁰ and self-gelation ²¹⁻²⁴. However, liquid-phase exfoliation of graphene coupled with dip-coating remains one of the simplest approaches to producing graphene-based pressure sensors. Pressure sensors can suffer from mechanically brittle performance or undergo considerable plastic deformation under compression which severely limits their applications. An ideal pressure sensor should have high endurance against structural collapse and negligible plastic deformation. One simple way to achieve these properties is to use commercially-available elastic foams with remarkable elasticity and considerable flexibility. Foams such as polyurethane sponges have been used by researchers to fabricate pressure sensors by simply placing a conductive network on their skeleton through dip-coating ²⁵⁻²⁶. Dong et al ²⁷ exploited the hierarchical structure of sea sponges as a substrate for rGO and silver nanowires. These sensors showed a large area detection range of 60% strain, a broad pressure range of up to 40 kPa, and excellent reproducibility above 7000 compression-release cycles. Ma and coworkers ²⁸ also used a hybrid rGO-MWCNT system to produce pressure-sensitive PU sponges. These low-density sponges demonstrated outstanding compression range with high sensitivity up to 5.6 kPa.

The sensing and measurement of temperature, as an important biological parameter, has become the focus of many studies. Wearable, flexible temperature sensors have therefore seen considerable attention recently ²⁹⁻³². These sensors have found applications in robotic sensors, soft devices, and electronic skin ³³⁻³⁶. Different types of flexible, wearable temperature sensors have been developed based on pyroelectricity, thermoresistivity, and thermistors. Pyroelectric effect is the change in polarization as temperature changes. Some

pyroelectric devices have been developed to measure temperature; despite their promising performance however, these devices were not flexible³⁷⁻³⁸. Resistive temperature detectors (RTDs), on the other hand, work based on the dependency of the electrical resistance of metals to temperature. Flexible RTDs have been developed based on pure metals such as copper, nickel, and platinum³⁹⁻⁴⁰. Although RTDs can measure a wide temperature range, their sensitivity is usually lower than the next class of temperature sensors, i.e., thermistors. A thermistor is an electrical resistor whose resistance can be significantly influenced by the change in its temperature. Thermistors can be divided into negative-temperature coefficient (NTC), which show a decrease in resistance with increasing temperature, and positive-temperature coefficient (PTC) types, which experience a rise in resistance as temperature goes up. First attempts at producing flexible temperature sensors were made by miniaturizing already available classical thermistors such as transistors on a flexible body². Recent efforts however rely on composite⁴¹ and nanocomposite materials based on carbon nanotubes⁴²⁻⁴⁴, Ni particles⁴⁵, and graphene⁴⁶.

In contrast to numerous studies on wearable, flexible sensors, fewer studies have dealt with multifunctional sensors. In addition, many of these multifunctional sensors can only sense different modes of only one stimulus: for instance, compression, strain, or torsion, which are different modes of mechanical deformation⁴⁷⁻⁴⁹. As a result, except for a few studies⁵⁰, the development of multifunctional sensors that can respond to different stimuli has seen much less attention. The aim of this study is therefore to propose a simple production route to multi-stimuli responsive sensors that are sensitive to both deformation and temperature using lignin-modified graphene and commercially-available sponges. Compared to literature, our method does not require any chemical other than water or any secondary conductive network based on nanotubes, nanowires, or conductive polymers such as PEDOT:PSS.

5.2 Experimental Methods

5.2.1 Materials

Natural graphite flake (43319, 10 mesh, 99.9%) was obtained from Alfa Aesar (USA). AL-lignin was purchased from TCI America (USA, TCI product number: L0082, softwood lignin) and used as received. Commercially available PU foams are used as elastic substrates on which graphene flakes are assembled. These foams show excellent elasticity and high durability.

5.2.2 Preparation of LMG

LMG was produced by adding pristine graphite to lignin aqueous solution (0.5 mg/ml) followed by tip sonication for 8 h based on a method reported in our previous work⁵¹. The content of LMG trapped between graphene layers was measured to be 10wt% using TGA.

5.2.3 Preparation of PU/LMG sensors

Sensors were produced by dip-coating of commercially available PU sponge in LMG aqueous suspensions and evaporating the water in an oven. This process repeated several times to achieve electrical conductivity in the sponges. Then two copper electrodes were planted on both sides of the sponges as current collectors.

5.2.4 Characterization

The PU/LMG sponges were observed under a JSM-7600F Schottky Field Emission Scanning Electron Microscope. Samples that were coated with Pt for 30 seconds. Dynamic mechanical analysis was carried out on a DMA Q800 (TA Instruments, USA). The resistance measurements were carried out using a two-probe setup on an Autolab apparatus (Metrohm Autolab, the Netherlands).

5.3 Results and Discussions

5.3.1 Preparation of PU/LMG Sensors

Figure 5.1 shows the process based on which from pristine graphite, lignin, and water multifunctional sensors are prepared. In this process, after sonication and centrifugation, the suspension is filtered and rinsed to remove free lignin. The LMG film is then re-dispersed in water through bath sonication to produce LMG aqueous suspension. PU sponge pieces are then dip-coated in LMG aqueous suspension and placed inside an oven to evaporate water. This step is repeated until the sponge becomes conductive. Afterwards, two copper tapes are attached on both surfaces of the sponge and reinforced by silver paste. These copper tapes will act as current collector and will be connected to an equipment that can measure and monitor electrical current.

Figure 5.1 Schematic representation of production of low-density PU/LMG multifunctional sensors.

5.3.2 Morphology of PU/LMG Sensors

Figure 5.2 A shows the morphology of a dip-coated PU sponge at rest at very low magnification. This figure gives an idea of the structure and the pore size of the sponge. To observe LMG on the skeleton of the sponge, an FESEM micrograph with higher magnification is presented in Figure 5.2 B showing LMG sheets attached to the skeleton. The percolated network created by these LMG sheets is responsible for the conductivity of these sponges. Figure 5.2 C shows that in addition to the connected skeleton, there are plenty of “dead-ends” in the sponge, which unlike the connected skeleton do not contribute to the conductivity of the sponge. The effect of compression on the structure of the sponge is seen in Figure 5.2 D. Here, the imposed pressure, in the horizontal direction, has dramatically warped the skeleton. As will be discussed in more detail in the following sections, the resistivity of the sponge decreases under compression. FESEM observations provide clear evidence as to why resistance falls under pressure.

As can be seen in Figure 5.2 E, under pressure, some dead-ends start to connect to the skeleton, which will create more pathways for electron transfer, resulting in a fall in electrical resistance. Figure 5.2 F shows another mechanism under which resistance falls with increasing pressure. It can be seen that adjacent PU skeletons come in contact with each other under compression. This allows the electrons to transport through the created contact points instead of traveling along the skeleton. The created shortcuts reduce the conduction path which is proportional to resistance.

Figure 5.2 low magnification FESEM micrograph of a dip-coated sponge at rest (A). high magnification FESEM micrograph of the same sponge at rest showing LMG sheets attached to the skeleton (B). Several dead-ends in PU skeleton not contributing to the conduction (C). Change in the shape of skeleton under compression (D). Dead-ends connecting under compression, increasing the total number of pathways (E). Adjacent skeletons coming in contact under compression creating shortcuts for electron transfer and reducing conduction path.

5.3.3 Electromechanical Properties of PU/LMG Pressure Sensors

Figure 5.3 shows the mechanical and electromechanical properties of a typical PU/LMG pressure sensor. The strain-stress curve shows a linear rise in stress as strain increases up to 40%, above which stress rapidly rises. Pressure-strain behavior of the sensors follows a similar trend. The non-linearity of pressure-strain curve is well-known for polymeric sponges and it is one of the main drawbacks of using sponges for pressure sensors. When resistance ratio, i.e., ratio of resistance after compression over its corresponding value before compression, is plotted against strain, a somewhat linear relationship can be observed. This linear relationship however is nonexistent between resistance ratio and pressure. The reason for this nonlinear behavior can be seen in Figure 5.3 B. Based on this graph it can be seen that an increase in pressure results in much higher compression at lower strains compared to higher strains. Since, the relationship between strain and resistance ratio is roughly linear, an increase in pressure results in much higher change in resistance ratio at lower pressures than higher ones. As shown in Figure 5.3 D, at low pressures the sensitivity is high, $S=0.25 \text{ kPa}^{-1}$, while at high pressures, the graph starts to level off and the sensor loses its sensitivity, $S=0.03 \text{ kPa}^{-1}$. Table 5.1 introduces different pressure sensing systems based on graphenic conductive networks and lists their sensitivities. Sensitivity is defined as the change in conductance of the sensors as a result of imposed pressure divided by conductance at rest (no pressure) normalized by corresponding change in pressure. To ascertain that the sensors are appropriate for prolonged use, the resistance ratio behavior of the sensors were monitored over numerous compression-release cycles, as shown in Figure 5.4 A. The comparison between initial cycles, Figure 5.4B, with final cycles, Figure 5.4C, suggests good repeatability of the electrical signal and high durability of sponge.

Figure 5.3 Typical stress-strain behavior (A) and pressure-strain behavior of a PU sponge (B). Resistance ratio versus strain (C) and versus pressure for a typical PU/LMG sensor (D).

Table 5.1 Pressure sensing systems based on different graphenic conductive networks and their sensitivities.

Pressure sensing system	Sensitivity (kPa^{-1})
Graphene–polyurethane sponge based on fractured microstructure design ⁵²	0.26
Foam-like structure based on laser-scribed graphene ⁵³	0.96
Self-assembled graphene flakes on PU sponge ⁵⁴	0.12
Reduced graphene oxide aerogel improved mechanically by water-soluble polyimide ⁵⁵	0.18
PDMS foams loaded with multilayer graphene nanoplatelets ⁵⁶	0.23
Carbonaceous nanofibrous aerogels with an ordered honeycomb-like structure ⁵⁷	0.43
Sea sponges and composites conductive networks of polydopamine reduced graphene oxides and silver nanowires ²⁷	0.016

Figure 5.4 Resistance ratio of a typical PU/LMG sponge over 5000 compression-release cycles (A). Resistance ratios in the beginning and the end of measurements for 50 compression-release cycles (B).

5.3.4 Electrothermal Response of PU/LMG Sponges

Another stimulus to which LMG is responsive is temperature. In general, two different strategies exist in producing flexible temperature-sensitive conductive nanocomposites. The first approach relies on the thermal expansion of a polymer matrix with a large expansion coefficient, e.g., PDMS, with a conductive network slightly above the percolation threshold. In this scenario, thermal expansion of the matrix can result in the conductive network to fall below its percolation threshold and experience a fall in conductivity, which results in a PTC behavior of the sensor. Yang *et al.* used this strategy to produce wearable graphene/PDMS temperature sensors³⁴. The second approach relies on the NTC behavior of graphene when the conductive network is slightly below the percolation threshold. Figure 5.5 shows the resistance ratio of PU/LMG sensors at different temperatures to the one at room temperature. It can be seen that the resistance falls with an increase in temperature. This drop, however, is more prominent at lower temperatures where the sensor has a high temperature sensitivity of $4.3\% \text{ } ^\circ\text{C}^{-1}$ and it becomes less prominent at higher temperatures. Here, the effect of temperature on the electrical resistance of the sensors is twofold: an increase in resistance due to the expansion of the sponge and a reduction in resistance due to the NTC behavior of graphene. The overall

thermal behavior of the sensor shows that the effect of the NTC behavior of graphene is much larger than the thermal expansion of the sponge because the sponges are slightly below the percolation threshold and therefore thermal expansion does not noticeably change electrical conductivity. Table 5.2 introduces different flexible, wearable temperature sensing systems and lists their sensitivities. Here, sensitivity is defined as the change in resistance of the sensors as a result of change in temperature divided by initial resistance, normalized by corresponding change in temperature.

Figure 5.5 Resistance ratio as a function of temperature

Table 5.2 Several temperature sensing systems based on different conductive networks and their sensitivities.

Temperature sensing system	Sensitivity %°C ⁻¹
GNW/PDMS nanocomposites ³⁴	21.4
Solar exfoliated reduced graphene oxide on PI substrate ⁵⁸	0.74
PEDOT:PSS/CNT temperature sensors ⁵⁹	0.61
Inkjet-printed temperature sensors, based on carbon and PEDOT:PSS ⁶⁰	0.25
deposited polyaniline on a PET substrate ⁶¹	1

5.3.5 Applications

Pressure sensors based on conductive sponges can have applications in diverse fields such as artificial intelligence, biomechanical studies, E-skin, and so forth. Because of their light weight they are particularly useful in smart clothes and wearables. Although current smart wearables are typically worn on wrist, the applications are being vastly extended beyond these common devices.

Smart clothing which is estimated to have a 2.4-million USD market share today is forecast to reach 1.2 billion USD by 2021. In hospitals, pressure sensors can be implemented in mattresses and bedsheets to monitor patients who are prone to bed sores to make sure that they move sufficiently in bed. They can also be integrated with soft robotics to empower patients who are vulnerable to fall. Shoe industry, in particular, has shown great interest in the implementation of pressure sensors in emerging smart shoes.

So much has changed since pumping the air into the sole of the shoes were the latest technology. Recent advances in technology have made shoes more than mere footwears. Shiftwear® sneakers, for example, can change their colors to match any outfit. Designs, still or animation, can be downloaded from the internet through a smartphone and transmitted to the shoes to be displayed on them. From Powerlace® shoes that can lace themselves to levitating Moonwalker® shoes to tailor-made 3D printed in-soles, the innovation in footwear technology is rapidly moving forward and with that developing light, flexible pressure sensors is getting more attention. Pressure sensors can be embedded in footwear and enable the shoes to track activity, count stairs, act as a pedometer and so forth. Although current wrist-top fitness trackers found on fitness bands and smart watches can perform these tasks as well, their accuracy is still questionable since these data are not measured directly but rather indirectly interpreted from accelerometer data. Moreover, smart shoes can gather additional data such as flight/contact time ratio, planar foot pressure, and feet strike patterns which cannot be collected by fitness bands. These data can be used for motion analysis in sports science to train athletes more efficiently or for rehabilitation purposes after injury. Figure 5.6, shows how our pressure sensors can distinguish the

pressure patterns created from walking and running, count steps, and measure flight/contact ratio. Pressure sensors can be used in other forms of smart wearables as well. Smart gloves are another form of smart wearables that can use pressure sensors to monitor the movement of fingers. Figure 5.7 shows how different finger movement can produce different electrical signals. One interesting application of smart gloves is the translation of sign language into speech.

Figure 5.6 Resistance ratios during walking and running gathered from a pressure sensor planted under the toe.

Figure 5.7 Change in resistance ratio for different finger movements

5.4 Conclusions

A sustainable, aqueous-only route to produce multifunctional pressure and temperature sensor was presented. Through a simple dip-coating of commercially-available sponges in the aqueous suspension of lignin-modified graphene, electrically conductive sponges with high sensitivities to pressure, $S = 0.25 \text{ kPa}^{-1}$, and temperature, $S = 4.3\% \text{ }^{\circ}\text{C}^{-1}$, were produced. These sensors showed high stability over 5000 compression-release cycles. PU/LMG pressure sensors can have applications in the emerging field of smart clothing. They can

be implemented in smart shoes to monitor activity, count steps and stairs, calculate flight/contact time ratio, map planar foot pressure, and track feet strike patterns or in smart gloves to monitor finger movement. It can be argued that this environmentally-friendly process can pave the way to the sustainable development of multifunctional sensors and materials.

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Chapter 6

Surfactant-Free, Aqueous Exfoliation of Graphite to Produce Skin-Conformal Electromechanical Sensors for Non-Invasive, Continuous Health Monitoring

Continuous health monitoring is an effective preventive measure that benefits patients' health and reduces healthcare costs. Here, a cheap, simple and environmentally friendly method to produce skin-conformal graphene-based polymer nanocomposite sensors for continuous health monitoring is presented. The sensors are facilely fabricated by aqueous exfoliation of pristine graphite using waterborne polyurethane (WPU) as stabilizer. WPU also plays the role of viscoelastic matrix in the nanocomposites, which improves skin conformality of the sensors. Using a filtration/precipitation method, a conductive network of exfoliated graphene flakes with a 3D random "house-of-cards" morphology is formed, resulting in noticeable electromechanical sensitivity at very small strains (gauge factor of ~ 70 at 0.1% strain). This 3D morphology also constrains time dependency of the electromechanical signal, which is frequently observed in sensors based on viscoelastic polymers. Owing to their high sensitivity and skin-conformality, these sensors can continuously monitor pulse, respiration, and minute soft-tissue deformations, as well as producing blood-pressure waveforms with marked precision.

6.1 Introduction

In Chapters 4, through an environmentally-friendly aqueous exfoliation, lignin was used to stabilize graphene in water. The produced lignin-modified graphene (LMG) was added to waterborne polyurethane (WPU) to prepare multifunctional WPU/LMG nanocomposites with fast self-healability and high UV-stability with antistatic coating applications. In Chapter 5, LMG was used to produce conductive PU sponges through a simple aqueous-only dip-coating process. These sponges showed high electrical sensitivity to deformation when subjected to pressure. They also showed electrical sensitivity to temperature changes as well. These multi-stimuli responsive capabilities made these sponges suitable for applications in smart clothing such as smart shoes and gloves. In this Chapter, this sustainable approach is taken one step further by attempting to remove lignin altogether. Polymers have shown to be great stabilizers for graphene exfoliation. If the polymer stabilizer and polymer matrix are the same, the final polymer/graphene nanocomposite will be void of any foreign stabilizer. In the previous chapter, pressure-sensitive electromechanical sensors were produced. Strain sensors are another type of electromechanical sensors that have attracted a lot of attention for their many potential applications, especially in continuous health monitoring.

Continuous health monitoring, such as constantly monitoring pulse, breath, and blood pressure waveforms beat-by-beat, can be a low-cost preventive measure that benefits patients' health and reduces healthcare costs. Recent advances in flexible and stretchable bio-electronic devices have introduced highly sensitive sensors that can deliver non-invasive continuous health monitoring. In particular, developing highly sensitive, flexible, electromechanical sensors based on graphene has become the current focus of the research community. For example, by infusing liquid-exfoliated graphene into natural rubber, Boland *et al.* produced conductive composites capable of monitoring bodily motions, breathing, and pulse.¹ Li *et al.*² used Marangoni effect to produce sensors capable of detecting pulse and recognizing sound signals. Shi *et al.*³ used graphene platelets, produced from thermally expanding a graphite intercalation compound, to fabricate highly sensitive, wearable strain sensors capable of detecting pulse, recognizing sound, and monitoring joint

movement. Similar studies have also been conducted by Zhao *et al.*,⁴ Wang *et al.*,⁵ Lin *et al.*⁶ and others.⁷⁻¹⁰ In general, increasing sensitivity by maximizing gauge factor, *i.e.*, the ratio of relative electrical resistance change to the applied strain, has been the primary focus of researchers. Nonetheless, it is also noted that high gauge factors obtained under simulated lab conditions may not necessarily result in excellent real-life performance of the sensors when attached on human body. To bridge this gap, one strategy is to improve skin conformality of sensors.

Skin-conformal sensors can have an intimate contact with the epidermis allowing them to pick up signals more precisely, resulting in higher spatial resolution and improvement in signal-to-noise ratio. The intimate contact also reduces the relative movement between the surface of epidermis and the sensor during high-speed motion detections. Several highly skin-conforming, ultra-sensitive sensors have been developed and employed to map macro and microvascular blood flow, thermally characterize human skin, study soft-tissue biomechanics, and monitor skin hydration.¹¹⁻¹⁴ These impressive devices, nevertheless, rely on sophisticated designs and complicated production routes. A relatively simpler approach to improve shape-conformality has been to attach an additional conformal layer on a sensor based on a non-conformal polymer. In a study, Pang *et al.*¹⁵ added an additional microhairy conformal layer to a sensor based on a non-conformal polydimethylsiloxane (PDMS) and increased signal-to-noise ratio by 12 times. Here, an effective yet simpler approach is presented that is to produce electromechanical sensors based on viscoelastic polymer matrices. Thanks to their viscous component, these polymers can conform to the shape of their substrates, while by combination with conductive fillers, the nanocomposites can maintain a level of elasticity that is necessary for sensors to function. The viability of using viscoelastic polymer bases for strain sensors have already been demonstrated. For instance, a sensor based on chewing gum and carbon nanotubes was produced by Darabi *et al.* and used for health monitoring.¹⁶ In another study, Boland *et al.* developed highly sensitive sensors capable of monitoring miniscule deformations, small pressures, and even impact by insects by incorporating graphene in a lightly crosslinked polysilicon, *i.e.*, Silly Putty.¹⁷ However, sensors based on highly viscoelastic polymers can show profound time dependency for the electrical signal, which is an undesired trade-off.¹⁷ To overcome this

trade-off, a graphene-based conductive network with a “house-of-cards” microstructure is desired. This microstructure may be stable enough to constrain the time dependency of the viscoelastic polymer matrix by immobilizing nearby polymer chains to form an elastic composite framework. Concurrently, the presence of tip-to-surface type of contact between graphene sheets in this structure may allow the conductive network to deform under even a slight external mechanical stimulus resulting in considerable sensitivity.

To realize a skin-conformal polymer nanocomposite with stable “house-of-cards” morphology, a cheap, simple, and environmentally friendly approach is formulated. Briefly, for the first time, waterborne polyurethane (WPU) was used as both a stabilizer to exfoliate pristine graphite and a viscoelastic polymeric matrix to enable skin-conformal polymer nanocomposites. Polymer stabilizers can create considerable spatial repulsion and provide sites for solvation while preserving the precious sp^2 structure of graphene.^{18,19} More importantly, the stabilizer-cum-matrix approach resolves a key issue arising from using small-molecule or “foreign polymer” stabilizers, i.e., detrimental effects of the small-molecules/foreign polymers on interfacial interactions and elastic performance of the resultant nanocomposites. For liquid exfoliation of graphite, only water which is the most economical and environmentally friendly solvent was used. Through a facile filtration-precipitation procedure, the exfoliated WPU-modified graphene (PMG) can form porous PMG films with “house-of-cards” microstructure, consisting of randomly oriented yet interconnected multilayer graphene sheets. After encapsulation with more WPU, the WPU/PMG nanocomposite films were studied in terms of electromechanical sensitivity, durability, and time dependency of their electrical signal. Herein, it will be demonstrated that skin-conformality of the nanocomposite films can indeed further increase the sensitivity of our sensors, which is already reasonably high at minute deformations with a gauge factor of 70 at 0.1% strain, and improve their real-life performance. Our sensors, owing to their high sensitivity and skin-conformality, can detect minute soft-tissue deformations and produce blood-pressure waveforms with marked precision, making them suitable for continuous health monitoring. The viscoelastic WPU endows the sensors with skin conformality without any time dependency for the electrical signal. What is more,

cyclic stability measurements show a narrow distribution for dynamic gauge factor, indicating satisfactory durability.

6.2 Experimental Methods

6.2.1 Materials

Natural graphite flake (43319, 10 mesh, 99.9%) was obtained from Alfa Aesar (USA). Waterborne polyurethane (WPU, Alberdingk ® U 3251) purchased from Alberdingk Boley Inc., USA, was an aqueous, anionic, low viscosity dispersion of an aliphatic polyester-polyurethane without free isocyanate groups. The average particle size by volume of WPU is about 85 nm and its Zeta potential is -40.4 mV at pH value of 7.0. Based on company's datasheet and verified by DSC measurement, the T_g of WPU is about -53 °C. The viscoelastic behavior of WPU was characterized using a dynamic mechanical analyzer in the linear viscoelastic region in the frequency range of 0.1 to 1 Hz.

6.2.2 Preparation of PMG

PMG was prepared by adding graphite to 200 ml WPU aqueous solution in a 250-ml beaker, followed by sonication. The mixture was then poured in 50 ml tubes and centrifuged at 600 rpm for 1.5 h, after which the top 30 ml was used and the bottom 20 ml was discarded. Different factors were considered to optimize the process. To investigate the effect of WPU concentration, WPU solutions with varying WPU contents ranging from 0.1 to 2 mg/ml were prepared. Then, 10 mg/ml of graphite was added to each solution and samples were sonicated for 4 h. To study the effect of initial graphite content, different amounts of graphite ranging from 10 to 80 mg/ml were added to 1.5 mg/ml WPU solutions and the mixtures were sonicated for 4 hours. Finally, to study the effects of sonication time, 10 mg/ml graphite was added to 1.5 mg/ml WPU aqueous solutions and sonicated for 2, 4, 6, and 8 hours.

6.2.3 Fabrication of WPU/PMG sensors

PMG porous films were produced using a process consisting of filtration of a PMG suspension through a 0.45 μm polytetrafluoroethylene (PTFE) membrane (Whatman®, Germany) for a few minutes, followed by turning off the vacuum pump to allow the suspension to precipitate slowly. Once a uniform porous PMG film was formed, excess suspension was removed meticulously, and the PMG film was dried. Afterwards, WPU was added onto the upper surface to infuse into the PMG films for reinforcement purpose. The WPU/PMG films were then removed from PTFE membranes, and cut into desired dimensions. Electrodes were planted on the bottom surfaces of the films, which were later coated with a layer of WPU.

6.2.4 Characterizations

UV-vis spectroscopy was performed on a UV-2501PC (Shimadzu Corporation, Japan). For each PMG solution, the absorbance was acquired by using a solution of the same WPU content as reference for background correction at the wavelength 660 nm. Transmission electron microscopy (TEM) was performed on a Libra® 120 Transmission Electron Microscope (Carl Zeiss, Germany). For TEM sample preparation, firstly, a graphene dispersion was diluted with water to produce an almost-colorless suspension. Then a drop of this suspension was placed on Cu grid. The grid was placed in an oven for the water to evaporate. Raman spectrometry was acquired with a confocal Raman microscope (alpha300, WITec, Ulm, Germany) equipped with a 488-nm laser source and a 20X Nikon objective lens. Each Raman spectrum was acquired for 60s using 0.5s integration time. Field emission scanning electron microscopy (FESEM) of graphene was carried out on a JSM-7600F Schottky Field Emission Scanning Electron Microscope. The cross-sectional FESEM micrographs of WPU/PMG nanocomposites were obtained from cryogenically fractured WPU/PMG nanocomposite films embedded in epoxy. Mechanical deformations were carried out by a Dynamic Mechanical Analyzer (DMA) Q800 (TA Instruments, USA). The resistance measurements were carried out using a two-probe setup on an Autolab apparatus (Metrohm Autolab, the Netherlands).

6.3 Results and Discussion

6.3.1 Preparation of WPU/PMG Nanocomposite Films

The viscoelastic polymer used in this work is a waterborne aliphatic polyester-polyurethane (WPU) with glass transition temperature (T_g) of $-53\text{ }^{\circ}\text{C}$. Figure 6.1 schematically presents the production route from WPU and pristine graphite to highly sensitive WPU/PMG sensors. Firstly, a mixture of graphite in WPU aqueous solution was sonicated and then centrifuged. In order to optimize the exfoliation process, vital parameters such as WPU content, duration of sonication, and initial graphite content were optimized based on the yield of the exfoliated PMG, estimated using UV-vis absorption of the PMG suspension.⁷ In Figure 6.2, graphs on the left side show UV-vis absorption curves and the ones on the right side show absorption values at the wavelength of 660 nm, corresponding to graphene yields. It can be seen in Figures 6.2 A and B that the PMG yield increases with increasing WPU content up to 1.5 mg/ml, above which the PMG yield decreases. An increase in the initial graphite content usually results in an increase in graphene yield.¹⁸ We, however, observed an optimum amount for initial graphite content, 20 mg/ml, above which the PMG yield started to fall drastically (Figure 6.2 C and D). In the end, the effect of sonication time on PMG yield was studied. Typically, an increase in sonication time results in a rise in graphene yield,¹⁹ albeit at the expense of lateral size of the obtained graphene flakes. Nonetheless, again, an optimum value for sonication time, i.e., 4h, was observed above which a sudden fall in PMG yield was observed (Figures 6.2 E and F).

To ensure that few-layer PMG is successfully produced, AFM was used to estimate the typical thickness of PMG. Our AFM scans on mica substrates, presented in Figure 6.3, show that the thickness of PMG layers on mica is less than 10 nm, proving successful production of few-layer PMG. AFM micrographs, together with FE-SEM micrographs of PMG layers on mica (Figure 6.4), can provide an idea of PMG flake size.

In Figure 6.5A, a typical TEM micrograph also shows a four-layer PMG with two single layers and one bi-layer, judging by their edges. Finally, Raman spectroscopy, which has

been widely used to confirm successful production of graphene, shows a dominant G band at ~ 1584 $1/\text{cm}$, attributed to sp^2 carbons, for both pristine graphite and PMG (Figure 6.5B). Nevertheless, an evident D band at ~ 1350 $1/\text{cm}$ is present for PMG. The increase in D/G ratio from 0.09 for pristine graphite to 0.45 for PMG is a clear sign of the presence of few-layer graphene. Figure 6.5C shows that the 2D peak of PMG also becomes wider with its full width at half maximum increasing from 62 to 77, and its position downshifts from 2732 to 2710 $1/\text{cm}$. All these results indicate successful production of few-layer PMG.

Figure 6.1 WPU/PMG sensors from production to application

In Figure 6.5A, a typical TEM micrograph also shows a four-layer PMG with two single layers and one bi-layer, judging by their edges. Finally, Raman spectroscopy, which has been widely used to confirm successful production of graphene, shows a dominant G band at ~ 1584 $1/\text{cm}$, attributed to sp^2 carbons, for both pristine graphite and PMG (Figure 6.5B). Nevertheless, an evident D band at ~ 1350 $1/\text{cm}$ is present for PMG. The increase in D/G ratio from 0.09 for pristine graphite to 0.45 for PMG is a clear sign of the presence of few-

layer graphene. Figure 6.5C shows that the 2D peak of PMG also becomes wider with its full width at half maximum increasing from 62 to 77, and its position downshifts from 2732 to 2710 $1/\text{cm}$. All these results indicate successful production of few-layer PMG.

Figure 6.2 UV-vis absorption curves (left) and absorption values at 660 nm (right) for PMG aqueous solutions prepared at different WPU contents (A,B), initial graphite contents (C,D), and sonication time (E,F).

Figure 6.3 AFM scans of PMG on mica substrate

Figure 6.4 FESEM micrographs of typical few-layer PMG on mica. The scale bar is 1 micron.

In Figure 6.5A, a typical TEM micrograph also shows a four-layer PMG with two single layers and one bi-layer, judging by their edges. Finally, Raman spectroscopy, which has been widely used to confirm successful production of graphene, shows a dominant G band at ~ 1584 $1/\text{cm}$, attributed to sp^2 carbons, for both pristine graphite and PMG (Figure 6.5B). Nevertheless, an evident D band at ~ 1350 $1/\text{cm}$ is present for PMG. The increase in D/G ratio from 0.09 for pristine graphite to 0.45 for PMG is a clear sign of the presence of few-layer graphene. Figure 6.5C shows that the 2D peak of PMG also becomes wider with its full width at half maximum increasing from 62 to 77, and its position downshifts from 2732 to 2710 $1/\text{cm}$. All these results indicate successful production of few-layer PMG.

Figure 6.5 TEM micrograph of typical PMG flakes showing two single-layer and one bi-layer PMG (A). Raman spectroscopy of the D band (B) and 2D band of graphite and PMG (C).

PMG porous films with conductance of 1247 S/m were produced using a process consisting of filtration for a few minutes, followed by slow precipitation without suction force. The purpose of the short filtration is to coat the polytetrafluoroethylene (PTFE) membrane with a thin layer of PMG, without which, precipitated PMG would precipitate in lumps owing to lack of affinity between PMG and PTFE, as shown in Figure 6.6. The subsequent precipitation forms randomly oriented, interconnected sheets akin to a “house-of-cards” morphology, as opposed to when it is completely filtered in which case a dominant parallel packing morphology is obtained. The replacement of parallel packing by “house-of-cards” morphology can in principle improve electromechanical sensitivity by changing the dominant electromechanical mechanism from direct contact resistance in the overlapping area of graphene flakes, in which case the correlation between strain and resistance is linear, to tunneling resistance, in which case the said correlation is exponential. It was also observed that sensors produced from PMG films with a randomly oriented 3D structure show higher electromechanical sensitivity to minute deformations compared to those prepared from PMG with a dominant 2D orientation. Since the PMG film is very thin and fragile at this stage, it can easily crack under any deformation. To reinforce the film, WPU was added to the upper surface to infuse into the PMG film, facilitating the removal of

WPU/PMG films from PTFE for fabrication of sensors. The proposed exfoliation route is advantageous compared to general exfoliation processes reported on literature since it can produce highly sensitive sensors from pristine graphite using only water.

Figure 6.6 Precipitation without a short initial filtration leads to PMG lumps instead of a uniform PMG film

6.3.2 Microstructures of PMG films and WPU/PMG nanocomposites

To gain a better insight into the microstructure of the sensors, the morphology of PMG film on PTFE membrane was studied (Figure 6.7). Low-magnification FE-SEM micrograph in Figure 6.7A shows a uniform precipitated PMG layer. At higher magnifications (Figures 6.7B and 6.7C), it can be observed that since there was no suction force, PMG layers have adopted a 3D random orientation instead of forming a parallel packing morphology.²⁰ This 3D morphology creates a porous medium that improves the diffusion of WPU into the film and improves the electromechanical sensitivity of the conductive network. Micrographs of the fractured surface of the PMG film, shown in Figures 6.7 D-F, reveal that due to PMG's random orientation, PMG cross section is largely porous. As can be seen, the PMG film is very brittle so to remove it from PTFE membrane without fracture, a layer of WPU must

be added on top it to infuse into the porous film. WPU infusion occurs so readily that it can easily reach the bottom side of the PMG film as can be seen in the FE-SEM micrograph of the bottom surface of the PMG film after coating its upper surface with WPU and its removal from PTFE membrane (Figure 6.8). Figures 6.7 G-I show the cryogenically-fractured cross-section of a WPU/PMG sensor embedded inside epoxy at different magnifications. It can be seen that the porous morphology of the PMG film is well kept inside the sensor, where the voids are filled by WPU, since the conductive network is stable enough so as not to collapse by WPU infusion. This porous, 3D orientation cannot be attained under filtration unless another component is introduced to create disorder.²¹

Figure 6.7. FE-SEM micrographs of the top-surface view of precipitated PMG film on PTFE membrane (A-C), cross-section view of precipitated PMG film on PTFE membrane (D-F), and cross-section view of the sensor prepared by WPU infusion in PMG film (G-I).

Figure 6.8 FESEM micrograph of the bottom side of the PMG film after infusion of its top-side with WPU and its removal from PTFE membrane. WPU infusion occurs so readily that it can easily reach the bottom side of the PMG film as shown in this micrograph by yellow arrows.

6.3.3 Sensing Performance of WPU/PMG Nanocomposites

The electromechanical properties of the sensors were studied using a dynamic mechanical analyzer (DMA), to create deformations, coupled with an Autolab, to monitor the electrical signal induced by DMA. Resistance-change ratio is widely used in studies on electromechanical sensors to quantify the relationship between deformation and electrical signal and it is defined as:

$$\text{Resistance change ratio} = \frac{R - R_0}{R_0} \quad (1)$$

Where R_0 and R are resistance values before and after deformation, respectively. Studying the effects of different strains, ranging from 0.1 to 2% at a fixed frequency of 0.1 Hz, shown in Figure 6.9A, unravels an increase in resistance-change ratio of the sensors with

increasing strain. Gauge factor is another important parameter that is used to quantify the sensitivity of the sensors, which can be calculated by dividing resistance-change ratio by its corresponding strain. The gauge factors at different strains, shown in Figure 6.9B, indicate that these sensors are most sensitive at the lowest strain, with gauge factor reaching as high as about 70 at 0.1% strain, which makes them particularly suitable for low-strain sensing applications such as minute soft-tissue deformation measurements or monitoring blood-pressure waveforms. Gauge factor, however, falls significantly with increasing strain and reaches to about 10 at the strain of 2%, following a power-law model. Our analysis on the effect of frequency, at the fixed strain of 0.6%, presented in Figure 6.9C, suggests that an increase in frequency results in a fall in the resistance-change ratio and, in turn, the sensitivity of the sensors. The resistance-change ratio of about 10 at the frequency of 0.1 Hz can fall to about 5 at the frequency of 5 Hz. By contrast, a decrease in frequency can lead to a rise in resistance-change ratio to 16 at 0.03 Hz and 70 at 0.007 Hz, as can be seen in Figure 6.9D. This is a profound increase in sensitivity, which is equivalent to the gauge factor of 115 at this strain. Table 6.1 lists the resistance change ratios and gauge factors at different strains. Table 6.2 compares strain ranges and gauge factors of several wearable, flexible strain sensors based on different polymers and conductive materials.

Table 6.1 Typical resistance change ratios and gauge factors at different strains

Strain (%)	Resistance change ratio	Gauge factor
0.1	6.8±0.1	68±1
0.3	10.8±0.9	36±3
0.6	11.8±0.9	20±2
1	14.8±2.66	15±3
2	21.1±4.4	11±2

The stability of the sensors is an important feature that ensures their long-term durability.²²⁻

²⁴ It is important that the sensitivity of the sensors does not change noticeably over their expected lifespan. Here, the sensitivity of these sensors was measured by resistance-change ratio of the samples at the strain of 1% and frequency of 0.1 Hz for 5000 stretch-release cycles, Figure 6.9E. It can be seen that, notwithstanding minor fluctuations, resistance-change ratio does not change noticeably. Figure 6.9F can also provide a clearer view of

repeatable electrical response for 12 selected cycles. By plotting the distribution of dynamic gauge factor over all cycles, shown in Figure 6.9G, a narrow distribution can be observed, with a coefficient of variation of only 4.96%, indicating that the sensitivity does not vary significantly thanks to the structural stability of the sensors.

Table 6.2 Comparison of strain range and gauge factors of several resistive strain sensors based on different polymers and conductive materials

Polymer	Conductive material	Gauge factor	Reference
PEDOT:PSS and PU	CNT	8.7-62.3	Roh <i>et al.</i> ²⁵
PEDOT:PSS and PU	AgNW	1.07–12.4	Hwang <i>et al.</i> ²⁶
PDMS	CB	1.8-5.5	Kong <i>et al.</i> ²⁷
TPE	CB	20	Mattmann <i>et al.</i> ²⁸
PDMS	Graphene foam	15-29	Jeong <i>et al.</i> ²⁹
PDMS	CNT	0.82	Yamada <i>et al.</i> ³⁰
PDMS	CB	29	Lu <i>et al.</i> ³¹
PDMS	AgNW	2-14	Amjadi <i>et al.</i> ³²

Finally, an interesting feature that sets these sensors apart from previously reported sensors with viscoelastic matrices, such as the ones based on Silly Putty,¹⁷ is the time-independent behavior of the electrical response for our sensors. Time-dependency of electrical responses can be a major concern when using a viscoelastic matrix since an ideal electrical response should only be dependent on deformation. To examine time dependency, the change in resistance of the sensors was monitored at a constant strain. At a relatively low strain rate, the sensors still showed an almost linear rise in resistance, as can be seen in Figures 6.9H. More impressively, when the strain was kept at 1% the electrical response remained nearly constant as well. In other words, although the WPU matrix is viscoelastic, the composite sensors show a time-independent electrical response to the strain. This much-desired time independency can be attributed to the 3D randomized morphology of PMG in the nanocomposite films, as well as possible immobilized WPU in its vicinity, resulting in the formation of an elastomer-like “house-of-cards” structure, which is weak enough to deform under a small external strain but stable enough to constrain time dependency in electrical signal of the sensor.³³⁻³⁴ This time-independent electrical behavior

can be observed repeatedly in these sensors as shown in Figure 6.10. It can also be seen that after the removal of the external strain the sensor recovers its original resistance even after a long hold at 1%.

Figure 6.9. Resistance-change ratios for different strains at 0.1 Hz (A), Gauge factors for different strains at 0.1 Hz following a power-law model (B), Resistance-change ratio for different frequencies at 0.6% strain (C), Resistance-change ratio at the very low frequency of 0.007 Hz at 0.6% strain (D), Resistance-change ratio over ~5000 cycles at 1% strain and 0.1 Hz (E), Resistance-change ratio for 12 selected cycles from graph E (F) Gauge factor distribution for graph E showing an average GF of 12.7 and coefficient of variation of 4.96% (G) Resistance response of the WPU-based sensor showing a time-independent behavior at a constant strain and full recovery after release (H).

Figure 6.10 Resistance as a function of time for sensors experiencing linear increase in strain up to 1%. The strain is then kept constant at 1% for some time followed by release.

6.3.4 Shape Conformality of Sensors

Our sensors can be employed to monitor bodily motions and deformations that are too small to be recorded clearly. This is in part due to the high sensitivity of the 3D conductive network, as well as the choice of polymer matrix, which can play a major role in enhancing sensitivity by improving signal-to-noise ratio. For skin-mounted sensors, skin-conformality is an important feature, which is often overlooked since most of the sensors reported in literature are based on PDMS, which is not shape-conformal due to its high elasticity. Figures 6.11A and 6.11B demonstrate the difference in shape conformality between a viscoelastic WPU/PMG sensor and an elastic PDMS-based one on a fractured epoxy substrate with an irregular surface. For the WPU/PMG sensor, clear shape conformality can be observed as it completely conforms to the irregular surface of the epoxy substrate, whereas in case of the PDMS-based one shape conformality is non-existent.

Figure 6.11. Surface conformality of sensors based on viscoelastic WPU (A) and elastic PDMS (B).

6.3.5 Continuous Monitoring of Pulse, Breathing, and Blood Pressure Waveform

The combination of skin conformality and high strain sensitivity allows our sensors to detect precise blood-pressure waveforms. In Figure 6.12A, the dotted red line is the original signal collected by a WPU/PMG sensor that is placed on the wrist of a healthy subject. To see the blood-pressure waveform more clearly, a segment consisting 7 pulses is magnified and shown in the top-left inset. The inset shows waveform variability, which is useful in studying different physiological parameters such as mental and emotional stress.³⁵⁻³⁷ A more detailed look at an individual pulse indicates that our sensors can detect not only the pulse and heartbeat variability but also all the stages of blood-pressure waveform in an individual peak, namely: systolic uptake, peak systolic pressure, systolic decline, diastolic notch, and diastolic runoff. By monitoring these peaks and analyzing their locations relative to one another, experts can continuously monitor vascular and tissue health,³⁸ vascular dysfunctions,³⁹ diabetes, renal dysfunction, and aging⁴⁰ in high-risk patients in a non-invasive manner. Going back to the original signal, in the dotted red line, one can observe another pattern over a longer period. For clarification purposes, the original signal is smoothened, as shown by the superimposed thicker solid black line. From the smoothened curve, it can be observed that in the beginning when the subject held his breath, the black line does not show much variation. However, as the subject starts to grasp for air, from $t=10s$ to $t=35s$, fluctuations in the black line can be observed. After $t=35s$, the subject starts to take regular breaths with increasing depths. After repeating this experiment with

different sensors to eliminate any possible source of error, it was verified that these fluctuations in electrical signal are in fact caused by respiration.⁴¹⁻⁴³

Figure 6.12. Signal collected by a sensor placed on the wrist of a healthy subject, shown in top-right inset, over a minute, shown as the dotted red line; top-left inset shows 7 selected pulses more clearly; top-middle inset shows all the stages of an individual pulse; The thick black line superimposed on the dotted red line is smoothed to remove pulse in order to show the effect of breathing on blood-pressure waveform more clearly (A). Evident electrical signal created by minute soft-tissue deformation as a result of squeezing a tennis ball (B).

Although precise monitoring of blood-pressure waveform by highly sophisticated skin-conformal electrothermal sensors had already shown the effect of respiration on blood-pressure waveform, this is the first time that a graphene-based electromechanical sensor is

sensitive enough to detect the same phenomenon. What is more, our sensors can also be used in the study of soft-tissue biomechanics. Figure 6.12B shows a signal created from soft-tissue deformation resulting from squeezing a tennis ball. Here, a minute deformation in forearm muscles, palmaris longus in particular, can create sharp spikes in the resistance of the sensor, the heights of which depend on the strength of squeezing the ball.

6.4 Conclusions

In this work, WPU is successfully utilized as a polymeric stabilizer for aqueous exfoliation of pristine graphite to multilayer graphene. Viscoelastic WPU, in contrast to conventional elastic polymeric bases like PDMS, also endows the resultant WPU/PMG sensors with shape-conformality, resulting in improvement in signal detection by creating intimate contact between sensors and epidermis. The sensors owe their high sensitivity to the 3D randomized “house-of-cards” morphology of their conductive network formed by precipitation of exfoliated PMG. This morphology should also be responsible for constraining time dependency, which has been observed in sensors based on viscoelastic polymers. The combined effects of high electromechanical sensitivity and skin conformality creates potentials for several applications, such as continuous monitoring of pulse, respiration, and blood pressure waveforms, and study of soft-tissue biomechanics. What sets this work apart from similar reports in literature is that only water is used to produce these sensitive sensors from pristine graphite. The multifunctional role of WPU as a stabilizer, matrix, and shape conforming layer should also be highlighted.

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Chapter 7

Conclusions and Outlook

In this chapter, key conclusions from Chapters 4, 5, and 6 are summarized and connected to paint the big picture. The results from our experiments are briefly mentioned to evaluate the success of the design/performance target set forth in Chapter 1. The novelties and major contributions of this work are then highlighted. Finally, the possibilities on expanding on this study based on some reconnaissance studies as well as possibilities for research on related materials are presented.

7.1 Conclusions

In this study, the importance of designing sustainable products in a circular economical model was highlighted. Two different strategies were adopted simultaneously to develop sustainable, environmentally-friendly, multifunctional polymer/graphene nanocomposites. The first strategy aims to substitute conventional, synthetic compounds with their naturally-occurring counterparts. The second strategy aims to eliminate components by assigning their roles to the remaining multifunctional ones.

In the first work, lignin was used to substitute conventional, synthetic, graphene stabilizers and produce lignin-modified graphene (LMG). It was then added to waterborne polyurethane (WPU) to produce WPU/LMG nanocomposites. Thanks to the non-covalent nature of modification by lignin, the sp^2 structure of graphene which is responsible for its unique functional properties, e.g., electrical conductivity, remained unchanged. Since the resulting conductive nanocomposites were intended for conductive coating applications, their outdoor durability was improved by introducing self-healability against environmental damage and UV-resistance against the sun. These functional properties, however, were not obtained by the addition of self-healing agents or synthetic UV blockers but rather by the excellent photothermal conversion and anti-UV properties of non-covalently modified graphene. The remarkable photothermal conversion in LMG, which is crucial for fast self-healing, is due to its non-covalently modified nature and unperturbed sp^2 structure. LMG also does not increase the T_g of WPU and, therefore, does not constrain self-healing entropically. Antioxidant properties of LMG stem from a combination of preventative and radical scavenging activities. LMG can improve antioxidant property by reducing the diffusion of oxygen inside the bulk of the polymer, which is necessary for the creation of reactive oxygen species, and preventing degradation through absorbing some of the harmful UV irradiation and converting it into heat. Although this heat may result in thermal degradation of WPU to its initial reagents, because of excellent impermeability of LMG, these volatile chemicals cannot easily escape the bulk of the polymer, and some of them may reversibly bond to form WPU again after the external heat source, i.e., UV illumination, is removed.

These strategies were carried over to Chapter 5, where LMG was used to produce sensors through a simple dip-coating process. Thanks to multi-stimuli responsiveness of LMG, these sensors showed high sensitivity to pressure, $S=0.25\text{kPa}^{-1}$, and temperature, $S=4.3\% \text{C}^{-1}$, opening the door to many attractive potential applications for wearable electronics such as smart shoes and smart gloves. These sensors showed high structural and electrical stability over 5000 compression-release cycles. The results from Chapter 4 and Chapter 5 show that LMG can indeed provide multifunctionality to nanocomposites.

In the third work, this design philosophy was taken to the next level by eliminating lignin as an aqueous stabilizer for graphene and substituting it with WPU. WPU proved to be an effective stabilizer for the LPE of graphene by preventing reaggregation through steric hindrance. By adopting WPU as the polymeric matrix as well, WPU/graphene nanocomposites with no external stabilizer were produced. These nanocomposites were highly conductive and showed remarkable electrical response to deformation making them suitable for electromechanical sensing applications. The high electrical sensitivity of these sensors is the result of the 3D randomized structure that is produced through a novel filtration-precipitation process. This randomized structure made tunneling resistance, which changes exponentially with deformation, the dominant form of electromechanical transduction. Due to viscoelastic nature of WPU, these sensors were shape conformal which further improved their sensitivity by improving signal-to-noise ratio. These sensitive sensors can have applications in continuous monitoring of pulse, respiration, and blood pressure waveforms, and the study of soft-tissue biomechanics

7.2 Novelty and Significant Contributions

This PhD study presents several novel and significant contributions. Firstly, for the first time, an aqueous-only approach was used to produce multifunctional nanocomposites from pristine graphite, with no other chemical used in the fabrication process. A variety of structural and multifunctional properties such as mechanical reinforcement, photothermal conversion, antioxidant properties, UV-absorption, electrical conduction, and thermo-responsive resistivity can be achieved by using non-covalently modified graphene with

unperturbed sp^2 structure. The need for additional components such as self-healing agents and synthetic UV stabilizers can also be obviated by assigning multifunctional roles to the components. Moreover, A new filtration-precipitation process was proposed which can produce highly sensitive electromechanical sensors.

Exploiting multifunctionality from all components of a nanocomposite have not been sufficiently focused on by the researchers. Here, LMG acted as both a graphene stabilizer and, synergistically with graphene, as a UV stabilizer. WPU also acted as both a graphene stabilizer and viscoelastic polymer matrix, which enabled shape conformality and eliminated the need for an additional skin-conformal layer¹. Considering the results of this study, it can be argued that the design/performance targets set forth in Chapter 1 have been met and perhaps exceeded. This study set forth a design philosophy for future studies to improve sustainability by moving towards natural components and multifunctionality.

Theoretically, this study presents a clear mechanism for the self-healing behavior of WPU/LMG nanocomposites. For the first time, the superb anti-UV property of non-covalently modified graphene was showcased and the underlying mechanisms behind this property was thoroughly explained. In the end, the underlying mechanism as to why the filtration-precipitation process can produce highly sensitive yet time-independent electrical response was described.

7.3 Future Work

7.3.1 Multi-Stimuli Self-Healability of WPU/LMG Nanocomposite Coatings

In Chapter 3, we reported on IR-induced self-healing of WPU/LMG nanocomposites. In addition to IR irradiation, other stimuli can be used to induce self-healing in WPU/LMG systems as well. For example, UV light has been used to trigger self-healing in a PU-based network containing UV-sensitive chitosan chains and mechanical-stress-sensitive oxetane rings. External damage breaks stress-sensitive oxetane rings more predominantly than other chemical bonds. Upon UV irradiation, self-healing takes place when chitosan chain

scission releases free radicals that can react with oxetane, created by damage, to form new crosslinking bonds ². Burnworth used UV-absorbent ligands that can convert UV light into heat and drive effective chain diffusion at the crack ³. LMG has also shown UV-absorbent ability which can be exploited for photothermal-induced self-healing in WPU/LMG nanocomposites. In case of electrically-conductive polymer nanocomposites, electrical self-healing can be employed as well. LMG conductive network can act as a heating network by converting the electrical energy into Joule heating ⁴⁻⁵. Upon the application of a proper voltage, heat will be generated at the cracked surface and induce chain diffusion. Similarly, electromagnetic waves can be used to produce heat in the WPU as well since LMG π structure should act as nanoscale heater by absorbing the electromagnetic wave and converting it into heat ⁶. These additional modes of self-healing can significantly expand the self-healing options for WPU/LMG nanocomposite coatings.

7.3.2 Multi-Stimuli Responsive Electromechanical PU/LMG and WPU/PMG Sensors

Flexible, wearable infrared (IR) detectors can find many applications in remote sensing, biological monitoring, and healthcare ⁷⁻⁹. Since IR illumination can modulate the electrical conductance of graphenic materials, they are suitable for IR sensing applications ¹⁰. In Chapter 5, multifunctional PU/LMG pressure/temperature sensors were prepared. In addition to being sensitive to pressure and temperature, these sensors showed electrical sensitivity to IR irradiation as well. As can be seen in Figure 7.1, the resistance of PU/LMG sensors falls instantly as they are illuminated by an IR lamp.

Similar to PU/LMG pressure sensors, WPU/PMG strain sensors also respond to IR irradiation as well as can be seen in Figure 7.2. The nature of response, nonetheless, contrasts with what is observed in Figure 7.1. Here, IR illumination results in an increase in the resistance of the sensors. The nature of the response is clearly dependent on the intensity of the lamp which is controlled by changing the distance between the lamp and the surface of the graphene sensor. The nature of these IR responses should be further investigated to determine the reason behind this rather contradictory response to IR in these two systems. Further characterizations such as cyclic response, resistance vs. intensity, and

so on should be carried out for these two systems. The unique combination of mechanical, temperature, and IR sensitivities can create unparalleled potentials for these sensors which should be exploited.

Figure 7.1 The effect of IR illumination on the resistance of PU/LMG multifunctional sensors.

Moreover, WPU/PMG strain sensors also show sensitivity to touch and pressure as well. Figure 7.3 shows the resistance response of a sensor after being touched and gently pressed. The sensor shows obvious bumps even after being touched and an evident spike after being pressed. This, however, is only a qualitative demonstration which should be complemented by detailed qualitative measurements such as pressure/resistance behavior and cyclic compression-release stability tests. Being responsive to strain, pressure, and IR irradiation simultaneously can create opportunities for attractive applications.

Figure 7.2 IR response of WPU/PMG strain sensors

Figure 7.3 Pressure sensitivity of WPU/PMG strain sensors. The resistance of the sensor shows small bumps as it is touched and an obvious spike even after it is gently pressed.

7.3.3 Sustainable Liquid-Phase Exfoliation of Other 2D Networks

Liquid exfoliation of other 2D materials such as transition metal oxides (TMOs), transition metal dichalcogenides (TMDs), boron nitride, tungsten disulfide, bismuth telluride, and bismuth selenide can be a source of 2D materials with unique functional properties^{1, 11-12}. Some of these layered materials have already been exfoliated in water. For example, Liu *et al.*¹³ exfoliated MoS₂ into single- and few-layer nanosheets in aqueous media with the help of lignin as naturally-occurring stabilizer. They also demonstrated the suitability of alkali lignin in aqueous exfoliation of other 2D materials such as tungsten disulfide and boron nitride. Based on some of our reconnaissance studies, successful aqueous exfoliation of MoS₂ was carried out with WPU as stabilizer. Similar aqueous-only processes can be employed to exploit the functional properties of polymer nanocomposites based on these 2D materials¹⁴.

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