©2019

ARAB HAMMADI HUSSEIN

ALL RIGHTS RESERVED

NOVEL EXFOLIATION-BASED PROCESSING AND CHARACTERIZATION OF GRAPHENE- AND *h*-BN-REINFORCED POLYMER MATRIX NANOCOMPOSITES

by

ARAB HAMMADI HUSSEIN

A dissertation submitted to the

School of Graduate Studies

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Doctor of Philosophy

Graduate Program in Mechanical and Aerospace Engineering

Written under the direction of

Stephen D. Tse and Assimina A. Pelegri

And approved by

New Brunswick, New Jersey

October, 2019

ABSTRACT OF THE DISSERTATION

NOVEL EXFOLIATION-BASED PROCESSING AND CHARACTERIZATION OF GRAPHENE- AND *H*-BN-REINFORCED POLYMER MATRIX NANOCOMPOSITES

By Arab Hammadi Hussein

Dissertation Directors:

Stephen D. Tse and Assimina A. Pelegri

Nano-additives are important and integral in a vast range of practical applications, especially for enhancing the mechanical properties of composite materials. The development of cost-effective methods to fabricate high-quality nanocomposite materials at high yield is essential. In this work, graphene flakes are delaminated from graphite particles loaded in a high-viscosity liquid polymer solution using a concentric-cylinder shear device. Using poly (methyl methacrylate) (PMMA) as the polymer, with 1%wt graphite loading, shearing for 6 hours leads to the formation of a graphene-reinforced polymer matrix composite (r-PMCs) when subsequently solidified. Here, PMMA dissolved in acetone at four different concentrations, i.e., 0.4, 0.5, 0.6, and 0.7 g/ml, is studied. Among the four different cases, during the exfoliation process, the polymer

solution from the 0.7 g/ml concentration exhibits a more pronounced non-Newtonian fluid behavior (i.e., significant shear thinning) and gives the best exfoliation performance. Furthermore, high PMMA/acetone concentration corresponds to high mixture viscosity, which at a high-speed rate (2500 RPM), results in very-high shear stress, increasing the total number of mechanically-exfoliated flakes produced within the PMCs. The liquidphase UV-Visible spectra analysis shows that 0.225 mg/ml of graphene is created in the G-PMMA during the process at 0.7 g/ml polymer/acetone concentration. The solution is then heat injection molded into a sample at 200°C prior to mechanical testing. The resulting graphene-reinforced PMC exhibits a maximum enhancement of elastic modulus (E) and hardness (H) of about 31% and 28.6% respectively. Additionally, Raman spectroscopy reveals the critical 2D peak to D peak intensity (I_{2D}/I_G) ratio to be about 0.92, which correlates to bilayer graphene flakes (n=2). The I_{2D}/I_G ratio dramatically changes from 0.45 to 0.92, as the polymer/acetone solution concentration varies from 0.4 to 0.7 g/ml, demonstrating the dependence of the degree of exfoliation on solution viscosity.

The effect of shear exfoliation time (i.e., 2, 6, and 12 hours) on the production of graphene in the liquid phase of the PMMA/acetone solution is evaluated. The Raman spectra show that the number of graphene layers ($n \le 2$) reduces with increasing processing time, with the I_{2D}/I_G ratio reaching a maximum of about 1.2 after 12 hours.

Using the same conditions (i.e., PMMA/acetone concentration 0.7 g/ml and processing time 6 hrs), few-layer graphene (G) and hexagonal boron nitride (h-BN) nanoflakes are investigated in terms of their production through exfoliation, along with the properties of the resulting polymer matrix containing them. The process produces both single layer and few-layer 2D nanoflakes, which immediately bond to the surrounding polymer without any external contamination. With pure PMMA as reference, mechanical characterizations, including nanoindentation testing (multi-load testing) and nano-dynamic mechanical analysis (nanoDMA), are conducted on the reinforced polymer matrix nanocomposites. As expected, the H and E of reinforced PMMA increase markedly with the 2D nano additives, in conjunction with heat treatment at 200°C. The results show that there are maximum increases of E and H by 32% and 31%, respectively, for the graphenereinforced PMMA nanocomposite, whereas the increases are 27.1% and 24.8% for h-BNreinforced PMMA nanocomposite. The surface morphology and interfacing of the nanoadditives with the polymer matrix are investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), showing one to four layers of either graphene or *h*-BN flakes with excellent interfacing between the matrix and the nanoflakes. Raman spectroscopy is used to assess the number of layers and the dispersion of the 2D flakes in the matrix, via the distributions of peak positions and intensities as a function of wavenumber. The *h*-BN peak or E_{2g} mode appears at 1367 cm⁻¹ in *h*-BN-PMMA after exfoliation, with a shift of 2 cm^{-1} (1365 cm⁻¹ for bulk *h*-BN). As in the previous study for

G-PMMA, the average I_{2D}/I_G ratio increases notably to 0.92 at a polymer/acetone concentration 0.7 g/ml. This average value indicates bilayer graphene flakes, with many monolayer graphene flakes (n=1) present also according to TEM imaging.

Finally, microfibers are fabricated by electrospinning the processed PMMA/acetone solution with graphene nanoplatelets for reinforcement. G-PMMA fiber mats with good dispersion of 2D-graphene flakes in the polymer matrix (according to TEM imaging) are produced in the diameter size range from 3 to 6 μ m. Nanoindentation testing is performed on the reinforced fiber, as well as the pure polymer fiber for reference. The nanoindentation technique reveals that the mechanical properties of individual graphene-reinforced PMMA microfibers are enhanced (with elastic modulus by 19% and hardness by 17.2%) as compared to those of pure PMMA microfiber produced in the same manner.

Acknowledgments

I would like to thank my advisors, Professor Stephen D. Tse and Professor Assimina A. Pelegri, for all the outstanding guidance, patience, encouragement, and support throughout my graduate studies. I wish to thank Professor Bernard Kear for his support and advice during the research work. I am very appreciative to all my lab-mates, especially, Dr. Zhizong Dong and Dr. Gang Xiong for all of their support and tips. Thank you to Daryll T. Munoz and Ashley M. Pennington for all of their assistance in the UV-Vis characterization. I am extremely thankful to John Petrowski for all his help in building my experimental setup. I am grateful to my friends, Mustafa Mozeal, Omer Alabdelkareem, Omar Jumaah, Jonathan Shi, Asaad Shaikh and Matthew Waizer, for their support.

Last but certainly not least, many thanks to the financial support from the higher committee for education development in Iraq (HCED) and the teaching assistantship program of Mechanical and Aerospace Engineering at Rutgers, The State University of New Jersey.

Dedication

This dissertation is dedicated to my parents, my wife, and my kids, Sarah and Ali, who have supported me through my whole life, making my successful studying and work

possible. My most profound gratitude is given to them.

Preface

The bulk of this dissertation focuses on novel reinforced-PMC processing by exfoliation of graphene and *h*-BN by high shear in a polymer solution, along with nanoscale characterization of the final product. Much of the content in Chapters 4, 5, 6, and 7 is from papers that are to be submitted for publication shortly [1-3] with permission from the coauthors to utilize the work in this dissertation. Additionally, other chapters contain similar or identical wording to that in the papers referenced below.

References

[1] Arab H. Hussein, Zhizhong Dong, Jennifer Lynch, Bernard Kear, Jerry Shan, Assimina Pelegri, Stephen Tse " Processing of Graphene Reinforced Polymer Matrix Nanocomposites by In- situ Mechanical Shear Exfoliation of Graphite " Manuscript prepared

[2] Arab H. Hussein, Zhizhong Dong, Bernard Kear, Stephen Tse, Assimina Pelegri " Fabrication, Structure Analysis, and Mechanical Property Characterization of Graphene and h-BN Nanosheets Reinforced Poly (methyl methacrylate) Polymer Composites " Manuscript prepared

[3] Arab H. Hussein, Zhizhong Dong, Bernard Kear, Assimina Pelegri, Stephen Tse " Manufacturing and Characterization of Electrospun Poly(methyl methacrylate) Nanocomposite Fibers Reinforced by Graphene Nanosheets "Manuscript prepared

| ABSTRACT OF THE DISSERTATIONii |
|---|
| Acknowledgmentsvi |
| Dedication |
| Prefaceviii |
| Table of contentsix |
| List of Tables xiv |
| List of Figures xv |
| Chapter One 1 |
| 1. Introduction 1 |
| 1.1 Motivation |
| 1.2 Research Aims |
| 1.3 Research Approach |
| 1.4 Dissertation Outline |
| Chapter Two |
| 2. Literature Review and Background7 |
| 2.1 Graphene Background |
| 2.1.1 Graphene Properties |
| 2.1.2 Graphene Preparation and Manufacture 10 |
| 2.1.2.1 Micromechanical Exfoliation12 |

Table of contents

| 2.1.2.2 Liquid Phase Exfoliation 1 | 13 |
|---|----|
| 2.2 Hexagonal Boron Nitride 1 | 18 |
| 2.2.1 Properties and Applications | 19 |
| 2.3 Polymer Matrix Nanocomposites Background | 21 |
| 2.3.1 Polymer Matrix Nanocomposite Synthesis Methods | 22 |
| 2.3.2 Polymer Matrix Nanocomposite Applications | 25 |
| Chapter Three | 29 |
| 3. Experimental Setup and Analytical Instruments | 29 |
| 3.1 High Shear and Reinforced Polymer Setup | 29 |
| 3.2 Electrospinning Fiber Setup | 31 |
| 3.3 Characterization Techniques | 32 |
| 3.3.1 Raman Spectroscopy | 32 |
| 3.3.2 UV-Vis Spectroscopy | 34 |
| 3.3.3 In-situ Shear Rheology Test | 35 |
| 3.3.4 Transmission Electron Microscopy (TEM) | 37 |
| 3.3.5 Scanning Electron Microscopy (SEM) | 38 |
| 3.3.6 Scanning Helium Ion Microscopy (HIM) | 39 |
| 3.3.7 Nanoindentation Test | 40 |
| 3.3.8 Viscoelastic Characterization - Dynamic Nanoindentation | 43 |
| Chapter Four | 46 |

| 4. Processing of Graphene Reinforced Polymer Matrix Nanocomposites by In-situ |
|---|
| Mechanical Shear Exfoliation of Graphite |
| 4.1 Introduction |
| 4.2 Experimental Methods |
| 4.2.1 Materials and Preparation |
| 4.2.2 Exfoliation Process |
| 4.3 Results and Discussion |
| 4.3.1 Characterization of Graphite |
| 4.3.2 Characterization of Exfoliated Graphene Reinforced PMMA Nano- |
| composites |
| 4.3.2.1 Raman Spectroscopy |
| 4.3.2.2 Solid Phase UV-Visible Analysis of π to π^* Transition |
| 4.3.2.3 Graphene Quantification via Liquid Phase UV-Visible Spectroscopy56 |
| 4.3.2.4 Nano-indentation Measurement |
| 4.3.2.5 Nanoindentation Mapping and Thermal Effect on The Mechanical |
| Properties |
| 4.3.2.6 X-ray Diffraction Test |
| 4.3.2.7 In-Situ Rheology Test |
| 4.3.2.8 SEM, TEM, and HIM Analysis70 |
| 4.4 Effect of Time on The Exfoliation of Graphene and Reinforced Polymer |
| Nanocomposites |

| 4.5 | Summary | . 77 |
|------|--|------|
| Cha | pter Five | . 78 |
| 5. F | Fabrication, Structural and Mechanical Characterization of Graphene and h-BN | |
| | Nanoflakes Reinforced Poly (methyl methacrylate) Nanocomposites | . 78 |
| 5.1 | Introduction | . 78 |
| 5.2 | Materials | . 80 |
| 5.3 | Experimental Procedure | . 81 |
| 5.4 | Results and Discussion | . 82 |
| | 5.4.1 Raman Spectroscopy | . 82 |
| | 5.4.2 Morphological Investigation | . 85 |
| | 5.4.3 Mechanical Properties-Nanoindentation Test | . 90 |
| | 5.4.4 Dynamic Mechanical Analysis (nanoDMA) | . 93 |
| 5.5 | Summary | . 99 |
| Cha | pter Six | 100 |
| 6. E | Exfoliation of Graphene in Water-Based Poly(vinylpyrrolidone) Solution | 100 |
| 6.1 | Introduction | 100 |
| 6.2 | Materials | 101 |
| 6.3 | Experimental Procedures | 101 |
| 6.4 | Raman Spectroscopy | 103 |
| 6.5 | Nanoindentation Test | 105 |
| 6.6 | Summary | 107 |

| Chapter Seven |
|--|
| 7. Manufacturing and Characterization of Graphene-Reinforced Electrospun Poly(methyl |
| methacrylate) Nanocomposite Fibers 109 |
| 7.1 Introduction |
| 7.2 Experimental Section |
| 7.2.1 Materials Preparation |
| 7.2.2 Electrospinning Processing |
| 7.2.3 Characterization and Measurements 116 |
| 7.2.3.1 Mechanical Properties116 |
| 7.2.3.2 Raman Spectroscopy 119 |
| 7.2.3.3 Scanning Electron Microscopy (SEM) 120 |
| 7.2.3.4 Transmission Electron Microscopy 123 |
| 7.3 Summary 125 |
| Chapter Eight |
| 8. Conclusion and Future work |
| 8.1 Conclusion |
| 8.2 Future Work |
| References |

List of Tables

| Table 2. 1 Some of the superb properties of graphene [36] 10 |
|---|
| Table 2. 2 Demonstrates the influence of processing time and exfoliation medium (solvent) |
| on the graphene concentration by using sonication method, adapted from [46] 15 |
| Table 2. 3 Shows the effect of processing time and exfoliation medium on the graphene |
| concentration by using a high-shear exfoliation method, adapted from [46] 16 |
| Table 3. 1 List of characterization techniques. 32 |
| Table 4. 1 Graphene concentration, graphite conversion, and the total mass of graphene in |
| the synthesized sample |
| Table 4. 2 Summary of mechanical properties of exfoliated graphite reinforced PMMA |
| nanocomposites |
| Table 5. 1 Summary of mechanical properties of PMMA composites |
| Table 5. 2 Mechanical proporties of PMMA nanocomposites evaluated by nano_DMA98 |
| Table 6. 1 crystallite size of graphene. 105 |
| Table 6. 2 Summary of mechanical properties of PVP composites |
| Table 7. 1 Summary of mechanical properties of electrospun nanocomposite fiber 118 |

List of Figures

| Figure 1. 1 scheme of the general approach used in this study |
|--|
| Figure 2. 1 Graphene is 2-D structural forming of carbon atoms. It can be rolled into 0D |
| fullerene, folded into 1D nanotubes, or agglomerated together into 3D graphite, adapted |
| from [18] |
| Figure 2. 2 Publications on Graphene from 2000 to 2016, adapted from [19] |
| Figure 2. 3 a process flow chart of graphene synthesis, adapted from [16] 11 |
| Figure 2. 4 Micromechanical exfoliation of graphene using scotch or adhesive tape from |
| highly oriented pyrolytic graphite (HOPG) [17, 43] |
| Figure 2. 5 Schematic shows the experimental liquid phase exfoliation process via |
| sonication with snapshots of centrifugate after exfoliation, adapted from [55] 14 |
| Figure 2. 6 The exfoliation mechanism for graphene production by shearing, collision, and |
| cavitation, adapted from [63]16 |
| Figure 2. 7 Schematic a high shear mixer of the exfoliation graphite with PVP or SC |
| solution. The graphene-polymer mixture was then centrifuged to extract unexfoliated |
| graphite particles, adapted from [64] 17 |
| Figure 2. 8 (a) A liquid-phase peeling of graphene in a beaker (b, c) mixing head rotor and |
| stator. (d) Graphene flakes are collected in the bottles after produced by high shearing with |
| N-methylpyrrolidone (NMP), adapted from [47] 18 |
| Figure 2. 9 <i>h</i> -BN-Structure. (A) Stereogram. (B) The 2D floor plan, adapted from [66]. 19 |

| Figure 2. 10 schematic diagrams showing some shapes for materials particles used in |
|---|
| reinforced polymers matrix, adapted from [82, 83]22 |
| Figure 2. 11 Diagram shows the preparation steps of polymer composites by direct mixing |
| of polymer solution with the fillers, adapted from [86]23 |
| Figure 2. 12 sketch show three types of composite polymer consisting of intercalation of |
| polymer chains with the nanofillers (silicate layers) (a) traditional phase separated process |
| (microcomposites) (b) the intercalated process of nanocomposite (c) the exfoliated process |
| of nanocomposite polymer, adapted from [88]24 |
| Figure 2. 13 Application fields of polymer matrix nanocomposite, adapted from [91]25 |
| Figure 2. 14 show the influence of nanofillers in nanocomposite polymer electrolytes |
| on the pathways system of lithium-ion conduction, which used to develop of next- |
| generation safe lithium-ion batteries, (a) nanoparticles, (b) random nanowires (NWs), |
| (c) aligned nanowires. The lithium-ion conduction of the NWs-nanocomposites exibited |
| higher performance and faster conduction system than nanoparticles- nanocomposites, |
| (d) The surface area of nanoparticles and NWs work as an booster way for Li-ion |
| conduction, adapted from [95]26 |
| Figure 2. 15 shows using polymer nanocomposites (polymer/glass plate) in building for |
| saving energy. The luminescent materials in the nanocomposites work as a solar |
| concentrator and absorb the incident radiation or sunlight and reemit the absorbed light at |
| a longer wavelength, adapted from [101] |

| Figure 3. 1 Schematic diagram of the experimental setup (a) high shear setup (b) Zoom in |
|---|
| of two concentric cylinders mixing chamber |
| Figure 3. 2 A typical schematic illustration electrospinning setup of fabrication of |
| graphene-reinforced fibers |
| Figure 3. 3 Schematic diagram of Raman spectra equipment (Renishaw RM 1000) [108]. |
| |
| Figure 3. 4 Raman spectroscopy analysis of different carbon systems (reproduced from |
| [109]) |
| Figure 3. 5 Image of UV-Visible spectroscopy |
| Figure 3. 6 Schematic of Concentric cylinders demonstrating the rotating inner cylinder |
| and stationary outer cylinder with rotating directions |
| Figure 3. 7 Schematic diagram of Scanning Transmission Electron Microscope |
| (reproduced from [113]) |
| Figure 3. 8 Schematic diagram of scanning electron microscope (reproduced from [114]). |
| |
| Figure 3. 9 Schematic diagram of the scanning helium ion microscope (reproduced from |
| [115]) |
| Figure 3. 10 (a) schematic of the indentation cross section on the surface (reproduced from |
| [116]); and nanoindentation Vantage test explain (b) the Berkovich tip in the touching |
| with a PMMA sample surface |

| Figure 3. 11 Image of Hysitron, nanoindentation, used here for nanoDMA analysis 45 |
|---|
| Figure 4. 1 Schematic of the shear-exfoliation processing of graphite in the PMMA/acetone |
| solution |
| Figure 4. 2 Graphite characterization. (a) SEM image, (b) Raman spectra |
| Figure 4. 3 Raman spectrum (green) Raman spectra of G-PMC at concentration 0.4 g/ml |
| is multilayer graphene, (pink) Raman spectra of G-PMC at concentration 0.5 g/ml is few- |
| layers graphene, (blue) Raman spectra of G-PMC at concentration 0.6 g/ml few-layers, |
| (red) Raman spectra of G-PMC at concentration 0.7 g/ml is bilayer graphene |
| Figure 4. 4 I_{2D}/I_G for samples with different concentrations of polymer/acetone (viscosity). |
| |
| Figure 4. 5 Kubelka-Munk units of solid-phase UV-Visible Spectroscopy of pure PMMA |
| (black), and graphene/graphite in PMMA samples: 0.4 g/ml (green), 0.5 g/ml (pink), 0.6 |
| g/ml (blue), and 0.7 g/ml (red)55 |
| Figure 4. 6 Effect of polymer/acetone concentration ratio (viscosity) on the graphene |
| |
| quantification |
| quantification |
| quantification. 57 Figure 4. 7 Load–penetration depth curves of exfoliated graphite reinforced PMMA nanocomposites. 60 |
| quantification.57Figure 4. 7 Load–penetration depth curves of exfoliated graphite reinforced PMMAnanocomposites.60Figure 4. 8 Local hardness maps of G-PMMA and processed neat PMMA (both processed |

| unprocessed neat PMMA. Test conditions: $\pm~20~\mu m$ displacement amplitude for each |
|--|
| indentation step, 5 mN normal load65 |
| Figure 4. 9 Local reduced modulus of G-PMMA and processed PMMA (both processed at |
| 0.7 g/ml polymer concentration and then heat injected into mold at 200°C) and unprocessed |
| neat PMMA. Test conditions: \pm 20 μ m displacement amplitude for each indentation step, |
| 5 mN normal load |
| Figure 4. 10 The XRD pattern for PMMA and G-PMMA nanocomposite at heat injection |
| and unheated; show large peak at 2θ is 13.1 indicates its amorphous nature of PMMA. 67 |
| Figure 4. 11 Shear stress vs. shear rate, before and after 6 hours of exfoliation or processing. |
| |
| |
| |
| |
| |
| |
| 68 Figure 4. 12 Torque vs. Time behavior during exfoliation for 2hrs at constant speed 2500 RPM. Data was taken in 10min intervals, so resolution for 0.7 g/ml case will need to be investigated at increased time resolution to account better for oscillating behavior 68 Figure 4. 13 SEM micrographs of G-PMMA prepared at 0.7 g/ml (a,b) surface morphology, (c,d) higher magnification shows the interfacing of graphene flakes with PMMA matrix, |
| 68 Figure 4. 12 Torque vs. Time behavior during exfoliation for 2hrs at constant speed 2500 RPM. Data was taken in 10min intervals, so resolution for 0.7 g/ml case will need to be investigated at increased time resolution to account better for oscillating behavior 68 Figure 4. 13 SEM micrographs of G-PMMA prepared at 0.7 g/ml (a,b) surface morphology, (c,d) higher magnification shows the interfacing of graphene flakes with PMMA matrix, (e,f) uniform dispersion of graphene in the polymer matrix |
| 68 Figure 4. 12 Torque vs. Time behavior during exfoliation for 2hrs at constant speed 2500 RPM. Data was taken in 10min intervals, so resolution for 0.7 g/ml case will need to be investigated at increased time resolution to account better for oscillating behavior 68 Figure 4. 13 SEM micrographs of G-PMMA prepared at 0.7 g/ml (a,b) surface morphology, (c,d) higher magnification shows the interfacing of graphene flakes with PMMA matrix, (e,f) uniform dispersion of graphene in the polymer matrix |
| |

| Figure 4. 15 HIM images of exfoliated graphite reinforced PMMA nanocomposites |
|---|
| prepared at 0.7 g/ml (a) surface morphology, scale bar = 1 μ m (b) High magnification |
| image of graphene layers, scale bar = 100 nm (c,d) wrinkling graphene flakes adhesion |
| with amorphous PMMA, scale bar = 100 nm75 |
| Figure 4. 16 Raman spectra of G-PMMA composites (red) Raman spectra at 12 hrs |
| shearing (blue) Raman spectra at 6hrs shearing, (yellow) Raman spectra at 2hrs shearing, |
| and (black) Raman spectra of graphite76 |
| Figure 5.1 SEM images of filler particles: (a) synthetic graphite powder with an average |
| particle size of 8-10 μ m (b) h-BN powder with an average particle size of 8-10 μ m 81 |
| Figure 5. 2 Schematic of the shear-exfoliation processing of graphite and bulk <i>h</i> BN in the |
| |
| PMMA/acetone solution |

Figure 5. 5 Raman spectra at 633nm of (red) exfoliated *h*-BN with PMMA and (purple) bulk h-BN powder before exfoliation. The h-BN exfoliated peak is shifted forwards of \sim 2 cm⁻¹ while the intensity decreased. The curves were normalized to the intensity of pure Figure 5. 6 SEM images of fracture surfaces: (a) Graphene flakes in PMMA matrix composite; (b) Interfacing of graphene with PMMA matrix; (c) h-BN layers in the PMMA composite; (d) the unexfoliated h-BN-PMMA composite; (e) the exfoliated h-BN-PMMA Figure 5. 7 Representative TEM images of exfoliated, *h*-BN nanosheets prepared via high shear between two concentric cylinders at 2500 RPM (a-b) graphene nanoflakes in bond Figure 5.8 Nanoindentation results for Young's modulus vs. indentation depth as a function of the 2D reinforcing phase (graphene and h-BN) in PMMA. The nanoindentations are performed under load controll conditions and each point is the average of 8 individual Figure 5. 9 Nanoindentation results for hardness vs. indentation depth as a function of the 2D reinforcing phase (graphene and h-BN) in PMMA. The nanoindentations are performed under load control conditions and each point is the average of 8 individual nanoindents at

| Figure 5. 10 Storage modulus of nanocomposites polymer (red) of G-PMMA, yellow of |
|---|
| <i>h</i> -BN-PMMA and (black) of pure PMMA95 |
| Figure 5. 11 Loss modulus of nanocomposites polymer (red) of G-PMMA, yellow of h- |
| BN-PMMA and (black) of pure PMMA96 |
| Figure 5. 12 Loss tangent (tan δ) of nanocomposites polymer (red) of G-PMMA, yellow of |
| <i>h</i> -BN-PMMA and (black) of pure PMMA |
| Figure 6. 1 SEM image of graphite particles |
| Figure 6. 2 Schematic of the shear-exfoliation processing of graphite in the PVP/WATER |
| solution |
| Figure 6. 3 Raman spectra of PVP composites (red) Raman spectra of G-PVP at |
| concentration 0.6 g/ml in the water, indicated D, G, and 2D bands intensity (~1333, ~1584, |
| and ~2657.87 cm ⁻¹) is few layers graphene, (blue) Raman spectra of G-PVP at |
| concentration 0.4 g/ml in the water has a 2D peak at 2664.81 cm ⁻¹ as a multilayer graphene, |
| (black) Raman spectra of PVP as a reference (green) synthetic graphite as a reference.103 |
| Figure 6. 4 Load-penetration depth curves of exfoliated graphite reinforced PVP |
| nanocomposites and pure PVP |
| Figure 7. 1 Schematic of the shear-exfoliation processing of graphite in the PMMA/acetone |
| solution114 |
| Figure 7. 2 Show a graphene flakes after producing by LPE method |

| Figure 7. 3 A typical schematic illustration electrospinning setup of fabrication of |
|--|
| graphene-reinforced fibers |
| Figure 7. 4 Photograph of an electrospun fibers mat made of (a)Pure PMMA (b) |
| PMMA/graphene nanocomposites116 |
| Figure 7. 5 Sketches of the electrospinning fiber mounted to the aluminum stub for |
| nanoindentation test |
| Figure 7. 6 Nanoindentation load-displacement curves of electrospun PMMA fiber at a |
| constant load of 300 µN 118 |
| Figure 7. 7 Raman spectra of PMMA nanocomposites (red) Raman spectra of Graphene- |
| PMMA indicated D, G, and 2D bands intensity (~1351, ~1584, and ~2671 cm ⁻¹) is bilayer |
| and few layers graphene, (black) Raman spectra of PMMA as a reference 120 |
| Figure 7. 8 SEM images of (a) electrospun graphene-PMMA nanocomposite fiber at |
| different magnification, and (b) electrospun pure PMMA fiber122 |
| Figure 7. 9 TEM images (a) electrospun nanocomposite fiber, (b) few layers' graphene |
| covered by PMMA (c,d) uniform dispersion of graphene flakes in the fibers, (e,f) high |
| magnification of graphene flakes in the fiber |

Chapter One

Introduction

Polymeric materials have affected almost every aspect of modern life. Polymer products are extremely widespread; for example they are used in furniture, clothes, household utensils, cosmetic surgery, 3D printing, automobiles, and so on. The polymer matrix performance could be improved by mixing or incorporating various fillers to form polymer matrix composites (PMCs). Polymer matrix nanocomposites are solids consisting of two or more phase-separated materials aligned together within the matrix structure, where one or more dispersed phase(s) is/are in nanoscale(s); and a polymeric matrix is the main phase. The polymeric matrix is most likely the weaker link in that structure; thus the dispersed phase provides a significant improvement in the mechanical, electrical, and thermal properties [1-5]. In nanotechnology, nanocomposites based on polymer/nanoadditives are becoming very interesting multifunctional nanomaterials, providing superb mechanical and electrical properties, even at low nanofiller content [6, 7]. Nowadays, polymer-based composites form nearly half the weight of Boeing's 787 Dreamliner airplane [8]. Thus, the development of cost-effective methods for fabricating high-quality reinforced polymer matrix composites (PMCs) at high yield has become increasingly essential for many applications.

Generally, polymer-based nanocomposites consist of various fillers such as (1D nano-fibers, 2D nano-plates, and 3D nano-particles) bound together by a polymer matrix structure. Two-dimensional nano-plates (nanofillers), such as graphene, hexagonal boron

nitride, and molybdenum disulfide, possess unique characteristics that are conducive in a plethora of applications [9]. Recently, studies in scientific research have found that polymers reinforced by 2D nanomaterials present a unique combination of properties such as excellent thermal, electrical, mechanical properties, even at low nanoparticle content [10]. Furthermore, 2D nanomaterials are lightweight because of their lower density as compared to other materials; thus, they have the capacity to be integrated within a polymer without a significant increase in the weight or density of the polymer nanocomposite. This feature is essential for various applications such as in aerospace industries which require very low weight and exceptionally high performance.

1.1 Motivation

In recent years, polymer matrix nanocomposites (PMCs) have been widely used in many fields where other materials and metals were previously employed because of unparalleled levels of characteristics (e.g., high tensile strength, stiffness, lightweight, high fracture toughness, corrosion resistance, and low cost). Such superb properties with lightweight PMCs are the basis of their usefulness in the aircraft industry, aerospace industry, aeronautical industry, and automotive industry, as well as being incredibly useful for structures that utilize lightweight yet strong materials [11]. Furthermore, an increase of global demand for new polymeric materials that can be produced with high quality at large quantity and reduced production costs, has led to the suggestion of various manufacturing processes characterized by high producing performance [12].

Advances in scientific research have observed that inclusions of 2D-nanofillers (e.g., graphene, *h*-BN, etc.) in the reinforced polymer matrix present a significant increase in the

mechanical properties [13]. The 2D-nanofillers provide desirable properties unavailable in the polymer matrix or the filler material alone. Moreover, the uniform dispersion of nanofillers in a polymer matrix as well as a strong link between them are required to achieve high performance of reinforced polymer nanocomposites. Using different polymers, the in-situ polymerization and high shear for exfolication occur simultaneously, resulting in high filler dispersion and reinforcement of the matrix. The results may be attributed to increasing the polymer chains that grow in the presence of the 2D-nanofillers, which is convenient for low and high concentration of additives [10, 14]. Various techniques for the preparation of 2D materials have been developed over the last ten years, such as mechanical, thermal exfoliation, and chemical vapor deposition [15]. Thus, an effective technique that can exfoliate 2D materials and reinforce polymers simultaneously would be a tremendously breakthrough. The liquid phase exfoliation (LPE) method is probably the most common method for extracting mono-layer and few-layer flakes from graphitic materials [16]. In this study, a variation of it is used as the main process to peel off the 2D materials in a liquid phase polymer, while simultaneously reinforcing the polymer matrix. Thus, the major aim of this research is developing a novel exfoliation method and observing the fluid dynamic (rheology) behavior during the process. To complete the study, the final product is tested via nanoscale characterization techniques to understand the quality of the new materials, assess the manufacturing capability, and optimize the production.

1.2 Research Aims

Reducing processing time, increasing cost-efficiency, enhancing quality, and fostering scalability are major objectives for recent studies. Thus, the goal of this research is to explore a novel exfoliation method for producing 2D nanomaterials directly from their natural resources, and then using nanoscale characterizations to evaluate them. This processing method innately produces polymer nanocomposites at high levels of matrix reinforcement, given molecular interactions at the nanoscale between nanofiller and polymer. This research also examines the effects of post heat treatment on the mechanical properties of the formed G-PMC samples. Finally, electrospinning of the reinforced nanocomposite materials into fibers are investigated.

1.3 Research Approach

In this work, the approach for in-situ liquid phase exfoliation (LPE) of graphene and/or hexagonal boron nitride (2D nanofiller) and matrix reinforcement consists of four main parts as depicted in Figure 1. 1. The results from the nanoscale-characterizations help direct the project, and a number of different parameters are investigated for the polymer nanocomposite. This parametric study of in-situ liquid phase exfoliation (LPE) and nanoscale characterization provides the opportunity to understand the exfoliation mechanisms of 2D nanofiller and the influence of this additive on the PMMA matrix.



Figure 1. 1 scheme of the general approach used in this study

1.4 Dissertation Outline

Chapter 1 gives an introduction and background to the study and provides a research summary with an explanation of the motivation behind the work. The approach is presented in a flow chart. Chapter 2 gives a literature review of 2D nano-additives, specifically graphene and hexagonal boron nitride, along with the nanocomposite polymers and their applications. Chapter 3 identifies the general project tools, including experimental setups and characterization instruments (nanoscale-characterizations facilities), which are employed in this study. Chapter 4 presents the processing of graphene-reinforced polymer matrix nanocomposites by in-situ mechanical shear exfoliation of graphite in a PMMA/acetone solution. Several parameters are investigated in this chapter, such as polymer/solvent concentration and post heat treatment of the samples. The exfoliation efficiency and mechanical properties of the final G-PMMA nanocomposites are correlated to the examined parameters. Chapter 5 discusses the fabrication, structure analysis, and mechanical properties of the graphene and hexagonal boron nitride nanosheet reinforced poly (methyl methacrylate) polymer nanocomposites. Chapter 6 describes the exfoliation of graphene in the water-based poly(vinylpyrrolidone) solution. Chapter 7 details the manufacturing and characterization of graphene-reinforced electrospun poly(methyl methacrylate) nanocomposite fibers.

Chapter Two

Literature Review and Background

2.1 Graphene Background

Graphene consists of crystalline carbon atoms aligned in a two-dimensional layer of sp2. The carbon atoms are tightly bundled into a hexagonal honeycomb crystal lattice (Figure 2. 1) with a distance between carbon-carbon bond about 0.142 nm [17]. Graphene is the foundation of graphite and other graphitic materials of different dimensions. Thus, it can bring together into 3D multi-layers as in graphite and diamond structures, rolled into 1D carbon nanotubes, or enfolded into 0D fullerenes (see Figure 2. 1) [18].

Experimental and theoretical studies of graphene have been performed at a remarkably increasing rate since the beginning of the 21st century, which can be noted by the rise of annual publications (Figure 2. 2) [19]. In 1961 and for the first time, Boehm and co-workers are succeeded to separate and then characterized the monolayers graphene flakes by using X-ray diffraction and TEM [20]. In 2004, Andre and Konstantin reported a producing of large quantities of graphene flakes in the lab [21, 22]. The method they used by detaching graphene layers from graphite onto paper via a graphite pencil and then picking the graphite up using sticky tape until graphene was found [17]. Andre and Konstantin granted the Nobel Prize in Physics in 2010 for their work [23].



Figure 2. 1 Graphene is 2-D structural forming of carbon atoms. It can be rolled into 0D fullerene, folded into 1D nanotubes, or agglomerated together into 3D graphite, adapted from [18].



Figure 2. 2 Publications on Graphene from 2000 to 2016, adapted from [19].

2.1.1 Graphene Properties

Graphene has many exciting and desirable properties, such as a high electrical conductivity, which makes it an ideal material that can be utilized in many novel electronic Graphene also exhibits interesting thermal, mechanical, and optical applications. properties, as illustrated in Table 2. 1. Monolayer graphene flake is classified as excellent transparent material with a capacity to scale up the light absorption per each new layer added. The amount of white light absorbed per layer of graphene added is about 2.3% [24], and the reflectance is less than 0.1% in the visible region [25]. Graphene layers possess a relatively high broadband transmission level with high optical absorbance for each graphene sheet, which is essential for transparent conductive electrodes. Additionally, fully transparent sheets of graphene may be only observed at single and double layers as a result of Pauli blocking [26, 27]. The thermal conductivity of monolayer graphene flakes at room temperature is around 3,000-5,000 W m⁻¹ K^{-1 [28]}, dropping to 600 W m⁻¹ K⁻¹ when it is stuck to another material substrate. The drop is caused by hindered phonon movement in the region where the graphene interfaces with a substrate, which causes dissipation of phonons in that region. This aspect is different from plain graphene sheets, in which the paths that the phonons take are continuous and without a barrier. Even at this drop in the thermal conductivity, graphene is still more thermally conductive than copper, i.e., ~ 400 Wm⁻¹K⁻¹ [29, 30].

A monolayer of carbon atoms in 2D hexagonal lattice or called Graphene is considered to be one of the harder and stronger materials known, even harder than diamond and 200 times stronger than steel [31-33]. A monolayer graphene sheet possesses a high Young's modulus of ≥ 1.0 Tpa, giving it the ability to carry stresses up to 42 Nm⁻¹ [34]. The unique properties of graphene platelets have attracted considerable interest from researchers who want to use it to reinforce a wide range of thermoset and thermoplastic polymers [35]. The graphene nanoflake reinforced polymer has increased intrinsic strength and elastic modulus to enhance the performance of bulk polymer composites, which is currently used in several applications in modern life.

| Some basic properties | Graphene |
|----------------------------|---|
| Young's modulus | ~1100 GPa |
| Fracture strength | 125 GPa |
| Thermal Conductivity | \sim 5000 W m ⁻¹ K ⁻¹ |
| Mobility of charge carrier | $2 \times 105 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ |
| Specific Surface area | $2630 \text{ m}^2 \text{ g}^{-1}$ |

Table 2. 1 Some of the superb properties of graphene [36].

2.1.2 Graphene Preparation and Manufacture

In recent years, different strategies have been suggested for the producing and synthesis of graphene. Graphene can be obtained from one of two specific synthesis approaches, i.e., the "top down" approach and "bottom up" approach, which are shown in Figure 2. 3. The "top-down" synthesis method involves extracting a monolayer or few-layers from pre-

existing 3D graphite crystals, whereas the "bottom-up" processing refers to self-assembly via small molecules of carbon into graphene. The "top-down" and "bottom-up" process have been broadly utilized over recent years to fabricate graphene and are classified as following: liquid and mechanical exfoliation [37], chemical or plasma exfoliation [38], and chemical synthesis [39] are "top-down" methods, while thermal and chemical vapor deposition (CVD) are "bottom-up" methods [40] (as shown in Figure 2. 3). Also, some additional new synthesis methods are capable of fabricating different layers of graphene (single-layer graphene and few-layer graphene), such as microwave synthesis [41] and mechanical cleavage via using AFM tips [16].



Figure 2. 3 a process flow chart of graphene synthesis, adapted from [16].

2.1.2.1 Micromechanical Exfoliation

The mechanical exfoliation process is the first observed method to produce graphene flakes from its natural resource. It is described as a "top-down" approach method because it is carried out by supplying a longitudinal and transverse force on top of the materials' surface structure. The natural structure of graphite consists of many single-layer graphene flakes stick together via relatively weak forces is called van der Waals force. In the 3D-graphite structure, the interlayer spacing and bond energy between the graphene single layers are about 3.34 Å and 2 eV/nm², respectively, requiring an external force of about 300 nN/lm² to peel off one single-layer graphene from its natural structure in the 3D graphite [16, 42]. Several micromechanical exfoliation methods can be used to exfoliate graphite into graphene, such as adhesive tape [43] and sonication [44], etc.

In the micromechanical exfoliation process, graphene platelets are detached from a natural structure of graphite using adhesive tape as in Figure 2. 4. Once the initial peeling is done, the result is a multiple-layer graphene stack on the tape. It is then repeatedly peeled so that the multiple layers will exfoliate into much smaller layer graphene. Afterwards, the tape is stuck to a substrate, and the adhesive is dissolved by acetone, or another solvent, in order for the tape to be removed. Finally, one more peeling step via using new tape is performed so that the graphene sheets can be collected [45].


Figure 2. 4 Micromechanical exfoliation of graphene using scotch or adhesive tape from highly oriented pyrolytic graphite (HOPG) [17, 43].

2.1.2.2 Liquid Phase Exfoliation

Liquid phase exfoliation (LPE) is classified as a top-down process method, which can perform excellent exfoliation of graphitic materials into a 2D few-layers or a monolayers flake, and these flakes are defect-free at relatively high concentration. Therefore, LPE can be a practical method compared to most of the other techniques; and LPE process of graphene flakes is expected to become an essential method in the near future. The preparation of graphene nanosheets by this approach involves the peeling of natural graphite particles via sonication or high-shear mixing in the organic solvents [46-51].

LPE of graphite was first observed by Coleman et al. [52] using sonication in Nmethylpyrrolidone. In LPE via sonication technique, the graphene flakes are obtained from the dispersion of natural graphite in aqueous solutions or another organic solvent, such as dimethylformamide (DMF) and N-methylpyrrolidone (NMP), etc., which is then followed by centrifuging to remove aggregated particles, as illustrated in schematic diagram of Figure 2. 5.

One advantage of the liquid exfoliation process via sonication is that the preparation of graphene flakes is generally easy, while the disadvantage of this method is a very low graphene concentration of about 0.01 mg mL⁻¹, which can be increased up to 1.2 mg mL⁻¹ and 4 wt % of monolayers by using drastically longer sonication times of about 460 hours [37, 53] (see Table 2. 2). Another disadvantage of the sonication method is the need for expensive solvents, which could hinder the ability to use this method in commercial applications [37, 46]. The largest produced quantity of monolayers graphene that has been reported is about 29% from sonication of graphite particles in the organic solvents [54].



Figure 2. 5 Schematic shows the experimental liquid phase exfoliation process via sonication with snapshots of centrifugate after exfoliation, adapted from [55].

| No | Method | Exfoliation Medium | Time (h) | Concentration (mg mL ⁻¹) |
|----|-------------------------|----------------------------|----------|---|
| 1 | Bath sonication | NMP | 0.5 | 0.01 |
| 2 | Sonication | NMP | 460 | 1.2 |
| 3 | Bath sonication | O-DCB | 8 | 0.0066 |
| 4 | Sonication (sequential) | NMP | 8 | 0.43 |
| 5 | Tip sonication | NMP/azobenzene | 3 | 0.07 |
| 6 | Bath sonication | NMP/NaOH | 1.5 | 0.07 |
| 7 | Bath sonication | Water/SC | 430 | 0.3 |
| 8 | Sonication | Water/SC | 12 | 0.25 |
| 9 | Sonication | Water/PVP | 1 | 0.42 |
| 10 | Bath sonication | Water/ammonia solution | 8 | 0.058 |
| 11 | Sonication | Water/Triton X-100 | 12 | 0.7 |
| 12 | Sonication | Low boiling point solvents | 48 | 0.5 |

Table 2. 2 Demonstrates the influence of processing time and exfoliation medium (solvent) on the graphene concentration by using sonication method, adapted from [46].

Other studies have come up with several recommendations to scale up the exfoliation techniques in the liquids and achieve high exfoliation performances of graphene. Some ideas include: prolonging the processing time (see Table 2. 2 and Table 2. 3), increasing the initial graphite concentration, mixing-up with polymers and surfactants, using solvent exchange methods, enhancing cavitation and collision effects, and supplying high shear force mixing in term of fluid events which is known by high shear exfoliation methods, (see Figure 2. 6 and Figure 2. 7) [37, 56-58].

| No | Exfoliation Medium | Exfoliation Time (h) | Concentration (mg mL ⁻¹) |
|----|-----------------------|-------------------------|--------------------------------------|
| 1 | NMP | 0.5 | 0.01 |
| 2 | Water/SC | 2 | 1.1 |
| 3 | Water/PVP | 2 | 0.7 |
| 4 | Water/Black liquor | 10 | 10 |
| 5 | Water/Black tea | 0.25 | 0.032 |
| 6 | NMP | 1 | 0.65 |
| 7 | 40 vol % IPA-water | 1 | 0.27 |
| 8 | NMP | 1 | 1 |
| 9 | NMP | 6 | 0.251 |
| 10 | OCDB | 1.5 | 0.03 |

Table 2. 3 Shows the effect of processing time and exfoliation medium on the graphene concentration by using a high-shear exfoliation method, adapted from [46].

Recent developments in liquid-phase exfoliation techniques predict that the high shear method could substitute sonication in the near future because of its ability to peel graphite into graphene flakes effectively with high quality and large quantities (see Figure 2. 7) [59]. It was found that the effective cleavage of graphene sheets occurs when the local shear rate exceeds 10^4 s⁻¹ during the LPE process [46, 60], which could be improved by enhancing the liquid viscosity or increasing the mixing speed and processing time [61, 62] (see Table 2. 3).



Figure 2. 6 The exfoliation mechanism for graphene production by shearing, collision, and cavitation, adapted from [63].



Figure 2. 7 Schematic a high shear mixer of the exfoliation graphite with PVP or SC solution. The graphene-polymer mixture was then centrifuged to extract unexfoliated graphite particles, adapted from [64].

In 2014, Coleman and co-authors presented important breakthroughs in evolving exfoliation techniques via high shearing of natural graphite particles in organic solvents [47], which was a substantial advancement in shear exfoliation for producing graphene flakes. The study illustrated that high-shearing of graphite particles in suitable solvents could lead to high-concentration dispersions of graphene nanoplatelets (see Figure 2. 8) [46, 60].

LPE via high shear mixing is an advantageous method which can open new opportunities to produce graphene at a significant yield rate and low-cost. Such a method can prepare graphene flakes with minor-defects, and dispersed in various liquids at high quality and large quantity. The produced graphene could be evaluated using different characterizations methods, such as TEM, SEM, Raman spectroscopy, UV-vis-IR absorption spectroscopy, and atomic force microscopy (AFM), etc. [47].



Figure 2. 8 (a) A liquid-phase peeling of graphene in a beaker (b, c) mixing head rotor and stator. (d) Graphene flakes are collected in the bottles after produced by high shearing with N-methylpyrrolidone (NMP), adapted from [47].

2.2 Hexagonal Boron Nitride

Boron nitride (BN) is an inorganic layered material with a hexagonal crystalline lattice, similar to graphite's carbonic networks. It is also commonly known as 'White Graphite.' Structurally, the hexagonal boron nitride (*h*-BN) is very much like to a graphene sheet patterns, possessing 2D-bonded layers (two-dimensional materials), as shown in Figure 2. 9, which consists of boron (B) and nitrogen atoms (N) arranged together in honeycomb crystals patterns, making the *h*-BN structure extremely robust with highly stable and isoelectronic [65]. In many applications, *h*-BN is selected as an alternative substance to graphene because of its unique properties and significant affinity with carbon, making it important in many applications and industries where carbon cannot be used.



Figure 2. 9 h-BN-Structure. (A) Stereogram. (B) The 2D floor plan, adapted from [66].

2.2.1 Properties and Applications

Monolayer hexagonal boron nitride has superb properties such as high Young's modulus (~0.865TPa) and fracture strength (~70.5GPa) [9]. Studies show that theoretically, monolayer *h*-BN possess a specific surface area of about 2,600 m²/g, which leads to excellent performance in the interfacing and interactions between BN and polymer matrix chains, by forming several bonds in the BN-based polymeric nanocomposites. [67]. According to Ouyang [68], hexagonal boron nitride- nanoribbons have thermal conductivities from 1700 to 2000 W/(m·K), which is relatively similar to the experimentally-measured values of graphene sheets. Theoretical studies have pointed out that the zigzag edge *h*-BN-nanoribbons, which can be employed as the main components in devices that require excellent heat characteristics [68]. Atomically thin films of hexagonal boron nitride have demonstrated better oxidation resistance behavior in comparison to that of graphene layers. Li and coworkers [69] concluded that the oxidation

temperature of single-layer hexagonal boron nitride nanoplates is 700°C and can withstand up to 850°C in the atmosphere, while bilayer and few-layer hexagonal boron nitride nanoplates have even higher oxidation temperatures. Moreover, the 2D-*h*-BN sheets have a slightly larger thermal stability or heat resistance of about 1000°C in the atmosphere and 1400°C in vacuum [69]. Investigations in the electronic and dielectric properties reveal that the 2D-*h*BN is considered electrically insulating substances because the nitrogen (N) atoms tend to be surrounded by pi-electrons in the molecular structure, which form electronegativity differences between the N - B pair atoms [65, 70-73]. *h*-BN is an excellent electrical insulator and thermal conductor with a large bandgap of about 5.97eV and high optical transparency, thus *h*-BN sheets could be utilized as a tunnel barrier for various devices [74].

The technological applications of *h*-BN sheets have been broadly categorized according to usage, ranging from metallurgy sector to photo-electricity, semiconductors, catalysts, and even cosmetic products [66]. Currently, BN components are used in industrial fields such as automotive, device (e.g., in oxygen sensors as a seal), and coatings (because of high chemical stability). Also, *h*-BN in its powdered form can be utilized as a core material for thermal management of electronic devices [75]. By using LPE methods, *h*-BN, graphene, and other 2D layered materials can be employed to reinforce polymers (e.g., including polyvinylchloride (PVC), PMMA, PVP., etc.). The results in the current and previous studies demonstrate that such reinforcement enhances the tensile strength and Young's modulus to 3 GPa and 240 MPa, respectively. This augmentation of key properties is due to the nanolayer alignment, uniform dispersion, and strain induced delamination [76, 77].

2.3 Polymer Matrix Nanocomposites Background

Nowadays, one of the hottest research areas in the field of nanotechnology is the development of polymeric materials, especially the polymer matrix nanocomposites. In the beginning of the 20th century, Baekeland started the study of composites materials by reinforcing clay by thermosetting a resin called Bakelite [78, 79]. The earliest academic studies of exfoliated and reinforced nanocomposite polymer by silicate nanofillers were performed by Carter in the 1950s [80]. However, the industrial development of polymeric nanocomposite materials only began forty years later, after the Toyota Motor Corporation reported a significant increase in the mechanical properties of reinforced Nylon-6 matrix by using montmorillonite (Mt) as a filler [2].

Historically, polymer matrix nanocomposites were efficiently prepared by adding different nanoscale fillers such as, nano-fibers, nano-plates, and nano-particles (Figure 2. 10) into the polymer matrix structure to enhance their physical and chemical properties [30]. Among the various types of nanocomposites, carbon-reinforced polymer matrix composites (C-PMCs) have already attracted considerable attention from researchers. Polymers have been reinforced by carbon nanotubes (CNT's) and carbon nanofiber (CF's). Graphitic reinforced polymer matrix composites have shown a substantial enhancement in desired polymer properties. The unique specific characteristics (e.g., high strength and stiffness, light weightiness, and excellent electrical and thermal conductivities) make polymer matrix composites the key building/functional materials in many fields [81].



Figure 2. 10 schematic diagrams showing some shapes for materials particles used in reinforced polymers matrix, adapted from [82, 83].

2.3.1 Polymer Matrix Nanocomposite Synthesis Methods

Polymer nanocomposites could be prepared by using either chemical-approach or mechanical-approach of depositing and bonding nanofillers substances in a bulk polymer matrix. Excellent dispersion and interaction between the nanofillers and the matrix are the most essential requirement for a polymer matrix-based compound to achieve maximum reinforcement. Uniform dispersion and good compatibility of nanofillers in the polymeric matrix are considered one of the most important issues when creating a reinforced polymer nanocomposite. There are some physical parameters necessary to form a nanocomposite polymer, such as low agglomeration energy, suitable melting viscosity or liquid phase viscosity of the polymer, and high shear stress during the process. Different types of preparation methods are reported for the fabrication of polymer nanocomposites, the most common methods being [10, 84]: *i* intercalation method, *ii* in-situ intercalative polymerization technique, *iii* melt blending, *iv*) direct mixing of polymer matrix with

fillers (see Figure 2. 11), *v*) template process , *vi*) polymerization process, and *vii*) sol-gel method, solution casting [85].



Figure 2. 11 Diagram shows the preparation steps of polymer composites by direct mixing of polymer solution with the fillers, adapted from [86].

The recent studies of polymer matrix nanocomposite structures highlight their preparation method and research developments. These studies provide an opportunity to understand the reinforcement mechanism and predict the required properties for a nanocomposite matrix based on the nanofiller types (e.g. graphene, CNT, *h*-BN, and Clay nanoparticles ..etc.) [1, 87]. A most realistic description of nanocomposite structure has been suggested by Alexandre and co-authors [88], which classifies the nanocomposite polymers into three main types based on the natural properties of the components (i.e., fillers, solvent, and matrix) and the synthesis methods (see Figure 2. 12). By using the silicate layers as a filler, the first type of composite polymer has the same properties of traditional microcomposites (Figure 2. 12a), which is obtained when the matrix chains cannot intercalate between the nanofiller sheets; thus, the phase separated composite is induced. The intercalation is occurred between the matrix and fillers, as given in Figure 2. 12b, when the polymer chains intercalating with the silicate sheets and then arrange in a multi-layer form with matrix chains. The nanocomposite polymer, as shown in Figure 2.

12c, is obtained when the fillers are completely exfoliated and dispersed in the matrix, leading to significantly improved nanocomposite performance [88].

Incorporation of various nanoadditives such as graphene sheets, silicate layers, carbon nanotubes, nanofibers and silica nanoparticles into the polymer matrix have been shown to improve notably the mechanical, thermal, and barrier characteristics of the composite, along with clear enhancements in adhesion, rheological properties, and processing behavior in that new product. [89].



Figure 2. 12 sketch show three types of composite polymer consisting of intercalation of polymer chains with the nanofillers (silicate layers) (a) traditional phase separated process (microcomposites) (b) the intercalated process of nanocomposite (c) the exfoliated process of nanocomposite polymer, adapted from [88].

2.3.2 Polymer Matrix Nanocomposite Applications

The discovery of polymer nanocomposites attracts considerable interest throughout all sectors of industry and polymer science technology, owing to their unique mechanical, electrical, and thermal properties [90]. Nowadays, polymer nanocomposites are commonly used in almost all industrial fields with a wide range of applications, such as packaging, environmental remediation, energy saving, radiation absorption, sensors manufacturing, transportation resources, defense manufacturing, information devices, novel catalysts, and cosmetic products, etc. [91] (see Figure 2. 13).



Figure 2. 13 Application fields of polymer matrix nanocomposite, adapted from [91].

Polymer nanocomposites are used in storage energy applications, such as lithium-ion batteries (see Figure 2. 14), which enhance the battery cell performances via increasing voltage, capacity, and lifetime expectancy, as well as having low toxicity and higher rates of performance [91-93]. Another usage of nanocomposites in the storage energy field is electrochemical capacitors, which are characterized by high storage capacity and provide high amounts of energy as well as prolongs lifetimes. This capacitor has attracted the attention of scientists and recent studies for developing and scaling up for future use in electric vehicles, aerospace applications (drones), and electronic devices [94].



Figure 2. 14 show the influence of nanofillers in nanocomposite polymer electrolytes on the pathways system of lithium-ion conduction, which used to develop of next-generation safe lithium-ion batteries, (a) nanoparticles, (b) random nanowires (NWs), (c) aligned nanowires. The lithium-ion conduction of the NWsnanocomposites exibited higher performance and faster conduction system than nanoparticles- nanocomposites, (d) The surface area of nanoparticles and NWs work as an booster way for Li-ion conduction, adapted from [95].

One of the more promising applications is energy saving by using polymer nanocomposites to reduce fossil fuel consumption and help to decrease environmental pollution. Particularly, the lightweight feature of polymer nanocomposites has contributed to reducing fuel consumption significantly via using it in manufacture various parts of vehicles, airplanes, etc. Additionally, approximately 30-40% of primary energy utilized by buildings go towards heating, cooling, ventilation, and lighting. Therefore, polymer nanocomposites can offer a high-efficiency insulation and environmental protection in sustainable construction or green building application [91, 96]. Smart windows (solar smart glass) are an innovative strategy that are effective in controlling the exchange of energy between the exterior and interior of buildings, through the use of windowpanes with solar heat control properties [97, 98](see Figure 2. 15). The energy-saving applications also lead to an improved economy by reducing the energy consumptions [99]. Polymer nanocomposites can also be used for chemical pollution absorption, solid sorbents, and filters of the separation systems [91, 100].



Figure 2. 15 shows using polymer nanocomposites (polymer/glass plate) in building for saving energy. The luminescent materials in the nanocomposites work as a solar concentrator and absorb the incident radiation or sunlight and reemit the absorbed light at a longer wavelength, adapted from [101].

Polymer nanocomposites can also be used to protect materials and metals against oxidation, corrosion, and wear. There has been a heightened interest in using polymeric nanocomposites products for metallic corrosion protection via coating or painting [102]. Different organic paints using polymer nanocomposites, such as polyvinyl butyral, acrylic polymers, water-based latex, vinyl, alkyd resins, epoxy resins and polyurethanes, strontium chromate, are frequently used to curtail corrosion of mechanical substrates. It is well known that paint can create a barrier closing the passage of water and oxygen, which maximizes the resistance of the ion transfer at the metallic surface and thus restricts the flow of electrons from the metal surface to the outside oxidizing environments or materials [103, 104]. Polymer nanocomposites in paintings or coatings can thus lead to enhanced barrier blocking properties and increase the lifetime of the organic paints [105].

Chapter Three

Experimental Setup and Analytical Instruments

3.1 High Shear and Reinforced Polymer Setup

A schematic of the high shear setup is exhibited in Figure 3. 1, possessing a design similar to the shear rotational rheometer (concentric cylinder) with the ability to generate high shear stress. However, in the present study, the high shear events setup consists of two coaxial cylinders, with a solid inner cylinder/spindle and a hollow outer cylinder as the container. The outer cylinder is supported by and connected to a fixed torque gauge (Ametek digital torque gauge). Our setup is designed to generate a high shear rate in the small gap between the two concentric cylinders to effectively exfoliate high quality 2D materials in the liquid phase. If a liquid polymer is used, then a reinforced polymer matrix composite can be simultaneously obtained after the exfoliation process. Also, the chamber is sealed by a special cover, designed to prevent the evaporation of solvent or loss of material, while keeping under pressure. The setup has been calibrated for rheological capability using N1000 standard oil purchased from SCP SCIENCE.

Here, graphite and/or BN is employed to produce a nanocomposite polymer by exfoliating the bulk additive by rotating the inner cylinder at constant speed for 6 hrs. For example, PMMA/acetone/graphite mixture is injected into the 6.5 mL gap between the inner spindle and the container. The shearing chamber is maintained at 25°C by a water chiller during the whole process. Also, the torque gauge is zeroed upon water circulation to eliminate its effect on the torque reading, prior to operating the shearing process. By

changing the PMMA/acetone concentration of the solution, the effects of viscosity on the graphite peeling efficiency can be assessed, and the properties of the resulting reinforced-PMCs can be tuned.



Figure 3. 1 Schematic diagram of the experimental setup (a) high shear setup (b) Zoom in of two concentric cylinders mixing chamber.

3.2 Electrospinning Fiber Setup

The electrospinning setup, as shown in Figure 3. 2, consists of three parts: (1) a 10 ml syringe attached to a syringe pump to eject the polymer solution at a fixed flow rate via spinneret needle with blunt flat tip [1.27 mm outer diameter(OD) 0.83 mm internal diameter (ID)]; (2) a ground electrode of aluminum substrate utilized as a fiber mat polarity collector; and (3) a high voltage power supply 12 kV (Glassman high voltage, Inc.) establishing an electric field between the spinneret needle and electrode substrate (separated by a gap of 15 cm).



Figure 3. 2 A typical schematic illustration electrospinning setup of fabrication of graphene-reinforced fibers

In the following research, the graphene reinforced PMMA nanocomposite, produced by our novel LPE method, is diluted by acetone to a PMMA/acetone concertation of 0.35 g/ml at ambient temperature with adequate stirring for 3 hours, and then loaded into the syringe that holds the polymeric solution mixture for electrospinning. The polymer solution is ejected towards the fiber collector substrate at a constant and controllable flow rate (0.04 mL/min) by the syringe pump. High voltage 12kV is applied to the needle at room temperature 25 ± 1 °C and $40\pm1\%$ RH. This process leads to the formation of a continuous individual solid fiber.

3.3 Characterization Techniques

Equipment used to characterize the reinforced polymer nanocomposite and its nanofillers are summarized in Table 3. 1.

| Technique | Equipment | |
|--|--|--|
| Raman spectroscopy | Renishaw 1000, laser excitation 633 nm | |
| Scanning electron microscopy | Zeiss Sigma 8100 | |
| Transmission electron microscopy | JEOL 2010F | |
| UV-Vis spectroscopy | Thermo evolution 300 | |
| X-ray diffraction | PANalytical X-ray diffraction | |
| Scanning Helium Ion Microscopy | Carl Zeiss ORION PLUS microscope | |
| Nanoindentation | NanoTest Vantage-Micromaterials, UK | |
| Dynamic Mechanical Analysis (nanoDMA) | Hysitron, UTi-750, USA | |

Table 3. 1 List of characterization techniques.

3.3.1 Raman Spectroscopy

Raman (Figure 3. 3) is a spectroscopic technique and is commonly used to characterize the molecular structure of the materials via vibrational, rotational, and translational modes.

According to this technique, many carbon systems and other related materials (e.g., graphite, high and low sp3 amorphous carbon, metallic materials and semiconducting single-walled nanotubes etc.) can be analyzed from the relation between the Raman frequency shift vs. intensity (see Figure 3. 4) [106, 107].

Herein, Raman spectra is measured by a Renishaw Raman microscope 1000 using a 633 nm He-Ne laser as excitation source. The laser spot size is between $1-2 \mu m$, with light collected by a 50X lens magnification. The Raman shifts cover the spectral range from 500-3200 cm⁻¹ for graphene fillers with the polymer and from 1200-1420 cm⁻¹ for *h*-BN fillers. An average of 20 scans is used for spectral analysis for each sample. The sample for Raman is prepared by casting and compressing small amounts of as-obtained polymer matrix nanocomposites between two ITO coated glass slides to obtain a 1 mm flat thin layer, and then letting it dry in s fume hood for 48 hours.



Figure 3. 3 Schematic diagram of Raman spectra equipment (Renishaw RM 1000) [108].



Figure 3. 4 Raman spectroscopy analysis of different carbon systems (reproduced from [109]).

3.3.2 UV-Vis Spectroscopy

The UV-visible absorption spectroscopy is performed by a thermo evolution 300 UV-Vis spectrophotometer (Figure 3. 5). The UV-Vis samples are prepared from the same molded specimens. Each sample's diffuse reflectance is measured by using the Praying Diffuse Reflectance Accessory. Pure PMMA is also analyzed as the control group. Each sample is placed in the micro-sample cup and inserted into the accessory. Incident light, ranging from 200 nm to 600 nm in wavelength, is aimed at the catalyst bed, and the percent reflectance is recorded. By transforming the diffuse reflectance data into Kubelka-Munk units (KMU), the samples' patterns of absorbance can be obtained.



Figure 3. 5 Image of UV-Visible spectroscopy.

3.3.3 In-situ Shear Rheology Test

Rheological behavior of the graphite exfoliation and formation of the polymer nanocomposites during processing is assessed, as the interfacing of the liquid polymer matrix and the suspension particles evolve. To understand the fundamental mechanisms and optimize the fabrication process, it is important to know the rheological properties and the structural transformation of composite material during processing, which may experience heterophase viscoelastic behavior [110].

The torque involved during the exfoliation process of the graphite/PMMA is measured by a torque gauge which is connected to the outer cylinder. All the results are collected at a constant temperature of 25°C. Three steps are used to measure the torque.

1- Determine torque (shear stress) before graphite exfoliation by changing rotating velocity (shear strain rate) (0-1000) RPM.

- 2- Determine torque with time at constant speed 2500 RPM for 2hr during exfoliation process.
- 3- Determine torque (shear stress) after graphite exfoliation (step2) by changing rotating velocity (shear strain rate) (0-1000) RPM.

The shear rate and shear stress of the small gap between two concentric cylinders as shown in Figure 3. 6, can be calculated by using the following equations [111, 112].

Shear stress
$$au = \frac{T}{2\pi R_i^2 L}$$
 (3.1)

Shear rate
$$\dot{\gamma} = \frac{2 \omega_1 R_o^2 R_i^2}{R^2 (R_o^2 - R_i^2)}$$
 (3.2)

For small gap approximation:

 $R \cong R_o \cong R_i$

Shear rate
$$\dot{\gamma} = \frac{2\pi \times R \times rpm}{\Delta R \times 60}$$
, $\Delta R = R_o - R_i$ (3.3)

Where: -

 $R_{\rm i}$ = radius of the spindle, m

 R_o = radius of the stationary cylinder, m

T= Torque, N.m

$$\omega_1$$
 = Inner cylinder rotates (angular velocity)

R=the radius at which shear rate is being measured ($R = \frac{R_o + R_i}{2}$)



Figure 3. 6 Schematic of Concentric cylinders demonstrating the rotating inner cylinder and stationary outer cylinder with rotating directions.

3.3.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM), Topcon JOEL 2010F (Figure 3. 7), is used at 200 keV with SAED to observe the morphology and crystal structure of the exfoliated graphene and h-BN in the PMMA matrix structure. The TEM samples are prepared by milling of molded of nanocomposites sample by using silica abrasive pads to obtain a fine powder. The small amount of powder is suspended in isopropanol and ultrasonicated for 5 minutes to achieve high dispersion. Then, the drops of this suspension are placed on the 3mm ultrathin copper grid and are dried overnight to be ready for TEM testing.



Figure 3. 7 Schematic diagram of Scanning Transmission Electron Microscope (reproduced from [113]).

3.3.5 Scanning Electron Microscopy (SEM)

A Zeiss Sigma Field Emission (Figure 3. 8) scanning electron microscopy (SEM) is used with an acceleration voltage of 5 kV, inlens or SE2, to assess the surface morphology and dispersion of graphene in PMMA and to see the interactions of graphene particles with the sample's inner structure. The samples of SEM are prepared by fracture of the molded specimens. Then, mounted vertically on the aluminum studs and coating by gold to thickness 5 nm via using sputter coater. Those samples are placed under vacuum for 24 hrs prior to observation.



Figure 3. 8 Schematic diagram of scanning electron microscope (reproduced from [114]).

3.3.6 Scanning Helium Ion Microscopy (HIM)

Helium ion microscopy, as shown in the Figure 3. 9, is conducted using a Carl Zeiss ORION PLUS microscope to visualize the overlapping of graphene flakes within the polymer matrix composite and to give the high-resolution images for exfoliated graphene flakes. HIM samples are prepared by using the same PMMA/graphene powder that is used with TEM test. The HIM sample is prepared by grinding the PMMA/graphene into fine powder. Then, the small amount of powder is sonicated in isopropanol for 5 minutes to achieve high dispersion. Finally, the drops of this suspension are placed on the 3mm ultrathin copper grid and dried overnight to be ready for HIM test.



Figure 3. 9 Schematic diagram of the scanning helium ion microscope (reproduced from [115]).

3.3.7 Nanoindentation Test

Nanoindentation testing requires the use of a diamond tipped indenter whose properties are well known. This tip is indented into a sample of unknown properties, with a set load, which gives a certain maximum depth. By analyzing the relation between the depth and load, the mechanical properties of the material can be calculated. Multiple indents can be done to analyze the various properties that may occur over a large surface in the material.

For the nanoindentation observations of unreinforced PMMA as reference and PMMA/graphene or *h*-BN nanocomposites, the processing materials are cast into cylindrical pellets (thickness = 1.5 mm and diameter = 10 mm) by hot injection at 200 °C into a cylindrical mold. These circular films are polished by a NANO 2000T polisher with

a polishing cloth disc to make sure that the specimen's faces are flat. They are then affixed onto aluminum stubs with a thin layer of glue. The nanoindentation experiment is performed using a NanoTest Vantage (Micromaterials, UK) equipped with a Berkovich tip (three-sided pyramidal diamond indenter) (see Figure 3. 10). Due to the sensitivity of the mechanical properties (i.e., elastic modulus, hardness) to the tip geometry, the tip contact area function is calibrated by using a standard fused quartz specimen before taking measurements. The different indentation effective parameters, such as loading, unloading rates, and holding time at maximum load, are determined with available literature data of Oliver [116]. Herein, indentation tests are performed at a force control, ranging from 0.1 to 10 mN, as well as at a holding time and unloading time of 30 seconds. Results are then picked from depths of 140 to 1350 nm. A matrix of eighty indentations are made at different locations for each sample, and the average values of the nanomechanical properties are carried out by using the Oliver–Pharr method [116]. The contact area $A(h_c)$ for Berkovich type-nanoindenter tip, where h_c is the contact depth, is defined in Equation 3.4 [116].

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \tag{3.4}$$

Reduced modulus (E_r) is calculated as in equation 3.5.

$$E_r = \frac{S\sqrt{\pi}}{2\beta\sqrt{A}} \tag{3.5}$$

Reduced modulus (E_r) is related to Young's modulus for sample (E_s) and the nanoindeter tip (E_s) , and we can determine it as in the equation 3.6 [116].

$$\frac{1}{E_r} = \frac{(1 - \nu_s^2)}{E_s} + \frac{(1 - \nu_i^2)}{E_i}$$
(3.6)

The Indentation hardness measurements (H) are performed depending on the equation 3.7 [116].

$$H = \frac{(P_{max})}{A(h_c)} \tag{3.7}$$

where P_{max} is the maximum load supply by indenter, h_{max} the maximum penetration depth, *S* the elastic contact stiffness of the unloading curve, and ε the geometric constant as ~0.75. β is a constant that depends on the indentation probe geometry and the projected contact area *A*. v_s is the Poisson's ratio of the sample ~ 0.35 for the PMMA. E_i and v_i are the Young's modulus and the Poisson's ratio of the Berkovich-nanoindenter tip most often considered for diamond. Thus, the experimental values for the probe tip are E_i =1141 GPa and v_i =0.07.



Figure 3. 10 (a) schematic of the indentation cross section on the surface (reproduced from [116]); and nanoindentation Vantage test explain (b) the Berkovich tip in the touching with a PMMA sample surface.

3.3.8 Viscoelastic Characterization - Dynamic Nanoindentation

Nanoindentation-dynamic mechanical analysis (nanoDMA) technique is utilized for characterizing the viscoelastic properties of soft materials as a function of frequency. It supplies an oscillatory load during an indentation on the material surface, and records the phase shift for the total indentation displacement and load to calculate the materials' dynamic properties [117]. The results of nanoDMA measurements, such as storage

modulus (E'), loss modulus (E''), and the loss tangent (tan δ), are considered to be major parts in identifying the viscoelastic behavior of soft materials. The storage modulus (E') is often related to the stiffness (k) and associated with Young's modulus (E), which is also relative to the energy stored of a viscoelastic material during a loading cycle. However, the loss modulus is often related to internal friction and propensity to lose energy, which is sensitive to various aspects such as structual morphology, relaxation of material structure, molecular motions, and other structural properties [118, 119]. The loss tangent or damping factor is indicated by the damping capabilities of a viscoelastic material. Moreover, higher loss tangent means a higher damping coefficient (C), leading to higher performance for viscoelastic materials, which corresponds to a more effective absorption and dispersal of energy [120, 121]. The specific values for storage and loss modulus can be determined as given in Equations (3.8),(3.9), and (3.10). These equations demonstrate that the damping coefficient of materials can be defined as a ratio of the out-of-phase counterpart to the inphase stiffness for the storage modulus. Thus loss tangent is often represented as the ratio of the loss modulus to the storage modulus (E''/E') [122].

$$E' = \frac{k\sqrt{\pi}}{2\sqrt{A}} \tag{3.8}$$

$$tan\delta = \frac{C\,\omega}{k} \tag{3.9}$$

$$E'' = \frac{\omega C \sqrt{\pi}}{2\sqrt{A}} \tag{3.10}$$

In this project, dynamic nanoindentation analysis is performed using the Hysitron, nanoindentation, USA (Figure 3. 11) with analysis using the nanoDMA theoretical

equations. Testing is done by applying a quasi-static load of 100 μ N and an oscillatory or dynamic load of 3 μ N with a sampling frequency range of 10-160 Hz. One hundred nanoDMA indentations are made at different points on the specimen's surface, and the average values are picked for each sample. In this study, storage modulus, loss modulus, and loss tangent of PMMA and its composites are tested at room temperature 25±1°C. The samples for nanoDMA are prepared the same way as the nanoindentation test samples.



Figure 3. 11 Image of Hysitron, nanoindentation, used here for nanoDMA analysis.

Chapter Four

Processing of Graphene Reinforced Polymer Matrix Nanocomposites by In-situ Mechanical Shear Exfoliation of Graphite

4.1 Introduction

Polymer matrix composites have been used in various fields [81, 123, 124], especially as key building/functional materials for diverse applications such as electrical/electronics industry, biomedical engineering, household utensils, 3D printing, automobiles, and aerospace (e.g., polymer-based composites form nearly half the weight of Boeing's 787 Dreamliner airplane [125-127]). More recently, polymer matrix nanocomposites have been successfully obtained by incorporating nanoscale additives, such as nanofibers, nanoplates, and nanospheres, into the polymer matrix structure to enhance the overall physical and chemical properties [2-5]. Among the various nanocomposites, carbon-reinforced polymer matrix composites (C-PMCs) stand out, attracting significant research interests. For example, carbon nanotubes (CNTs) and carbon nanofiber (CFs) have already been used to reinforce polymers. Accompanied by the development in graphene research, studies have found that graphene-reinforced polymers matrix composites (G-PMCs) can lead to substantial improvement of the desired polymer's performance [13].

Bulk cleavage of graphite through exfoliation, namely mechanical, thermal, and electrochemical, can produce graphene with high quality, at large quantity and low cost [37]. The mechanical method peels graphite flakes by overcoming the van der Waals attraction between adjacent graphene layers. In general, both normal and shear forces are

involved in the mechanical exfoliation of graphite into graphene, irrespective of whether processing involves sonication, spinning, mixing, or ball-milling [37]. Sonication of graphite in organic solvents yields graphene flakes with low defect content [128], but acceptable graphene concentration is small, typically ~0.01 mg mL⁻¹) [37]. Graphene nanoflakes have also been produced in a high-shear rotor, using a solvent, surfactant, or liquid-polymer dispersant [129, 130].

Many methods have been devised for processing G-PMCs, as discussed in recent review articles [5, 127, 131]. However, the challenge of scaling the technology for general industrial use has not yet been resolved. Even so, kilogram quantities of G-PMCs are being produced and tested for a broad range of potential applications [2, 132]. Because of their unique characteristics (i.e., high strength and stiffness, low density, excellent electrical and thermal conductivity), G-PMCs are attractive candidates for commercialization. For example, a recently developed integrated high-shear mixing/injection molding process is versatile, scalable, and cost-effective [133, 134].

In this work, a process to fabricate G-PMC composites is described, wherein highpurity grapheite is shear-exfoliated into graphene flakes that are bonded directly to the polymer matrix (without any external or handling contamination), thus yielding enhanced mechanical properties. The setup involves high-shear only strain events between two concentric cylinders where graphite is added to a liquid-phase polymer (PMMA/acetone). Such mechanical exfoliation of graphite in a solvated polymer appears to be an effective means to produce large quantities of G-PMCs at relatively low cost. Moreover, the experimental setup is fundamentally conducive for investigating the mechanisms involved, including the effect of liquid polymer viscosity on the exfoliation efficiency, along with the coupled effects of graphite/graphene loading on the rheological behavior (e.g., viscoelastic) of the solution during processing [135]. After drying, the structure and morphology of the as-obtained G-PMCs are studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and helium ion microscopy (HIM). The mechanical properties are characterized by nano-indentation.

4.2 Experimental Methods

4.2.1 Materials and Preparation

The poly(methyl methacrylate) (PMMA) powder and acetone use in this work are both purchased from Fisher Scientific. Synthetic graphite powder with an average flakes size of 8-20 μ m (TC 301 High Purity) was supplied by Asbury Carbons Inc. NJ.

First, the graphite powder is dried in an oven at 150°C for 8 hours, and the PMMA is dried by a vacuum drier for 8 hours. The PMMA powder is loaded by 1wt% of graphite powder; then dissolved in acetone forming the liquid phase PMMA solution for varying PMMA/acetone concentrations, i.e., 0.4, 0.5, 0.6, and 0.7 g/ml, respectively. Finally, the graphite/PMMA/acetone solution is sonicated for 60 minutes in a low power sonication bath to achieve high dispersion of graphite in the polymer solution forming a homogenous mixture, where all the PMMA powder is fully dissolved in the acetone.
4.2.2 Exfoliation Process

A schematic showing the sequence of steps involved in the shear-exfoliation process is presented in Figure 4. 1. Well-crystallized graphite particles (8-20 μ m) at 1wt% loading are ultrasonically dispersed in a PMMA/acetone solution, and subjected to shear exfoliation in a simple rotor (concentric cylinders) device. The inner shaft of the device rotates at constant angular speed while the outer cylinder is held stationary. During processing, a high-shear rate imparted to the graphite-added PMMA/acetone solution serves to exfoliate efficiently and disperse the graphite particles, resulting in a uniform distribution of graphene nanoflakes. The effect of liquid-solution viscosity on exfoliation efficiency is investigated using different polymer/acetone solution concentrations (i.e., 0.4, 0.5, 0.6, and 0.7 g/ml), with fixed graphite loading (1wt%). Structure and morphology of as-processed G-PMCs are examined by analytical-electron microscopy techniques.

The shearing device, Figure 4. 1, consists of a solid inner shaft and a co-axial hollow outer cylinder. The outer cylinder is connected to a sensitive digital torque gauge and fixed with respect to the rotating inner cylinder. Such an arrangement generates a high-shear rate within the small gap, corresponding to a volume of 6.5 mL, between shaft and cylinder, thus facilitating graphite exfoliation into graphene. A cover plate is used to prevent acetone evaporation, keep the solution under pressure, and prevent the solution from migrating out of the gap. In a typical experiment, the shaft is rotated at 2500 rpm for 6 hours, with the liquid phase maintained at 25°C by active water cooling. Thus, the influence of changes in liquid-phase viscosity on graphite-exfoliation efficiency can be determined, while also tailoring the mechanical properties of the resulting G-PMC.



Figure 4. 1 Schematic of the shear-exfoliation processing of graphite in the PMMA/acetone solution.

After drying, the final solid G-PMC (in comparison with pure PMMA processed in the same manner) is characterized by various techniques. Raman spectra is measured using a Renishaw Raman microscope with 633nm HeNe laser. UV-visible absorption spectroscopy is performed using a Thermo Evolution 300 UV-Vis spectrophotometer, with diffuse reflectance measured using the Praying Diffuse Reflectance Accessory. By transforming the diffuse reflectance data in Kubelka-Munk units (KMU), the pattern of absorbance can be obtained. Nano-indentation is conducted on polished samples to determine mechanical properties, using a NanoTest Vantage-micromaterials indenter equipped with a Berkovich tip (three-sided pyramidal diamond indenter).

The morphologies of graphene-reinforced PMMA composites are investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and helium ion microscopy (HIM). Scanning electron microscopy (A Zeiss Sigma) is used with an acceleration voltage of 5 kV and in-lens to reveal the surface morphology,

dispersion, and interaction of graphene flakes within the PMMA matrix. JOEL 2010F Transmission electron microscopy is used at 200 kV with selected area electron diffraction (SAED) to observe the morphology and crystal structure of the G-PMCs, giving a detailed analysis of the exfoliated graphene flakes. Scanning helium ion microscopy, which does not induce charging in the carbon nanostructures, is conducted using a Carl Zeiss ORION PLUS microscope to reveal the overlapping of graphene flakes within the PMC and produce high resolution images for exfoliated graphene flakes.

4.3 **Results and Discussion**

4.3.1 Characterization of Graphite

An SEM image and Raman spectra of as-received graphite powder are shown in Figure 4. 2 (a) and (b), respectively. Graphite particle size is 8-20 μ m, and surface area is ~6.0 m²/g. Raman G and 2D peaks are located at 1573 and 2701 cm⁻¹, respectively, along with a small D peak at 1352 cm⁻¹. The I_{2D}/I_G ratio of 0.4 corresponds to graphite [136]. The D peak indicates the defect level and degree of G disorder in the powder particles. The edges of graphite particles are observed during Raman analysis as defects because the laser spot includes them. The D peak, therefore, appears even when the graphite particles are perfect and free of defects [136].



Figure 4. 2 Graphite characterization. (a) SEM image, (b) Raman spectra.

4.3.2 Characterization of Exfoliated Graphene Reinforced PMMA Nanocomposites

4.3.2.1 Raman Spectroscopy

The Raman spectra of G-PMMA samples produced by exfoliating graphite particles at high shear in varying concentrations of PMMA/acetone solution are shown in Figure 4. 3. The plot elucidates the effects of solution viscosity (based on polymer-acetone concentration) on the mechanical cleavage of graphite into graphene. Typically, the I_{2D}/I_G intensity ratios, along with the G and 2D peak positions, have been used to evaluate the number of graphene layers [137].



Figure 4. 3 Raman spectrum (green) Raman spectra of G-PMC at concentration 0.4 g/ml is multilayer graphene, (pink) Raman spectra of G-PMC at concentration 0.5 g/ml is few-layers graphene, (blue) Raman spectra of G-PMC at concentration 0.6 g/ml few-layers, (red) Raman spectra of G-PMC at concentration 0.7 g/ml is bilayer graphene.



Figure 4. 4 I_{2D}/I_G for samples with different concentrations of polymer/acetone (viscosity).

The I_{2D}/I_G ratio increases notably with increasing polymer/acetone concentration, which corresponds to higher solution viscosity and thus higher shearing, as shown in Figure 4. 4. The ratio reaches 0.92 at a polymer/solvent concentration of 0.7 g/ml, which correlates to bilayer graphene flakes [138]. Figure 4.3 shows that the positions of G and 2D bands are red-shifted slightly with increasing polymer/solvent concentrations to be 1579, 1581, 1582, 1584 for G band and 1673, 1674, 1672, and 1671 for 2D band at 0.4g/ml, 0.5g/ml, 0.6g/ml, and 0.7g/ml polymer/solvent concentrations, respectively. As seen, the G and 2D peak positions are maximally shifted (i.e., 11 cm^{-1} and ~ 30 cm^{-1} , respectively) at the polymer/solvent concentration of 0.7 g/ml, as compared to those of bulk graphite, as presented in Figure 4.2 b. The D and D' bands are associated with defects and disordered structures of graphene [139]. Here, the D, D' intensity, and I_D/I_G ratio increase noticeably with decreasing polymer/solvent concentration (corresponding to lower solution viscosity). This Raman result could then be attributed to the edge/basal defects [137], along with average distance between those defects L_D [140]. The result also implies smaller particle size of the graphene flakes.

Figure 4. 3 shows that the PMMA peak intensities decrease with increasing polymer/acetone concentration, corresponding to the graphene achieving higher exfoliation and dispersion in the polymer matrix. As a result, the Raman graphene bands (G, D, and 2D) become more easily observed with better graphene dispersion in the PMC.

4.3.2.2 Solid Phase UV-Visible Analysis of π to π^* Transition

To analyze the solid-phase UV-Visible Spectra of the graphene/graphite in the PMMA matrix, 0.022 mL μ-samples are loaded into an Evolution 300 UV-Vis spectrometer

(*ThermoFisher*) equipped with a Praying Mantis Diffuse Reflectance Accessory (*Harrick Scientific*). The absolute diffuse reflectance (R_{∞}) is measured, with a Spectralon® disk as a reference. The absolute reflectance measured across the range of 200 nm to 600 nm is converted to Kubelka-Munk units, $F(R_{\infty}) = KMU = \frac{(1-R_{\infty})^2}{2R_{\infty}}$, which is analogous to absorbance for diffusely reflected samples.



Figure 4. 5 Kubelka-Munk units of solid-phase UV-Visible Spectroscopy of pure PMMA (black), and graphene/graphite in PMMA samples: 0.4 g/ml (green), 0.5 g/ml (pink), 0.6 g/ml (blue), and 0.7 g/ml (red).

As shown in the Figure 4. 5, pure PMMA, along with the other graphite-loaded samples which also contain PMMA, display an absorbance peak at approximately 220 nm. This peak corresponds to the energy difference between the HOMO and LUMO of PMMA, i.e., 5.6 eV [141]. The graphite containing samples also exhibit signals with maxima varying from 282 nm to 296 nm, which may be attributed to the π - π ^{*} transitions in the

carbon-carbon double bonds [142]. The redshift in the peak position has been previously reported to correspond to the region of the aromatic system [143]. As the grams of PMMA per ml of acetone concentration increases, a shift in the peak can be seen, as the 0.4 g/ml, 0.5 g/ml, 0.6 g/ml, and 0.7 g/ml samples have peak maxima at 282 nm, 287 nm, 290 nm, and 298 nm respectively. In additional to the redshift, the intensity of the peaks also grow. Both the increases in intensities and redshift of the peaks indicate the production of graphene from graphite, resulting in increase of the surface area of the aromatic system by shearing 3-D graphite into 2-D graphene. To determine better the amount of graphene produced, liquid phase UV-visible spectroscopy is conducted.

4.3.2.3 Graphene Quantification via Liquid Phase UV-Visible Spectroscopy

The amount of graphene produced from shearing graphite in the samples can be determined by analyzing the liquid-phase UV-Visible spectra of the graphene/graphite-PMMA composite suspended in acetone. For the suspensions, 0.014 g of each sample is suspended in 3.2 ml of acetone and sonicated for 10 minutes in order to produce 5 solutions, each with 0.003 g/ml of sample to acetone. The UV-Visible spectra % transmittance for each sample is measured across the range of 600 nm to 750 nm using an Evolution 300 UV-Vis Spectrometer (ThermoFisher).

The percent absorbance, $%A_{Graphene}$, of each sample at 660 nm is used to determine the concentration of graphene in the sample. Since the graphene in each sample is produced via exfoliation of graphite in a PMMA mixture, it is pertinent to account for the absorbance of the graphite/PMMA sample that experiences no exfoliation from each of the exfoliated samples. Accordingly, the background from the graphite and PMMA is subtracted, leaving only the absorbance from graphene, i.e., $%A_{Graphene} = [%A_{Sample} - %A_{No Exfoliation}]$ [128, 143, 144].

The concentrations of graphene dispersions are determined using the Beer-Lambert law ($A = \alpha Cl$), where *l* is a path length, *C* the concentration, and α the absorbance coefficient of graphene, which is taken to be α = 6600 ml g⁻¹ m⁻¹, as used in Coleman's work [128]. As seen in the Figure 4. 6 and Table 4. 1, higher concentration of polymer to acetone corresponds to higher viscosity, producing more exfoliated graphene.



Figure 4. 6 Effect of polymer/acetone concentration ratio (viscosity) on the graphene quantification.

| Sample | Graphene in | Graphene | % Graphite |
|----------------|-------------|--------------------|------------|
| | Exfoliated | concentration in | Conversion |
| | sample (mg) | Exfoliation sample | |
| | | (mg/ml) | |
| No Exfoliation | 0.00 | 0.000 | 0.0% |
| 0.4 (g/ml) | 0.45 | 0.005 | 1% |
| 0.5 (g/ml) | 1.66 | 0.022 | 3% |
| 0.6 (g/ml) | 10.93 | 0.140 | 22% |
| 0.7 (g/ml) | 36.21 | 0.225 | 72% |
| | | | |

 Table 4. 1 Graphene concentration, graphite conversion, and the total mass of graphene in the synthesized sample.

The mass of graphene in the measured sample was calculated by multiplying the concentration of graphene obtained from the Beer-Lambert law by the volume of acetone used in the suspension.

The mg of graphite in the measured sample was calculated by taking 1% of the mass of sample (graphite was 1% of each sample prior to exfoliation).

Graphite conversion is measured as in the next relation

$$\frac{mg_{Graphite} - \Delta mg_{Graphite}}{mg_{Graphite}} = \frac{mg_{Graphite} - (mg_{Graphite} - mg_{Graphene})}{mg_{Graphite}}$$

Mass of graphene in the final synthesized sample was calculated by multiplying the conversion by the starting amount of graphite (50 mg). Percent of graphene in the final sample was calculated by dividing the mass of graphene in the final sample by the mass of the starting sample (5000 mg).

4.3.2.4 Nano-indentation Measurement

To obtain the mechanical properties, neat PMMA and graphene-reinforced-PMMA samples are tested by nanoindentation. The indentation tests are performed with a fixed maximum force of 5 mN, holding time of 30 s, and loading and unloading time of 30 s. The tip during the unloading period is held at 10% of the maximum load for 60 seconds for thermal drift correction. Eighty indentations are made at different points for each sample, and the average values of the nanomechanical properties are calculated by using the Oliver–Pharr method [116].

Figure 4. 7 shows load-penetration depth curves of neat PMMA, with and without processing in our shearing device, and graphene-reinforced PMMA processed by exfoliating graphite in different polymer/acetone concentrations (i.e., 0.4, 0.5, 0.6, and 0.7 g/ml). The overall behaviors of the samples are typical of soft materials with little elastic recovery compared to plastic deformation of the surface under the indenter [145].



Figure 4. 7 Load–penetration depth curves of exfoliated graphite reinforced PMMA nanocomposites.

 Table 4. 2 Summary of mechanical properties of exfoliated graphite reinforced PMMA nanocomposites.

| Sample | E (GPa) | Hardness | Max. Depth | Contact Depth |
|------------|---------------|----------------|-----------------|----------------------|
| | | (GPa) | (nm) | (nm) |
| PMMA | 3.96+/-0.052 | 0.206+/-0.005 | 1173.05+/-12.33 | 1043.66+/-12.96 |
| PMMA | 4.595+/-0.051 | 0.226+/-0.0041 | 1140.64+/-09.97 | 1010.60+/-10.20 |
| Processing | | | | |
| 0.4 g/ml | 4.678+/-0.120 | 0.235+/-0.0054 | 1118.79+/-12.56 | 987.07+/-12.05 |
| 0.5 g/ml | 4.897+/-0.106 | 0.241+/-0.0066 | 1098.16+/-13.61 | 970.50+/-13.80 |
| 0.6 g/ml | 5.034+/-0.083 | 0.251+/-0.0078 | 1077.40+/-15.54 | 950.92+/-16.04 |
| 0.7 g/ml | 5.193+/-0.086 | 0.265+/-0.0088 | 1035.86+/-14.66 | 910.04+/-15.65 |

The hardness, H, and elastic modulus, E, for each sample are analyzed using the Oliver–Pharr method [116]; and the results are listed in Table 4. 2. The properties of the exfoliated-graphene-reinforced PMMA increase markedly with PMMA/acetone

concentration during shearing. The values of neat PMMA processed under the same conditions but with no graphite loading are also given. Increases of *E* and *H* are 31% and 28.6%, respectively, under processing at the high-viscosity PMMA/acetone concentration of 0.7 g/ml. Neat PMMA processed at 200°C, but without graphite loading, has increases of 13% and 17.2% of *E* and *H*, respectively. The maximum penetration depths (Table 4. 2) are observed to decrease with increasing polymer/acetone concentration.

The large surface area of graphene nanoparticles could be the reason behind the improved *E* and *H* because of the increased interaction between the nanoparticles and the polymer matrix chains [146, 147]. In amorphous polymers, plastic deformation can result from nucleation and diffusion of shear bands. In unreinforced polymers, the shear bands diffuse without constraint, with no barriers to their movement. On the other hand, in reinforced polymer nanocomposites, the graphene can serve as obstacles to the motion of shear bands, causing the enhancements in hardness and elastic modulus [148]. Furthermore, wrinkled graphene sheets, as shown in Figure 4. 14 (a-b) and Figure 4. 15 (c-d), have regions that possess a nanoscale surface roughness of 0.4–0.5 nm. These regions may work as preferential nucleation sites for polymer growth of crystalline phases or short-range order [149]. Thus, the nanoscale surface roughness of wrinkled graphene sheets can increase adhesion and mechanical interlocking of graphene with the polymer chains [150], which can enhance the overall mechanical properties.

4.3.2.5 Nanoindentation Mapping and Thermal Effect on The Mechanical Properties

Nanoindentation tests are performed to evaluate the local near-surface mechanical properties of the graphene-reinforced polymer matrix composites. Reduced modulus and hardness surface mappings are conducted using a pendulum-based nanoindentation platform system (Nanotest Vantage indenter, UK) with a Berkovich tip (three-sided pyramidal diamond indenter). Due to the sensitivity of the mechanical properties to the tip geometry, the tip contact area function is calibrated by using a standard fused quartz specimen before measurement. The surface mechanical property behavior is determined by a nanoindentation grid (8x15) indent array with \pm 20 µm pitch mapping distribution on the top of the polished surface for G-PMMA, processed neat PMMA, and unprocessed neat PMMA. The spacing between individual indents is set in such a way as to illustrate the effect of graphene dispersion and processing method on mechanical behavior. The test settings for each sample are: 5 mN maximum indentation load with 30s holding time, loading and unloading time of 30 s, and holding the tip during unloading period at 10% of the maximum load for 60s for thermal drift correction. The Oliver and Pharr method is used as a standard procedure to determine the hardness and elasticity from the nanoindentation data [116]. The data are shown in Figure 4. 8 and Figure 4. 9. All of the measurements are collected under controlled environment with temperature and humidity at 25 ± 1 °C and $40 \pm 1\%$ RH, respectively.

To uncover the effects of graphene and experimental processing on the mechanical behavior near the surface of graphene-reinforced PMMA, a series of indentation tests are carried out under a constant load. The results are presented in Figure 4. 8 and Figure 4. 9.

Relative to the polymer matrix, the graphene flakes themselves have larger reduced modulus and hardness. The variation in local mechanical properties along the surface of the specimens, as the nanoindenters encounters graphene flakes versus polymer matrix is evident. Figure 4. 8 and Figure 4. 9 show the hardness and reduced modulus increase by nearly 9.7% and 16%, respectively, when neat PMMA is simply processed at hightemperature (200°C) injection. The mechanical properties may be enhanced because of polymer crystallinity [151] and/or thermo-residual stresses during the molding process, which is strongly related to the thermal manufacturing process of the glassy polymers [152], but the x-ray diffraction test of Figure 4. 10 demonstrates that, the PMMA and G-PMMA are amorphous under all the conditions (heat injection and unheated). Additionally, during thermal treatment ,which is associated with the manufacturing process, mechanical properties may be enhanced from stabilization of C-H bonds and methyl groups, crosslinking between the unadulterated graphene flakes with dangling bonds and surrounding polymer, modification of polymer chain structure in the matrix, and modifications in the side group of the polymer [153]. The mechanical properties of processed PMMA (under heat injection) vary from 5.23 GPa to 5.44 GPa in reduced modulus and from 0.23 GPa to 0.249 GPa in hardness. However, processed G-PMMA (under heat injection) vary from 5.5 GPa to 6.1 GPa in reduced modulus and from 0.24 GPa to 0.31 GPa in hardness. In future work, it is worth etching the samples with acetone while spinning to remove the effects of polishing, and then doing a nanoscratch test. The

Fourier-transform-filtered plot of the amplitude versus time should give an assessment of the graphene number concentration which can be compared to the UV-Vis-based concentration measurements.

While PMMA is amorphous (see Figure 4. 10), the mechanical properties of the polymer composites can correlate strongly with polymer morphology and fillers, especially if these fillers, such as graphene flakes, induce crystallization in the polymer matrix [151]. Also, the disparity in thermal expansion coefficient between the polymer matrix and graphene flakes can result in thermo-residual stresses from the manufacturing process, leading to mismatch deformation between the graphene flakes and the polymer matrix [154]. The degree of alignment of molecular chains are essential for enhancing the properties of polymeric materials. Polymer molecules are usually randomly twisted; and during the manufacturing process, they line up parallel to the flow direction. The polymer can achieve higher mechanical properties if the molecules become aligned parallel to the applied load.[155]. A polymer is usually very hard when its molecular chains are oriented parallel to or along the molecular backbone structure. However if the orientation of the molecules chains are randomly oriented, the inter-chain bonds become very weak; and the polymers display lower mechanical properties as in amorphous polymers, [156, 157]. All of these effects can contribute to the augmentation of mechanical properties.



Figure 4. 8 Local hardness maps of G-PMMA and processed neat PMMA (both processed at 0.7 g/ml polymer concentration and then heat injected into mold at 200°C) and unprocessed neat PMMA. Test conditions: \pm 20 µm displacement amplitude for each indentation step, 5 mN normal load.



Figure 4. 9 Local reduced modulus of G-PMMA and processed PMMA (both processed at 0.7 g/ml polymer concentration and then heat injected into mold at 200°C) and unprocessed neat PMMA. Test conditions: \pm 20 µm displacement amplitude for each indentation step, 5 mN normal load.

4.3.2.6 X-ray Diffraction Test

The X-ray curves, as presented in Figure 4. 10, show that samples of a pure PMMA and G-PMMA nanocomposite that have been heat injected (extruded) or just unheated and untreated have an amorphous nature that decreases when diffraction angle (20) increase. The curves of pure PMMA and G-PMMA nanocomposites show the wide peaks at diffraction angle 13.1°. These wide peaks indicate the polymer's amorphous nature, which appearing at that diffraction angle (13.1°) also corresponds to the diffraction pattern of [111]. The wide diffraction peaks in the X-ray spectrum curves suggest that the possibility of the existence of crystallites is rare. Thus, amorphousness seems to be the dominant nature, which is recognizable from the absence of any prominent peaks or high-intensity narrow peaks of all the PMMA samples even at 200 °C injection (extrusion) temperature. However, there exists the possibility that graphene flakes can heterogeneously crystallize the polymer under certain annealing conditions to produce a nanocrystalline structure, which will be explored in future work.



Figure 4. 10 The XRD pattern for PMMA and G-PMMA nanocomposite at heat injection and unheated; show large peak at 2θ is 13.1 indicates its amorphous nature of PMMA.

4.3.2.7 In-Situ Rheology Test

The rheology aspects of the exfoliation process are investigated. Specifically, four different concentrations of PMMA/acetone (0.4, 0.5, 0.6, and 0.7) g/ml with 1% wt. graphene/graphite are examined for their shear stress versus shear strain rate characteristics, as given in Figure 4. 11, along with their torque versus time response, as shown in Figure 4. 12. Figure 4. 11 reveals that the PMMA/acetone with graphene/graphite slurry exhibits a more pronounced non-Newtonian behavior at higher PMMA/acetone concentrations, e.g., 0.7 g/ml (shear thinning behavior), when compared with that at lower concentrations, i.e., 0.4, 0.5 and 0.6 g/ml. Shear thinning is a common behavior in some composites reinforced with nanofillers such as nanofibers, nanoclays, and silica [3].



Figure 4. 11 Shear stress vs. shear rate, before and after 6 hours of exfoliation or processing.



Figure 4. 12 Torque vs. Time behavior during exfoliation for 2hrs at constant speed 2500 RPM. Data was taken in 10min intervals, so resolution for 0.7 g/ml case will need to be investigated at increased time resolution to account better for oscillating behavior.

Figure 4. 11 divulges that the increase in shear stress with shear rate is significant at 0.7 g/ml, as compared to that at other polymer/solvent concentrations. Moreover, the difference in shear stress for a given shear rate is quite noticeable before and after exfoliation, at the high polymer/solvent concentrations. The interaction of the nanofiller with the polymer matrix leads to increase in the shear viscosity, which becomes even more significant when starting with a higher viscosity polymer solution [3]. In concordance, as the number density of graphene nanoparticles increases during the exfoliation process of graphite, the shear stress and viscosity of the polymer matrix nanocomposite increases, as a result of the growing number of polymer/graphene interfaces [158]. Notably, the increase in shear stress with shear rate is modest at lower polymer/solvent concentrations (low viscosity). Gallege et al. [159] found that graphene sheets did not cause a significant increase in the viscosity of the system compared to other nanofillers, such as MWCNT.

Figure 4. 12 shows that the torque needed to maintain a constant rotation rate at 2500 RPM increases with polymer/solution concentration. At the 0.7 g/ml polymer/solvent concentration, the oscillations or fluctuations in the torque manifest after 30 minutes of processing time, likely because of the growing number density of graphene nanoflakes from exfoliation of graphite in the polymer matrix. Einstein's theory [160] states that for a fixed volume fraction of spherical particles, the effective viscosity should remain the same for low loading in the dilute limit. However, in our case, as the graphite particles are sheared into fewer and fewer layers down to monolayer graphene, the aspect ratio changes significantly, affecting the effective viscosity. The oscillatory torque is likely due to viscoelastic behavior of the composite system. Note that the data were taken in Fig. 4.12 is only at 10 min intervals, and higher time resolution is needed in future work to

characterize better the phenomenon. With increasing graphene number density in the polymer solution, the fluid becomes more non-Newtonian, with signification interaction between the nanofiller and the polymer solution [161, 162]. Although the effective viscosity versus shear rate reveals shear thinning for all cases, the effective viscosity is near the practical processing limit for the 0.7mg/ml PMMA/acetone case, for the temperature condition investigated. Additionally, the composite system exhibits solid-like behavior and may have a 3D network structure at a uniform dispersion and low filler loading [163, 164].

4.3.2.8 SEM, TEM, and HIM Analysis

Of our cases tested, the best mechanical properties and performance are observed for the samples processed with higher polymer/solvent concentrations, namely 0.7 g/ml. Again, higher concentrations result in unstable torque needed to maintain a constant rotation rate (at 2500 RPM), and will be examined in future studies. Nonetheless, SEM, TEM, and HIM are conducted on the corresponding G-PMCs.

The SEM images of Figure 4. 13(a-b) show the morphology of graphene-reinforced PMMA nanocomposites. The surface of a fractured sample reveals good interfacing and adhesion of graphene with the polymer matrix. Separation and interfacing of graphene sheets with the polymer matrix are visible on the composite fracture surface as shown in Figure 4. 13a (indicated in the circle). Figure 4. 13b displays the excellent interfacing and adherence of the graphene flakes with the polymer. Also, Figure 4. 13b shows a bundle of polymer chains sticking out on top of a graphene-flake surface. Although the bundle looks like fibers (as indicated by the arrow after the break of G-PMMA sample for SEM test),

they are actually textured (likely aligned) PMMA that has broken off. The higher magnification images of Figure 4. 13(c-d) clearly show the interfacing of exfoliated graphene flakes with the polymer matrix (indicated by the arrows). Also, as in Figure 4. 13(e-f), the SEM images reveal a uniform dispersion of graphene in the polymer matrix, without any agglomeration of graphite on the fractured surface.

TEM investigations further evince the morphology of graphene sheets and the interfacing of graphene with the polymer matrix. Figure 4. 14(a-b) shows typical lowmagnification TEM images of few-layer graphene flakes ($n \le 4$) stacked together in wrinkled and folded shapes. For example, in Figure 4. 14a, the scrolled bottom and top edges of graphene are observed, with a strongly folded region in the middle. SAED patterns (insets of Figure 4. 14(a-b)) confirm typical diffraction rings for graphene. Figure 4. 14c displays a folded graphene sheet covered by very thin layer of amorphous polymer matrix. In Figure 4. 14d, high-resolution TEM image (HRTEM) of a graphene flake near its edge, corresponding to the circular region in Figure 4. 14c, shows 2 to 4 layers as indicated by the arrow [165]. The SAED pattern (inset of Figure 4. 14c) exhibits the typical diffraction rings of graphene. Interestingly, in Figure 4. 14e, a monolayer of graphene flake is found and indicated by the arrow. The SAED pattern (inset of Figure 4. 14c) exhibits typical reflection rings of monolayer graphene [37], with d-spacings of 0.345 nm, 0.207 nm, and 0.122 nm. Figure 4. 14f presents the HRTEM imaging of the circled region of Figure 4. 14c, which clearly divulges the featured honeycomb structure.

HIM imaging analysis further determines the morphology and interfacing of graphene with the polymer matrix. The morphology of the graphene reinforced polymer

is presented in Figure 4. 15a, which shows graphene flakes embedded within the PMMA polymer matrix. Figure 4. 15b shows the high magnification image of the circled region depicted in Figure 4. 15a, clearly indicating the folded layers of graphene sheet. Furthermore, Figure 4. 15c and Figure 4. 15d show wrinkled graphene flakes adhered to and folded with amorphous PMMA, as indicated by the arrow.



Figure 4. 13 SEM micrographs of G-PMMA prepared at 0.7 g/ml (a,b) surface morphology, (c,d) higher magnification shows the interfacing of graphene flakes with PMMA matrix, (e,f) uniform dispersion of graphene in the polymer matrix.



Figure 4. 14 TEM images (a, b) Multilayers graphene and SAED pattern, (c, d) few layers' graphene covered by PMMA and SAED pattern, (e) single-layer graphene flake and SAED pattern, (f) atomic resolution high magnification hexagonal honeycomb lattice.



Figure 4. 15 HIM images of exfoliated graphite reinforced PMMA nanocomposites prepared at 0.7 g/ml (a) surface morphology, scale bar = 1 μ m (b) High magnification image of graphene layers, scale bar = 100 nm (c,d) wrinkling graphene flakes adhesion with amorphous PMMA, scale bar = 100 nm.

4.4 Effect of Time on The Exfoliation of Graphene and Reinforced Polymer Nanocomposites.

The influence of processing time on the shearing of graphite into graphene flakes in the liquid-phase PMMA/acetone solution is investigated and characterized via Raman spectroscopy. The processing time for exfoliation into graphene between two concentric cylinders are studied at 2, 6, and 12 hours, while keeping the other conditions constant (i.e., 2500 RPM, 0.7 g/ml, and 25°C). The Raman spectra, as shown in Figure 4. 16 clearly illustrated the influence of time on the number of graphene layers for the exfoliated flakes. After 12 hours of shearing, the I_{2D}/I_G ratio of the flakes exhibits gradual increasing up to 1.22, which is considered to be bilayer and monolayer graphene. The Raman shift position of the 2D peak corroborates the I_{2D}/I_G results where the peak moves from 2701cm⁻¹ of graphite to 2665 cm⁻¹ of graphene.



Figure 4. 16 Raman spectra of G-PMMA composites (red) Raman spectra at 12 hrs shearing (blue) Raman spectra at 6hrs shearing, (yellow) Raman spectra at 2hrs shearing, and (black) Raman spectra of graphite.

4.5 Summary

An effective method is needed to fabricate the next generation of high-performance graphene-reinforced polymer matrix composites (G-PMCs). In this work, a versatile and fundamental process is described to produce high-quality G-PMMA composites via in-situ shear exfoliation of well-crystallized graphite particles in highly-viscous liquid PMMA/acetone solutions between two concentric cylinders (one of them rotating). After drying, observations by SEM, TEM, and HIM show uniform distributions of well-bonded graphene nanoflakes in a PMMA matrix (without external/handling contamination), which enhances stiffness and strength via a load-transfer mechanism. So far, best properties, such as elastic modulus (5.193 G Pa) and hardness (0.265 GPa), are achieved at 0.7 g/ml of acetone/PMMA concentration (the upper bound tested) during processing for 1% wt starting graphite loading. Characterization of structure, morphology, and properties of this new class of nanostructured composites reveal interesting trends. The nanoindentation test evaluates the near-surface mechanical properties of the individual components (graphene flakes and polymer matrix) for the reinforced nanocomposites. The results show noticeable improvement in the mechanical properties of G-PMMA in modulus (31%) and hardness (28.6%). Nonetheless, it is worth noting that the mechanical properties increased in heattreated and extruded neat PMMA by approximately 16% and 9.7% in modulus and hardness, respectively, likely because of alignment of the polymer chains, with respect to unprocessed neat PMMA. Also, the duration of exfoliation influences on the final graphene flakes is evaluated, demonstrating enhancing in I_{2D}/I_G ratio gradually up to 1.22 (1- and 2-layer graphene) for 12 hours shearing.

Chapter Five

Fabrication, Structural and Mechanical Characterization of Graphene and h-BN Nanoflakes Reinforced Poly (methyl methacrylate) Nanocomposites

5.1 Introduction

Polymer nanocomposites (PNCs) are a combination of strong reinforcing phases and nanofillers (e.g., three-dimensional nanospheres, two-dimensional nanoplatelets, and onedimensional nanofibers) bound together by a polymer or copolymer matrix [166, 167]. Nanofillers enhance the mechanical and functional performance of matrices providing tailorable properties unavailable in polymer matrices or filler materials alone, such as high strength and stiffness, and improved electrical and thermal conductivities [168], The nanocomposites' performance is directly related to the uniform dispersion of the nanofillers in the polymer matrices, and several methods have been proposed in order to identify and employ optimal conditions leading to high yield PNC processing. In-situ polymerization and high shear can accommodate a large range of nanofiller concentrations to reinforce different polymer matrices while providing superb filler dispersion and exceptional nanocomposite material properties [10, 14].

Two-dimensional (2-D) layered nanofillers, such as graphene, h-BN, and molybdenum disulfide (MoS₂) nanoplates, are very effective in enriching material matrices with many unique properties useful for a wide range of nanotechnology applications, such as nanocomposite materials, nanoelectromechanical systems, and sensing [9]. Literature reported values of the mechanical properties of high-quality monolayer graphene include

1.0 TPa for Young's modulus of and 130 GPa for fracture strength of [139], while the corresponding values for h-BN are 0.865 TPa and 70.5 GPa [9], respectively. These nanofillers could improve the performances of a polymer's matrix, due to the nano-size effect, the large specific surface area, and the reliable interfaces between the polymer chains and the nanofiller. Graphene or h-BN-based nanofillers may also affect the viscoelastic behavior of a polymeric nanocomposite matrix and necessitate viscoelastic response studies of the investigated PNC.

Viscoelasticity is examined using standard dynamic nanoindentation (nanoDMA), during which a controlled sinusoidal load (stress) is applied to the specimen and the resulting sinusoidal displacement (strain) is measured. The depth indentation mechanism of this technique is modeled based on the linear elasticity mechanism of Sneddon [169]. This unique technique is considered the most effective method for the study of viscoelastic behaviors of various classes of polymers and nanocomposites. Under cyclic loading, nanoDMA can illustrate the time-dependent deformation recovery within a loading cycle. The viscoelastic behavior plays a critical role in assessing quality control and predicting the lifetime of materials [170, 171], so it is crucial to test this behavior reliably. For example, polymer coatings, like those found on solar panels and medical devices, need to be studied by DMA nanoindentation to understand the transition between viscous and elastic properties. The behavior of polymers is greatly affected by time and temperature, which can alter the long-term functionality of a device. The results acquired here will be used to understand the life cycle of the polymer coating better. In this study, a series of graphene-PMMA and *h*-BN-PMMA nanocomposites are prepared by in-situ high shear and polymerization with a nanofiller content of 1 wt.%. During the high-shear mixing process, the outer layers of nanofiller are detached from their bodies as a result of the shear force generated during the exfoliation process. The structure and mechanical properties (i.e., elastic modulus, hardness, storage modulus, loss modulus, and loss tangent) of graphene-PMMA and *h*-BN-PMMA nanocomposites are experimentally evaluated according to the features of nanostructures and the alignment of molecular chains under stress.

5.2 Materials

Polymethylmethacrylate (PMMA) ($-CH_2C-(CH_3)$)CO₂CH₃)-) purchased from Fisher Scientific is mixed with a solvent to prepare a polymer solution that is utilized as the working fluid. Synthetic graphite (TC 301 High Purity) and bulk hexagonal boron nitride (BTBN5009) powders with an average flake size of 8-10 µm are supplied by Asbury Carbons Inc., New Jersey. The SEM images of both synthetic graphite and bulk *h*BN powders are shown in Figure 5.1.



Figure 5.1 SEM images of filler particles: (a) synthetic graphite powder with an average particle size of 8-10 μ m (b) h-BN powder with an average particle size of 8-10 μ m.

5.3 Experimental Procedure

The high shear setup consists of two coaxial cylinders (gap volume capacity of 6.5 mL), as shown in Figure 5. 2. It is designed to generate a high shear rate in that small gap between two concentric cylinders, which is used to exfoliate the graphite and *h*-BN powder in the liquid phase polymer. The outer container chamber connects to fast stream water circulating chiller to remove the heat generated and keep the temperature of the mixture inside the inner vessel constant at 25 °C. The exfoliated nanocomposite polymer is prepared as follows: (1) the graphite and *h*-BN powders are dried in an oven at 150 °C for 8 hours, and the PMMA powder is dried under a vacuum for 8 hours, (2) the PMMA powder is mixed with 1 wt% graphite or *h*-BN and dissolved in the acetone at a PMMA/acetone concentration of 0.7 g/ml, (3) the mixture is sonicated in a container for one hour in the low load sonication bath to make a uniform solution. Afterwards, the mixture is injected into the gap between the cylinders of the device and then closed tightly by a special cover which is designed to prevent evaporation of acetone and escape of

mixture while keeping it under pressure. The inner cylinder rotates at a constant velocity of 2,500 RPM, providing high shear exfoliation stress for six hours during the whole process. Then, the nanocomposite polymer mixture is taken out from the container and left to dry in the fume hood for 48 hours. Subsequently, the mechanical properties and DMA nanoindentation are characterized by nanoindentation using a NanoTest Vantage system from Micromaterials, UK, and aTbi-750 nanoindenter from Hysitron, USA.



Figure 5. 2 Schematic of the shear-exfoliation processing of graphite and bulk *h*BN in the PMMA/acetone solution.

5.4 Results and Discussion

5.4.1 Raman Spectroscopy

The Raman spectra of polymer composites are well investigated, as shown in Figure 5. 3, and almost all of the Raman-active peaks are assigned, confirming the existence of graphene and h-BN in the polymer matrix. The Raman shift is set to cover the spectral

range from 500-3200 cm⁻¹ and 1200-1420 cm⁻¹, for graphene and *h*-BN respectively.. The Raman-active regularity peaks for neat PMMA are observed at ~602, ~812, ~966, ~990, ~1450, ~1730, ~2844, ~2954, and ~3002 cm⁻¹. For the G-PMMA composite, there are three distinguished peaks at ~1351, ~1584, and ~2671 cm⁻¹, representing the D, G, and 2D bands of graphene, which are the emissions generated during the oscillation of carbon atoms in the graphene lattice [172]. For the *h*-BN-PMMA composite, there is one single band (E_{2g}) peak at ~1367 cm⁻¹, which corresponds to bilayer and few-layer h-BN flakes [173]. Moreover, the number of layers for graphene and h-BN flakes can be determined from the intensity, shape, and position of those peaks. It is interesting to observe the intensity ratio I_{2D}/I_G of 0.92 for graphene within the G-PMMA composite in Figure 5. 3 and Figure 5.4, which indicates the existence of bilayer and few-layer graphene [138, 174]. Additionally, the comparison between the graphite and graphene after six hours of exfoliation, as shown in Figure 5. 4, exhibits a red-shift in the 2D band of ~ 28 cm⁻¹; this band has a shape characteristic indicating bi-layer graphene [137]. Figure 5.5 shows the Raman spectra of *h*-BN before exfoliation, displaying a characteristic peak of 1365 cm⁻¹ for bulk *h*-BN. The scanned laser spots of Raman on the *h*-BN-PMMA surface is shown in Figure 5. 5. However, we have found that the *h*-BN peak or E_{2g} mode appears at 1367 cm⁻¹ in *h*-BN-PMMA after exfoliation, with a red-shift of ~ 2 cm⁻¹ (note that the Raman shift is 1365 cm⁻¹ for bulk *h*-BN). Also, the peak intensity becomes weaker for *h*-BN after exfoliation, corresponding to a decrease of h-BN layers [173, 175]. The full-width at halfmaximum (FWHM) of the E_{2g} peak is used to determine *h*-BN sheets; and it is 12 cm⁻¹ for *h*-BN-PMMA after exfoliation (while it is 9 cm⁻¹ for bulk *h*-BN).



Figure 5. 3 Raman spectra of PMMA composites. (red) Raman spectra of G-PMMA denoting D, G, and 2D peaks with band intensities of ~1351, ~1584, and ~2671 cm⁻¹ respectively; (blue) Raman spectra of *h*-BN-PMMA with a peak at 1367 cm⁻¹ indicating bilayer and few layers of *h*-BN; (black) Raman spectra of PMMA (reference). The curves are normalized to the intensity of the G peak (1584 cm⁻¹).



Figure 5. 4 Raman spectra at 633nm of (red) exfoliated graphene with PMMA and (black) synthetic graphite powder before exfoliation. The 2D peak of graphene is shifted backwards ~ 28 cm⁻¹ while the intensity ratio I_{2D}/I_G increased. The curves are normalized to the intensity of the G peak (1584 cm⁻¹).


Figure 5. 5 Raman spectra at 633nm of (red) exfoliated *h*-BN with PMMA and (purple) bulk *h*-BN powder before exfoliation. The *h*-BN exfoliated peak is shifted forwards of $\sim 2 \text{ cm}^{-1}$ while the intensity decreased. The curves were normalized to the intensity of pure BN peak (1365 cm⁻¹).

5.4.2 Morphological Investigation

The mechanical properties of reinforced PMMA-composites depend on the constitutive and interfacial composition, as well as on the geometry, volume fraction, and dispersion of fillers in the composite matrix. SEM and TEM imaging enables the morphological characterization and recognition of the different phases, i.e., *h*-BN, G, present in the PMMA composites at the micro and nanoscales.

The morphologies on the cutting surface of the reinforced G-PMMA and *h*-BN-PMMA composites and dispersion of fillers characterized by SEM are presented in Figure 5. 6. Figure 5. 6(a-b) illustrate G-PMMA with excellent interfacing and adhesion of G-flakes with the PMMA matrix (indicated by the arrows), and Figure 5. 6c demonstrates *h*-BN flakes embedding the PMMA matrix of the *h*-BN-PMMA composite; as noted, this

flake consists of a few layers of *h*-BN sheets (arrows indicate individual layers). Also, the morphologies on the fracture surface of bulk *h*-BN-PMMA and exfoliated *h*-BN-PMMA composites after the acetone evaporations are investigated in Figure 5. 6(d-e). The SEM image in Figure 5. 6d clearly shows the incompatibility of the components (fillers and matrix) with weakness in the cross-linked and interfacial bonding between them. The exfoliated *h*-BN-PMMA composites in Figure 5. 6e exhibit completely different morphology, presumably due to the effect of the exfoliated *h*-BN nanosheets improving resistance to crack initiation and propagation, as well as the cross-linking enhancement between the *h*-BN and PMMA, which might lead to improvement of the mechanical properties [176].



Figure 5. 6 SEM images of fracture surfaces: (a) Graphene flakes in PMMA matrix composite; (b) Interfacing of graphene with PMMA matrix; (c) *h*-BN layers in the PMMA composite; (d) the unexfoliated *h*-BN-PMMA composite; (e) the exfoliated *h*-BN-PMMA composite.

Typical TEM images of the G-PMMA and *h*-BN-PMMA composites are observed in Figure 5. 7. As shown in Figure 5. 7(a-b), graphene exhibits a thin, transparent, layer-like structure with few layers ($n \le 4$), that has a typical folding nature (indicated by the arrows) and is stacked together in a wrinkled and folded shape. Figure 5. 7b shows a graphene sheet surface which has proper interfacing and adhesion with amorphous PMMA matrix, Figure 5. 7(c-d) denotes that the *h*-BN nanosheets are a few-layers thick, and Figure 5. 7d demonstrates excellent *h*-BN interfacing with the PMMA matrix. Also, the selected area electron diffraction (SAED) pattern (Figure 5. 7(a-b) inset) demonstrates typical reflective rings of few-layer *h*-BN. However, the TEM results reveal that the number of exfoliated *h*-BN flakes in the *h*-BN-PMMA composite is less than that of exfoliated graphene flakes in the G-PMMA composite.



Figure 5. 7 Representative TEM images of exfoliated, *h*-BN nanosheets prepared via high shear between two concentric cylinders at 2500 RPM (a-b) graphene nanoflakes in bond with PMMA matrix (c-d) h-BN nanoflakes in bond with PMMA matrix.

5.4.3 Mechanical Properties-Nanoindentation Test

In amorphous polymers, the plastic deformation occurs as a result of nucleation and diffusion of shear bands. Therefore, in the unreinforced polymer, the shear band diffusion ensues without constraints, so there are no barriers in their movement's way. On the other hand, in reinforced polymer nanocomposites, the nanofillers work as obstacles to the motion of shear bands, which cause the enhancement in the hardness and elastic modulus [148].

Young's modulus E and hardness H of the PMMA/graphene or h-BN nanocomposites as a function of graphene or h-BN flake containment are shown in Figure 5.8 and Figure 5.9, respectively. Each point on the graph is the average of eight nanoindentations of the displacement range of (140–1350) nm [177]. It should be pointed out that in Figure 5.8, the elastic modulus E of the polymer-based 2D materials for each sample have been analyzed by using the Oliver–Pharr method [116]. The curves show that there is a clear decrease in the modulus and hardness of the materials as the displacement depth increases, until the values reach a plateau, as expected for soft compliant polymers [177]. As expected, the H and E of reinforced PMMA increase markedly by using 2D nanomaterials. As seen in Figure 5. 8 and Figure 5. 9, graphene exhibits superior performance to h-BN nanofillers as a PMMA reinforcing phase. The performed nanoindentations illustrate that the pure PMMA Young's modulus and hardness are measured as $E_{PMMA} = 4.02$ GPa and H_{PMMA} = 0.205 GPa, while the average graphene reinforced PMMA values are E_{G-PMMA} = 5.31 GPa and $H_{G-PMMA} = 0.270$ and the respective values of h-BN reinforced PMMa are $E_{h-BN-PMMA} = 5.11$ GPa and $H_{h-BN-PMMA} = 0.256$ GPa, as listed in Table 5. 1. Summarily, the maximum increase of *E* and *H* are 32% and 31%, respectively, for graphene reinforced PMMA nanocomposite, whereas they are 27.1% and 24.8%, for *h*-BN reinforced PMMA nanocomposite.



Figure 5. 8 Nanoindentation results for Young's modulus vs. indentation depth as a function of the 2D reinforcing phase (graphene and *h*-BN) in PMMA. The nanoindentations are performed under load controll conditions and each point is the average of 8 individual nanoindents at the same load and at different positions on the specimen.



Figure 5. 9 Nanoindentation results for hardness vs. indentation depth as a function of the 2D reinforcing phase (graphene and *h*-BN) in PMMA. The nanoindentations are performed under load control conditions and each point is the average of 8 individual nanoindents at the same load and at different positions on the specimen.

The presented method suggests that 2D nanosheets with intrinsically high strength are well dispersed in the polymer matrix, resulting in a high contact area and strong interfacial adhesion with PMMA chains, which consequently enhances the bonding with the folded and wrinkled graphene sheets, as seen in the inset of Figure 5. 7a (indicated by the arrows). Moreover, the wrinkled sheets have regions that exhibit nanoscale surface roughness of (0.4-0.5) nm [148]. These rough regions may work as preferential nucleation sites and can increase the growth of polymer crystalline phases when wrinkled graphene flakes are dispersed in the polymer matrix [178]. Thus, the nanoscale surface roughness

of the wrinkled sheets increases the adhesion and mechanical interlocking of nanofillers with the polymer chains [179], which likely enhances the mechanical properties.

| Sample | Young's modulus Hardness | |
|-------------------|--------------------------|----------------|
| | (GPa) | (GPa) |
| PMMA | 4.020 +/- 0.145 | 0.205+/- 0.007 |
| <i>h</i> -BN-PMMA | 5.112 +/- 0.134 | 0.256+/-0.013 |
| G-PMMA | 5.311 +/- 0.132 | 0.270+/-0.009 |

Table 5. 1 Summary of mechanical properties of PMMA composites.

5.4.4 Dynamic Mechanical Analysis (nanoDMA)

The dynamic viscoelastic properties of the two PMMA-nanocomposites and pure PMMA have been observed using the nanoDMA technique or dynamic nanoindentation (nanoDMA) method.

Typically, the storage and loss modulus for pure PMMA gradually becomes more significant with increasing frequency [180]. The response of the storage modulus as a function of frequency indicates that the storage modulus increases with the addition of *h*-BN and graphene nanoadditives and with increased frequency for the three PMMA nanocomposites tested, as shown in Figure 5. 10. The G-PMMA nanocomposite exhibits slightly higher E' (29.2%) than that of the *h*-BN-PMMA nanocomposite (18%), which is likely due to the lower concentration of exfoliated *h*-BN nanosheets in the polymer matrix than the concertation of graphene nanoflakes.

The more dominant behavior of the storage modulus increase associated to the frequency indicates a strain rate sensitivity of the polymeric composite. The latter appears to be related to the increased loading of the PMMA with graphene flakes as the rate of exfoliation increases at higher strain rates, i.e., higher frequencies. In addition, the pure PMMA viscoelastic behavior is intrinsically related to the relaxation time required for the polymeric chains to entangle. At lower frequencies the entanglement is loose as more relaxation time is afforded. At higher frequencies the relaxation time significantly shortens resulting in increased polymer chain entanglement and higher storage modulus for the pure PMMA and the associated nanocomposites [181, 182]. Similar behavior is reported by Tripathi et al. (2015)[183] and by Du et al. (2004)[184]. Du's group [185] argues the existence of a rheological percolation threshold at 0.5% RGO in PMMA that reinforces the PMMA-RGO interaction while restraining the motion of the polymer chains. It is suggested that similar behavior is exhibited by the graphene and *h*-BN nanoadditives in the PMMA nanocomposites, which enhances the storage modulus.

Another possible mechanism of the enhancement of the nanocomposites' mechanical properties [139] may be attributed to molecular level the interaction of the polymer matrix and the nanoadditives leading to better adhesion of the polymer chains to the filler surface, restricting the mobility of molecules and increasing the storage modulus [186]. The polymer chains intercalate with the nanosheets, and at the same time the chain molecules make a crosslink and interaction with the fillers, so, the load is transferred to both chains and nanofiller sheets which enhances the storage modulus.



Figure 5. 10 Storage modulus of nanocomposites polymer (red) of G-PMMA, yellow of *h*-BN-PMMA and (black) of pure PMMA.

The loss modulus at a frequency range (10-160 Hz) is plotted in Figure 5. 11, where a progressive increase of the loss modulus in the frequency range of 100Hz to 160 Hz is observed. As seen, both graphene and *h*-BN fillers enhance the E'' of PMMA compared its unreinforced values. The *h*-BN-PMMA nanocomposite loss modulus, E'', average value increases by 62.9% while the G-PMMA nanocomposite E'' increases by 33.2%, both when compared to the pure PMMA respective value. As discussed in Chapter 4 with comparison with ch5, the size of the *h*-BN multilayer flakes in the PMMA matrix is larger than that of the graphene monolayer (see Figure 4. 14(e-f)). That larger surface area of each *h*-BN flake or large size may cause increased friction with the matrix thus dissipating more energy and resulting in higher *h*-BN-PMMA loss modulus than that of the G-PMMA, (see Figure 5. 11).

It is noteworthy that as the frequency increases the spread of the storage (E') and loss (E'') moduli values, at the specific frequency, also increases. This increase in the loss modulus is possibly caused by the intercalation of the polymer chains with the nanosheets, while simultaneously the molecular chains crosslink with the fillers. The load is transferred to both the chains and nanofiller sheets, which enhances the internal friction which subsequently enhances the loss modulus [187].



Figure 5. 11 Loss modulus of nanocomposites polymer (red) of G-PMMA, yellow of *h*-BN-PMMA and (black) of pure PMMA.

During the production of the graphene and *h*-BN nanocomposites, the increase of the internal friction values due to the flakes existence and the stiffening of the molecular polymer chains may result to a decrease in the loss tangent or damping factor (tan δ) with frequency increase, demonstrated by Figure 5. 12. Loss tangent is commonly used to

characterize its damping ability, which means higher tan δ value indicates good damping performance of the structure as is also evident in $tan\delta = C \omega/k$, where C is the damping coefficient, ω is the frequency, and k is the stiffness of the of viscoelastic material which is associated with Young's modulus. The values of the loss tangent are not sensitive to the graphene content and fluctuate around the polynomial fitting curve [188], while it is sensitive to *h*-BN nanofillers content in the polymer matrix. Also, the experimental results exhibit that the *h*-BN-PMMA nanocomposite achieves a higher loss tangent (41%), while the G-PMMA nanocomposite is lower (3.67%). The significant increase of the damping factor (tan δ) of h-BN-PMMA may be attributed to the increase in the rate of energy loss (loss modulus, see Figure 5. 11). This also may be possible due to the relative decrease in storage modulus with the *h*-BN filler content (see Figure 5. 10). Also, the enhancement of storage modulus in the polymer composites via adding fillers could reduce the moveable in molecule chains inside the matrix. The damping factor of G-PMMA illustrates a different behavior compared with h-BN-PMMA. The significant increase in storage modulus combined with the decrease in the loss modulus of G-PMMA may cancel each other out, thus leading to no change in the damping factor.[187].

The error bar of Figure 5. 10, 11, and 12 illustrate that the viscoelastic behavior for the h-BN-PMMA nanocomposite has a significant variation in its performance that is frequency-dependent. All the quantitive results of viscoelastic behavior (storage and loss modulus, and loss tangent) have been included in Table 5. 2.



Figure 5. 12 Loss tangent (tan δ) of nanocomposites polymer (red) of G-PMMA, yellow of *h*-BN-PMMA and (black) of pure PMMA.

Table 5. 2 Mechanical proporties of PMMA nanocomposites evaluated by nano_DMA

| Sample | Ave storage | Ave loss | Ave loss tangent |
|-------------------|----------------|---------------|------------------|
| | modulus (Pa) | modulus (Pa) | |
| РММА | 14.225+/-1.831 | 0.63+/-0.210 | 0.045+/-0.018 |
| <i>h-</i> BN-PMMA | 16.868+/-3.391 | 1.03+/-0.415 | 0.063+/-0.022 |
| G-PMMA | 18.380+/-2.856 | 0.847+/-0.352 | 0.047+/-0.019 |

5.5 Summary

In this study, graphene (G) and hexagonal boron nitride (*h*-BN) nanosheets reinforcing poly(methyl methacrylate) (PMMA) composites are successfully produced by a novel insitu high shear method, where graphene and hBN micro powders are exfoliated to nanoscale sheets in liquid phase PMMA. During the shearing process, freshly exfoliated nanosheets immediately bond to the polymer matrix without any further possible contaminations leading to the formation of strong bonds between the nanosheets flakes and matrix, which cannot be achieved by traditional powder mixing approached. Mechanical characterizations of G-reinforced PMMA and h-BN-reinforced PMMA composites are performed by using nanoindentation tests (strength and stiffness) and dynamic mechanical analysis (DMA). The results show promising performance property enhancement for both G-reinforced PMMA and h-BN-reinforced PMMA composites by comparing with the results of pure PMMA polymer. The morphology, interface, and structure of the nanosheets with the PMMA polymer matrix are investigated using a scanning electron microscope (SEM), transmission electron microscope (TEM), and Raman spectroscopy, respectively. This novel polymer reinforcement method demonstrates a versatile way to produce a broad range of 2D nanosheet reinforced polymer nanocomposites, together with improved physical and chemical characteristics.

Chapter Six

Exfoliation of Graphene in Water-Based Poly(vinylpyrrolidone) Solution

6.1 Introduction

Poly(vinylpyrrolidone), PVP, is a synthetic water-soluble polymer that has a wellconnected structure with the monomer N-vinylpyrrolidone as a long chain. This polymer of non-toxic nature has excellent biocompatibility and is widely used in various technical applications [189]. Because of its brittleness, it is blended with other polymeric materials or nanofillers, such as graphene, CNT, and clay, to form a nanocomposite material with improved and excellent properties [190]. The exceptional features of nanocomposite materials needed to achieve two fundamental conditions are: (i) excellent dispersion of nanofillers in the polymer matrix, and (ii) strong interaction of nanofillers with molecular polymers chains [190].

In this work, graphene-PVP nanocomposites are prepared by in-situ high shear exfoliation in a polymer, with a filler content of 1wt.% graphene. During the continuous high-shear process, the outer sheets of graphite platelets are detached from their bodies as a result of the shear force generated by the inner rotating cylinder of the device. The structures and mechanical properties (i.e., elastic modulus, hardness, morphology, and chemical composition) of graphene-PVP nanocomposites are experimentally evaluated according to the features of micro and nanostructure properties.

Poly(vinylpyrrolidone), PVP was purchased from Sigma Aldrich. It is dissolved in DIwater to prepare a water-based polymer solution that is utilized as a working fluid. Asbury Carbons Inc. New Jersey supplied synthetic graphite (TC 301 High Purity) with an average flake size of 8-20 μ m (see Figure 6. 1), which is exfoliated by our device into graphene flakes.



Figure 6. 1 SEM image of graphite particles.

6.3 Experimental Procedures

The rotating high shear setup and manufacturing process, as shown in Figure 6. 2 has been presented previously in chapter 3 at Figure 3. 1; consists of two coaxial cylinders (volume capacity 6.5 mL), designed to generate a high shear stress in the small gap between the two concentric cylinders, which is then used to exfoliate the graphite particles in the liquid-phase polymer. The outer container chamber is connected to fast stream water circulating

chiller to remove the heat generation and keep the temperature of the mixture inside the inner vessel constant at 25°C. The exfoliated-nanocomposite polymer is prepared as follows; the PVP powder is mixed with 1wt% graphite and then dissolved in the water at two different concentrations of 0.4 g/ml and 0.6 g/ml. Then the mixture is sonicated for one hour in the low-load sonication bath to make a uniform solution. The mixture is fully injected into the gap between the cylinders of the mixer and then closed tightly by a special cover (vapor trap), which is designed to prevent evaporation of water and to prevent mixture migration out of the device while keeping it under pressure. The inner cylinder rotates at constant velocity of 2500 RPM and can provide high shear stress for exfoliation for 6 hours during the whole process. Finally, the nanocomposite polymer mixture is taken out from the container and left under the vacuum for a week.



Figure 6. 2 Schematic of the shear-exfoliation processing of graphite in the PVP/WATER solution.

6.4 Raman Spectroscopy

Raman spectra of polymer composites are well investigated, and almost all the Ramanactive peaks are assigned, confirming the existence of graphene in the polymer matrix, as shown in Figure 6. 3. Notably, the I_{2D}/I_G ratio increases from 0.4 of graphite to 0.65 of graphene in G-PVP, where graphene is peeled off of graphite at a polymer concentration of 0.6 g/ml water. Also, the 2D peak of graphene moves from ~ 2701 cm⁻¹ of graphite to ~2657.87 cm⁻¹ of few-layer graphene [191]. Preliminary results of Raman spectrometry have revealed good concentrations of graphene flakes in the polymer matrix, after six hours of processing.



Figure 6. 3 Raman spectra of PVP composites (red) Raman spectra of G-PVP at concentration 0.6 g/ml in the water, indicated D, G, and 2D bands intensity (~1333, ~1584, and ~2657.87 cm⁻¹) is few layers graphene, (blue) Raman spectra of G-PVP at concentration 0.4 g/ml in the water has a 2D peak at 2664.81 cm⁻¹ as a multilayer graphene, (black) Raman spectra of PVP as a reference (green) synthetic graphite as a reference.

Moreover, Figure 6. 3 demonstrates an increase in the Raman intensity of two separate disorder peaks: D (1333 cm⁻¹) and D' (1618 cm⁻¹). The disorder D peaks and G peaks are used to find the average defect ratio from intensity ratio I_D/I_G , which can then be utilized to determine the degree of disorder in the graphene layers [137]. The I_D/I_G integrated ratio determines how high the quality of the graphene is. The exfoliation of graphite in the water base solution of PVP (0.4 g/ml and 0.6 g/ml) leads to an increase in the disorder D peaks and is then used to find the I_D/I_G ratio increase from 0.1 up to 1.05 at 0.4 g/ml and from 0.1 to 0.93 at 0.6 g/ml.

Additionally, the I_D/I_G ratio from Figure 6. 3 can be used to evaluate the crystallite size (L_a) and average defect distance L_D by using Equation 6.1 and Equation 6.2 [192]. For the determination of L_a and L_D from the I_D/I_G ratio must know the Raman laser energy E_{laser} value, which is here about (E_{laser} =1.95eV) for the laser wavelength (λ_{laser} =633 nm). From Table 6. 1 the graphene is considered to be in the nanocrystalline graphite size as displayed by intensity ratios I_D/I_G, which confirms a reduction in the crystallite size after exfoliation [193]. The flake size of graphene might be able to be assessed from the average defect distance L_D because the Raman laser spot detects the flake edges as defects; thus, L_D may be able to be correlated with the average distance between graphene flakes, if each flake is single crystalline. Much more analysis and study is needed, but, the assessment can allow us to study morphology, structural, and mechanical properties of the graphene-PVP nanocomposite.

$$L_{a} = \frac{560}{E_{laser}^{4}} \times \left(\frac{I_{D}}{I_{G}}\right)^{-1}$$
(6.1)

$$L_D^{\ 2}(nm^2) = (2.4 \times 10^{-9})\lambda_{laser}^4 \left(\frac{I_D}{I_G}\right)^{-1}$$
(6.2)

| Parameters Samples | Id/IG ratio | L _a (nm) | $L_D(nm)$ |
|-----------------------|-------------|---------------------|-----------|
| Graphite | 0.1 | 387.30 | 107.49 |
| G-PVP prepared | 1.05 | 36.88 | 33.17 |
| at 0.4 g/ml | | | |
| G-PVP prepared | 0.93 | 41.64 | 35.24 |
| at 0.6 g/ml | | | |

Table 6. 1 crystallite size of graphene.

6.5 Nanoindentation Test

In amorphous polymers, plastic deformation occurs as a result of nucleation and diffusion of shear bonds. Therefore, in unreinforced polymers, the shear bands diffuse without constraint, with no barriers in the way of their movements. On the other hand, in reinforced polymer nanocomposites, the nanofillers act as obstacles to the motion of shear bands, which causes the enhancement in the hardness and elastic modulus.

Reduced modulus E_r and hardness H of the graphene-reinforced PVP shown in Table 6. 2. The values of each sample are collected by averaging the values from eight indentations at a constant force of 4 mN. The elastic modulus E of polymer fiber-based 2D materials for each sample is analyzed using the Oliver–Pharr method [116]. As expected, the H and Er of reinforced PVP increase markedly with the inclusion of 2D nanomaterials into the matrix. Additionally, using graphene to reinforce PVP leads to enhanced mechanical properties of the electrospun fiber of non-toxic nature, as shown in Figure 6. 4. The results illustrate the increasing of reduced modulus Er and hardness H by about 11% and 10.8% respectively, through reinforcement of the PVP matrix with graphene nanoflakes.

Analyses suggest that 2D nanoflakes with intrinsically high strength are well dispersed in the polymer matrix, perhaps presenting high contact areas and strong interfacial adhesion with polymer chains. Moreover, the polymer chains look more reactive or adhesive with the folding and wrinkling of the graphene sheets. The existence of graphene wrinkles may lead to and/or enhance the nanoscale surface roughness, which would likely increase mechanical interlocking and adhesion with the polymer matrix chains [179, 194].

| Samples | Reduce Modulus (GPa) | Hardness (GPa) |
|----------------|----------------------|-----------------|
| Pure PVP | 4.8382+/-0.1092 | 0.1843+/-0.0052 |
| G-PVP 0.6 g/ml | 5.3732+/- 0.1127 | 0.2043+/-0.0071 |

Table 6. 2 Summary of mechanical properties of PVP composites.



Figure 6. 4 Load–penetration depth curves of exfoliated graphite reinforced PVP nanocomposites and pure PVP.

6.6 Summary

In-situ high-shear graphite exfoliation in a water-soluble polymerization is employed to prepare a G-PVP nanocomposite. In this work, Poly(vinylpyrrolidone), PVP is reinforced by exfoliating 1wt.% graphite under high shear stress into graphene nanoflakes in an aqueous polymer solution. The results of Raman spectroscopy clearly shows the influence of high shear stress on the number of graphene layers in the produced flakes. Notably, the I_{2D}/I_G ratio of the filler increases gradually from 0.4 of graphite to 0.65 of graphene in the as-produced G-PVP, as graphene is peeled off at a polymer/DI-water concentration 0.6 g/ml. Nanoindentation tests conducted using a pendulum-based nanoindentation platform system (Nanotest Vantage indenter, UK) evaluates the near-surface mechanical properties

of the individual components (i.e., graphene flakes and polymer matrix) of the reinforced nanocomposites. The results show noticeable improvement in the mechanical properties of reduced modulus from 4.838 GPa to 5.373 GPa and hardness from 0.1843 GPa to 0.2043 GPa.

Chapter Seven

Manufacturing and Characterization of Graphene-Reinforced Electrospun Poly(methyl methacrylate) Nanocomposite Fibers

7.1 Introduction

Polymer matrix nanocomposites are defined as solid materials consisting of two or more phase-separated materials aligned together within the matrix structure, where one or more dispersed phases is/are nanoscale within the main polymeric phase. The dispersed phase delivers significant improvement to the mechanical, electrical, and thermal properties of the polymer matrix [1]. Nanoadditive/polymer-based composites have received much attention as multifunctional nanomaterials because their superb mechanical and electrical properties, even with low nanofiller concentration [6, 7]. The exploration of carbon-based nanostructured additives like two-dimensional (2D-layered) graphene nanosheets have attracted researcher's attention in recent years because of their remarkable properties, such as 1.0 TPa, Young's modulus and 130 GPa strength, high thermal conductivity about 5000 W m⁻¹K⁻¹, significant intrinsic mobility of 2×105 cm²V⁻¹s⁻¹, high specific surface area about 2630 m²g⁻¹, and high electrical conductivity [139].

A number of different techniques for the preparation of 2D nanomaterials have been developed over the last decade, such as mechanical and thermal exfoliation, gas-phase nucleation, and chemical vapor deposition [15]. Mechanical liquid-phase exfoliation (LPE) is an excellent method which extracts single- and few-layer graphene flakes from graphitic starting materials [16]. Thus, in order to create uniform polymer-matrix nanocomposites with high dispersions of graphene nanosheets, a novel application of LPE is developed here to peel off the 2D materials with high shear in a liquid-phase polymer, which will later form the 2D-nanofiller-reinforced-PMC.

Application-wise, polymer processing technology can be utilized for forming, molding, or replication of polymer composites, enabling cheaper manufacturing of new components and devices [7]. Electrospinning techniques have been extensively used in previous years as a versatile method for producing continuous polymer fibers at diameters ranging from several micrometers down to tens of nanometers [195, 196]. Electrospinning is an efficient method performed to produce fibrous structures using either polymer melts or polymer solutions, for applications that include textiles, sensing, drug delivery systems, wound dressings, filter membranes, and tissue engineering scaffolds [197]. The mechanism of the electrospun fiber fabrication process depends on the critical value of the electric field strength overcoming the surface tension of the liquid polymer drop, leading to the extraction of electrically charged liquid jets of polymer solutions [198]. The electrospun polymeric fibers are formed under the influence of two types of non-contact or electrostatic forces: electrostatic repulsion of two surface charges and the Coulombic attraction force applied by the external electric field along the straight line, joining the two charges [199].

Because of these electrostatic forces, the polymer droplet deforms into a conical shape, commonly referred to as the Taylor cone [200]. When the electric field intensity reaches a certain critical value, the electrostatic interaction will increase and exceed the surface tension of the polymer droplet; thus, the charged liquid is ejected from the tip of

the Taylor cone towards the collector substrate to collect the charged fibers mat [201]. The liquid jet travels away from the spinneret or nozzle; and during this process, it elongates and the solvent evaporates, forming a flat non-woven mat on the collector as is typical of polymer fibers. Fiber diameter, controlled morphology, and formation in space can be prepared by a precise setting of the processing parameters such as solution concentration, injection pressure, solution flow rate, and voltage supply. etc. [199, 202].

Electrospun fibers based on polymer/nanoadditive composites are becoming attractive multifunctional nanomaterials due to the combination of the superb mechanical and electronic properties of filler and the confinement-enhanced additives alignment within the fiber structure, which could significantly improve the fibers mechanical properties, along with the electrical and thermal performance. Thus, the microfiber mats based on PMMA solution with graphene nanoplatelets are prepared using the electrospinning technique as an application to reinforce fiber with 2D nanosheets such as graphene.

In this work, we report the manufacturing and performance characterization of fibers obtained by the electrospinning of reinforced nanocomposite PMMA with acetone. G-PMMA electrospun fiber has been produced and evaluated according to its morphology, structure, and chemical composition. The effects of graphene on the nanocomposite fibers mats, such as microstructural morphology, concentration dispersion of graphene nanoplatelets, and mechanical performance are determined respectively using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and nanoindentation testing. The results show excellent dispersion of nanoflakes in a polymer matrix within a nice G-PMMA fiber mat, along with enhanced mechanical performance of electrospun polymer fiber, as compared to the unreinforced PMMA fiber.

7.2 Experimental Section

The G-PMMA has higher strength and stiffness than does pure PMMA and can be used in various applications, such a manufacturing a reinforced G-PMMA fiber. The first step in involves mechanical exfoliation to obtain graphene by peeling off graphite in the liquid-phase of a PMMA/acetone solution. Liquid-phase exfoliation (LPE) has attracted considerable attention as a cost-effective, efficient, and versatile method that has the potential for large-scale production of defect-free graphene. Here, a modified LPE method is applied using two concentric cylinders: a stationary outer cylinder and an inner cylinder rotating at high rates. The high rotation rate creates high shear rate to exfoliate the graphite into graphene nanosheets, which leads to the formation of novel high-quality G-PMMAs.

The next step is to dilute the exfoliated graphene PMMA/acetone solution with more acetone to prepare it for electrospinning of solid G-PMMA fibers. The fiber will be shaped and dragged to the other side by supplying a high electric field on the mixture (graphene/PMMA/acetone). Consequently, the mechanical properties, morphology, structure, and structural density have been observed by nanoindentation (Hysitron nanoindentation, USA), Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

7.2.1 Materials Preparation

Polymethylmethacrylate (PMMA) and acetone, purchased from Fisher Scientific, are utilized to prepare the working fluid. Asbury Carbons Inc., New Jersey supplies synthetic graphite (TC 301 High Purity) with an average flake size of 8-20 μ m. The graphite particles are exfoliated into graphene nanoplatelets (see Figure 7. 2) by using a novel liquid-phase exfoliation method (LPE), whose setup is described in Figure 7. 1. The polymer/acetone solution at a concentration of 0.7 g/ml with 1% wt graphite is injected inbetween two concentric cylinders of a device that is run for six hours to achieve exfoliated high-quality graphene. This uniform PMMA/acetone solution with graphene is used to produce graphene-reinforced-PMMA nano- and microfibers.

Our setup is designed to generate high shear stress in the small gap between two concentric cylinders (with the inner one rotating and the outer one fixed) to exfoliate effectively bulk materials into high-quality 2D materials in a liquid phase. If a liquid-phase polymer is used, then a nanoflake-reinforced polymer matrix composite can be concurrently fabricated upon drying after the exfoliation process. This setup has been used to exfoliate starting microscale fillers of graphite or *h*-BN in a liquid phase of PMMA/acetone solution into nanoscale fillers.



Figure 7. 1 Schematic of the shear-exfoliation processing of graphite in the PMMA/acetone solution.



Figure 7. 2 Show a graphene flakes after producing by LPE method.

7.2.2 Electrospinning Processing

The electrospinning setup, as shown in Figure 7. 3, typically consists of three parts: (1) a 10 ml syringe that holds the polymer solution with a needle (blunt flat tip) as the spinneret [1.27 mm outer diameter(OD) 0.83 mm internal diameter (ID)] is connected to syringe pump to control the polymer solution flow rate; (2) a ground electrode substrate (i.e., aluminum foil) is used as a fiber polarity collector; and (3) a high voltage source (Glassman

high voltage, Inc.) is supplied between the spinneret needle and substrate (separated by a gap of 15 cm).



Figure 7. 3 A typical schematic illustration electrospinning setup of fabrication of graphene-reinforced fibers.

In this work, the graphene-reinforced PMMA solution that is produced from our novel method is diluted by acetone to PMMA/acetone concertation of 0.35 g/ml at ambient temperature and stirred for 3 hours. It is then filled into a syringe and ejected toward the fiber collector substrate at a constant and controlled flow rate (e.g., 0.04 mL/min) by a syringe pump. A high voltage source 12 kV at room temperature 25 \pm 1°C and 40 \pm 2 % RH is supplied to the needle tip of the syringe. This process leads to formation continuously of a solid fiber mat, as shown in Figure 7. 4.



Figure 7. 4 Photograph of an electrospun fibers mat made of (a)Pure PMMA (b) PMMA/graphene nanocomposites.

7.2.3 Characterization and Measurements

7.2.3.1 Mechanical Properties

The nanoindentation tests of neat PMMA as a reference and graphene-reinforced PMMA electrospun fibers are conducted. First, the individual fiber (diameter size = $6 \mu m$) is tied and mounted on top of a polishing Aluminum stub (see Figure 7. 5); and then the fiber is glued at both of its edges to ensure it is secure. The nanoindentation experiment is conducted using Hysitron nanoindentation, USA, equipped with a Berkovich tip (three-sided pyramidal diamond indenter). Because of the sensitivity of the mechanical properties (e.g., reduced modulus, hardness) to the tip geometry, the tip contact area function is calibrated using a standard fused quartz specimen before measurements and are calculated accordingly for the present cases.

In amorphous glassy polymers, plastic deformation happens as a result of nucleation and diffusion of shear bands [203]. Therefore, in the unreinforced polymer fiber, shear band diffusion occurs without constraint with no barriers in their pathways. On the other hand, in reinforced polymer nanocomposite fibers, the nanofillers serve as obstacles to the motion of the shear bands, resulting in enhancements in hardness and elastic modulus.

Young's modulus *E* and hardness *H* of the graphene-reinforced PMMA fiber as a without and with graphene inclusion are given in Table 1. The listed values of each sample are determined by averaging the collected measurements from eight indentations at a constant force of 300 μ N. The Young's modulus *E* of the graphene-reinforced polymer fibers are analyzed using the Oliver–Pharr method [116]. As shown in Figure 7. 6, graphene addition produces augmentation in the mechanical properties of the PMMA electrospun fibers by about 19 % and 17.2% of *E* and *H*, respectively.

The graphene nanosheets with intrinsically high strengths are well dispersed in the polymer matrix, resulting in high contact areas and strong interfacial adhesion with PMMA chains. Folded and wrinkled graphene sheets seem more effective, as seen from the inset of Figure 7. 9 (TEM images). Moreover, the wrinkled sheets have a region where the wrinkled structures possess nanoscale surface roughness of 0.4 –0.5 nm. These rough regions in the wrinkled graphene may work as nucleation sites in the matrix, which encourage the growing polymer chains to form new crosslinks [179, 194].



Figure 7. 5 Sketches of the electrospinning fiber mounted to the aluminum stub for nanoindentation test.



Figure 7. 6 Nanoindentation load-displacement curves of electrospun PMMA fiber at a constant load of 300 μ N.

Table 7.1 Summary of mechanical properties of electrospun nanocomposite fiber.

| Sample | Young's modulus (GPa) | Hardness (GPa) |
|--------------|-----------------------|-------------------|
| PMMA fiber | 1.7413+/- 0.3300 | 0.0995 +/- 0.0207 |
| G-PMMA fiber | 2.1080+/- 0.4038 | 0.1167 +/-0.0278 |

7.2.3.2 Raman Spectroscopy

Raman spectroscopy is conducted using a Renishaw Raman microscope 1000 using a 633 nm Helium-Neon laser with a focused spot size of 1-2 μ m and collection lens of 50X magnification. The Raman shift range from 500 to 3200 cm⁻¹ is examined, corresponding to that of the graphene/PMMA nanocomposite. The spectral analysis averages over 20 scans for each sample. Prior to electrospinning, the sample for Raman testing is prepared by casting a small amount of graphene-reinforced polymer matrix nanocomposites between two ITO coated glass slides to obtain a 1-mm flat thin layer and then letting it dry for 48 hours.

Comparison of the Raman spectra between graphene-reinforced PMMA and neat PMMA can be seen in Figure 7. 7. From this plot, the effects of adding graphene nanosheets to the PMC can be discerned from the shape of the Raman spectra. Typically, the G, D, and 2D bands of graphene are included together with the PMMA bands in the G-PMMA spectra (Figure 7. 7), while they are missing in the spectra of neat PMMA. Here, the I_{2D}/I_G intensity ratio and G, 2D peak position are used to determine the number of graphene layers [137]. The Raman-active regular peaks for neat PMMA are found at ~602, ~812, ~966, ~990, ~1450, ~1730, ~2844, ~2954, and ~3002 cm⁻¹. The three more distinguished peaks of G-PMMA nanocomposite are the D, G, and 2D bands of graphene at ~1333, ~1584, and ~2671 cm⁻¹, respectively, which are represented by the signals generated during the vibration of carbon atoms from the graphene lattice [172]. The intensity ratio $I_{2D}/I_G \sim 0.92$ (Figure 7. 7) of graphene in the PMMA matrix is indicative of bi-layer and few-layer graphene embedded in the polymer matrix [138, 174]. Also, in

Figure 7. 7, the comparison of graphite and graphene Raman curves reveal redshifting in the 2D peak of about $\sim 28 \text{ cm}^{-1}$, which is also characteristic of mono-layer and bi-layer graphene [137].



Figure 7. 7 Raman spectra of PMMA nanocomposites (red) Raman spectra of Graphene-PMMA indicated D, G, and 2D bands intensity (~1351, ~1584, and ~2671 cm⁻¹) is bilayer and few layers graphene, (black) Raman spectra of PMMA as a reference.

7.2.3.3 Scanning Electron Microscopy (SEM)

The SEM is a powerful investigative technique, which is used to provide extensive analysis possibilities with high-resolution images of a sample's surface topography. SEM (Zeiss Sigma 8100) is used to observe the average diameter of the electrospun fibers and their morphology. The SEM samples of G-PMMA fiber mat are prepared by coating them with a thin layer of gold (5 nm) to avoid the charging effect
[204]. Applying this technique to analyze G-PMMA electrospun fibers has created a powerful method to completely characterize not only the fiber's diameter, but also its morphology and orientation.

Figure 7. 8 clearly shows that all of the samples are in the continuous single fiber shape and randomly oriented. The SEM images in Figure 7. 8 display the typical morphology of reinforced G-PMMA electrospun fiber when using acetone as a solvent with PMMA. Higher magnification reveals the wrinkling of fibers without any bead formation on the fiber structure, while beads were observed to appear on the electrospun PMMA fiber (see Figure 7. 8b). The beads on the electrospun polymer fibers disappear with adding of graphene nanoflakes into the polymer solution before electrospinning process [205, 206]. Possible reasons for this effect may be due to increase of the electrospun fluid effective viscosity or increased polymer solution conductivity with graphene content [207].

The wrinkled surface topographies of electrospun polymer fibers may appear as a result of buckling instabilities during processing [208]. From the high magnification SEM images, the fiber diameter is determined to range from $3-6 \,\mu$ m.



Figure 7. 8 SEM images of (a) electrospun graphene-PMMA nanocomposite fiber at different magnification, and (b) electrospun pure PMMA fiber.

7.2.3.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) can be used to achieve understanding and characterization of the internal composition, interfacing, and nanofillers dispersion in the polymer matrix [209]. Along with SEM, TEM can corroborate the morphologies of the polymer nanocomposites.

The morphologies of the G-PMMA electrospun fiber and distribution of nanoadditives within it are visualized by TEM images (Figure 7. 9). The diameter of the fiber is determined to be around 3 μ m as exhibited in Figure 7. 9a. Figure 7. 9(b–c) evince proper interfacing and dispersion of graphene flakes in the G-PMMA fiber (as indicated by the arrows), while also clearly exhibiting the graphene flakes embedded in the polymer matrix. The high magnification image (Figure 7. 9c) shows the graphene surfaces having excellent interfacing and adhesion with the amorphous PMMA matrix. Therefore, the enhanced mechanical properties demonstrated in the nanoindentation tests are reasonably verified. The number of layers in the graphene flakes can be determined by high-resolution TEM images, as shown in Figure 7. 9e, indicating thin few-layer (n \leq 4) graphene flakes. On the other hand, the shear stress between the graphene layers during the exfoliation process has a strong influence on wrinkle- and ripple-formation of graphene flakes, which is observed in Figure 7. 9f and Figure 7. 9c (as circled).



Figure 7. 9 TEM images (a) electrospun nanocomposite fiber, (b) few layers' graphene covered by PMMA (c,d) uniform dispersion of graphene flakes in the fibers, (e,f) high magnification of graphene flakes in the fiber.

7.3 Summary

Nanofillers are an important and integral part in many nanotechnological applications, especially for enhancing the mechanical properties of the polymer matrix composite. In this work, graphene is exfoliated to nanoscale sheets in the liquid phase of a PMMA/acetone solution, which is then electrospun into nanocomposite fibers. However, the mechanical characterizations, including nanoindentation tests (i.e., to determine modulus and hardness) of the reinforced fiber, with neat polymer fiber as a reference, are performed using the nanoindentation technique (Hysitron, nanoindentation). The surface morphology and interfacing of the nanofillers with the polymer matrix are investigated with scanning electron microscopy (SEM) and transmission electron microscope (TEM). Additionally, Raman spectroscopy is utilized to determine the number of dispersion flakes in the matrix via knowing the dispersion of peak positions and intensities with wavenumber shift. The analysis indicates good dispersion of nanoflakes within the polymer matrix, resulting in overall uniform improvement in the mechanical properties. The graphenereinforced PMMA electrospun fibers have enhanced mechanical properties of 19% and 17.2% in E and H, respectively.

Chapter Eight

Conclusion and Future work

8.1 Conclusion

By using high shear-induced exfoliation of graphite within a liquid-phase polymer, highquality graphene-reinforced polymer nanocomposites can be directly produced. Moreover, our novel technique not only exfoliates the graphite, but also allows unadulteratedbonding/adhesion of the peeled-off graphene with the polymer, as well as uniform dispersion of graphene flakes in the polymer matrix without noticeable aggregation. The exfoliation efficiency is found to increase rapidly with increasing solution viscosity, which, for our examined cases, corresponds to a PMMA/acetone concentration of 0.7 g/ml. The results of the final nanocomposite show significantly improved mechanical properties, including elastic modulus and hardness, especially at the polymer/solution concentration e.g. 0.7 g/ml, with post-heat treatment at 200°C. The rheological behavior during the exfoliation process in the polymer solution suggests the fluid entering the non-Newtonian regime, with coupled interaction between the nanofiller and the polymer solution. When the graphene loading of the polymer solution increases to a critical value, the composite system exhibits solid-like behavior (viscoelastic behavior). Our novel exfoliation method may be used for other 2D materials, such as hexagonal boron nitride (h-BN) or molybdenum disulfide (MoS_2) to produce other reinforced polymer nanocomposites with unique properties.

This research investigates and contrastes the effects of two different nanofillers (i.e., graphene and h-BN) on the morphology, structure, and mechanical properties of the as-

obtained reinforced polymer nanocomposites, along with study of the viscoelastic behavior during processing, which gives insight into the final nanocomposite augmented properties. For best results in the range studied, the graphene-PMMA and h-BN-PMMA samples are fabricated under the processing conditions 0.7 g/ml and then post heat treated at 200°C. The resulting nanocomposite displays excellent dispersion and interfacing of graphene and h-BN nanofiller within the polymer matrix. Interestingly, graphene exhibits more folding and wrinkling than does h-BN after the exfoliation process. Moreover, the graphenereinforced PMMA possesses slightly higher enhanced mechanical properties (i.e., in E and H) than does the h-BN reinforced PMMA, perhaps reflected in the different viscoelastic behaviors during processing. The nano-dynamic mechanical analysis tests (nanoDMA) makes evident that the storage modulus increases significantly with increasing grapheneflake concentration, which may be attributed to strong links/bonding between the graphene flakes and PMMA matrix. In contrast, h-BN-reinforced PMMA nanocomposites achieve a maximum increase in the loss modulus in comparison to that of the G-PMMA nanocomposite. In contrast, h-BN-reinforced PMMA nanocomposites achieve a maximum increase in the loss modulus in comparison to that of the G-PMMA nanocomposite. Also, the results show that the *h*-BN nanofiller achieves a higher loss tangent or damping factor (41%), while the G-PMMA nanocomposite achieves a lower loss tangent (3.67%). This increase of the damping factor (tan δ) when using h-BN is due to the increase in the rate of energy loss (loss modulus). Adding fillers to the matrix could reduce the movement in molecule chains inside the matrix, thus increasing the internal friction, which results in an increase of energy loss and damping factor in the end [187].

As an extension of the novel exfoliation process and polymer reinforcement to waterbased polymers, graphene reinforced polyvinylpyrrolidone (G-PVP) is produced through high shear treatment of graphite particles at 0.4 and 0.6 g/ml of polymer/water concentrations. The characterization by Raman spectroscopy demonstrates high concentrations and dispersion of graphene sheets in the polymer matrix after six hours of processing, which is shown by the increasing of the I_{2D}/I_G ratio from 0.4 to 0.65. The mechanical properties exhibit clear improvement in the elastic modulus and hardness.

The processing time influence on the high-shear exfoliation performance is investigated, revealing increasing amount of monolayer graphene flakes produced in the polymer matrix with increasing shear application duration up to 12 hours. The Raman spectra of the G-PMMA samples display increase of the I_{2D}/I_G ratio gradually up to 1.22, with increasing processing duration.

As an application-motivated study, the nanocomposite polymer is electrospun into a graphene-reinforced PMMA fiber mat, and the mechanical and structure-property attributes of the fibers are assessed. The characterizations demonstrate that shear exfoliation of graphene in the liquid PMMA solution can achieve high dispersion of graphene in the polymer matrix, which can be retained in their processing into fibers, as observed from the TEM images. The mechanical properties of the fibers, as determined from nanoindentation tests, demonstrated significant improvement with graphene addition, i.e., by 19% and 17.2% for E and H, respectively.

8.2 Future Work

Although many topics related to reinforcing polymers using a novel exfoliation methods for 2D materials in the polymer liquid phase have been covered in this research, with the discussion of some parameters that may affect the exfoliation performance, there are still many suggestions or challenges that should be carried out for further improvement of the exfoliation processes and the manufacturing of nanocomposites.

The first suggestion is to improve the exfoliation performance by scaling up the novel high-shear apparatus design via increasing the polymer viscosity and heat treatment of the composite at the same time. This can happen by adding a hot stage into the setup, and then mixing the polymer at melting temperature with the fillers, which could achieve a high processing viscosity, resulting in high exfoliation and reinforcement performance.

Additives are an important parameter that can be studied towards achieving a superior nanocomposite polymer matrix. One can try mixing graphene and h-BN or MoSO₂ together to form a new hybrid structure of nanofillers whereby graphene/h-BN structures are stacked together. Currently, the experimental studies have achieved very limited success in producing such hybrid structures [210].

Another project, developing an electrospun method for producing antimicrobial electrospun biopolymer nanofiber mats via mixing of graphene oxide (GO) with silver nanoparticles (Ag) [211] in the Poly (vinyl pyrrolidone) (PVP) solution.

References

- 1. Müller, K., et al., *Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields.* Nanomaterials, 2017. **7**(4): p. 74.
- Potts, J.R., et al., Graphene-based polymer nanocomposites. Polymer, 2011. 52(1): p. 5-25.
- 3. Zhou, L., C. Gao, and W. Xu, *Simultaneous photoluminescence import and mechanical enhancement of polymer films using silica-hybridized quantum dots.* Journal of Materials Chemistry, 2010. **20**(27): p. 5675-5681.
- 4. Nosker, T., et al., *In Situ Exfoliation Method to Fabricate a Graphene-Reinforced Polymer Matrix Composite (G-PMC)*. 2013, Google Patents.
- 5. Tewatia, A., et al., *Characterization of melt-blended graphene–poly (ether ether ketone) nanocomposite.* Materials Science and Engineering: B, 2017. **216**: p. 41-49.
- 6. Tjong, S.C., *Structural and mechanical properties of polymer nanocomposites.* Materials Science and Engineering: R: Reports, 2006. **53**(3-4): p. 73-197.
- 7. Hanemann, T. and D.V. Szabó, *Polymer-nanoparticle composites: from synthesis to modern applications.* Materials, 2010. **3**(6): p. 3468-3517.
- 8. Peplow, M., *The plastics revolution: how chemists are pushing polymers to new limits.* Nature, 2016. **536**(7616).
- 9. Falin, A., et al., *Mechanical properties of atomically thin boron nitride and the role of interlayer interactions.* Nature communications, 2017. **8**: p. 15815.
- 10. Müller, K., et al., *Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields.* Nanomaterials, 2017. **7**(4): p. 74.
- 11. Assessment, U.S.C.O.o.T. *Advanced materials by design*. 1988. Congress of the US, Office of Technology Assessment.
- 12. Aleksendric, D. and P. Carlone, *Soft Computing in the Design and Manufacturing of Composite Materials: Applications to Brake Friction and Thermoset Matrix Composites*. 2015: Woodhead Publishing.

- 13. Mittal, G., et al., A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. Journal of Industrial and Engineering Chemistry, 2015. **21**: p. 11-25.
- 14. Fim, F.d.C., et al., *Thermal, electrical, and mechanical properties of polyethylene– graphene nanocomposites obtained by in situ polymerization.* Journal of Applied Polymer Science, 2013. **128**(5): p. 2630-2637.
- 15. Huo, C., et al., *2D materials via liquid exfoliation: a review on fabrication and applications.* Science bulletin, 2015. **60**(23): p. 1994-2008.
- Bhuyan, M.S.A., et al., Synthesis of graphene. International Nano Letters, 2016.
 6(2): p. 65-83.
- 17. Singh, V., et al., *Graphene based materials: past, present and future.* Progress in materials science, 2011. **56**(8): p. 1178-1271.
- Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nature materials, 2007. 6(3): p. 183.
- 19. Pham, V.P., et al., *Direct growth of graphene on rigid and flexible substrates: progress, applications, and challenges.* Chemical Society Reviews, 2017. **46**(20): p. 6276-6300.
- 20. Bondavalli, P., *Graphene and Related Nanomaterials: Properties and Applications*. 2017: Elsevier.
- 21. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. science, 2004. **306**(5696): p. 666-669.
- 22. Lee, H.C., et al., *Synthesis of single-layer graphene: A review of recent development.* Procedia Chemistry, 2016. **19**: p. 916-921.
- 23. Novoselov, S., The Nobel Prize in Physics 2010 honours two scientists, who have made the decisive contributions to this development. They are Andre K. Geim and Konstantin S. Novoselov, both at the University of Manchester, UK. They have succeeded in producing, isolating, identifying and characterizing graphene. 2010.
- 24. Novoselov, K.S., et al., *A roadmap for graphene*. Nature, 2012. **490**(7419): p. 192.
- 25. Pang, S., et al., *Graphene as transparent electrode material for organic electronics*. Advanced Materials, 2011. **23**(25): p. 2779-2795.

- 27. Bablich, A., S. Kataria, and M.C. Lemme, *Graphene and two-dimensional materials for optoelectronic applications.* Electronics, 2016. **5**(1): p. 13.
- Al-Juhani, A.A., Rheology, mechanical properties, and thermal stability of maleated polyethylene filled with nanoclays. Journal of Nanomaterials, 2015.
 16(1): p. 394.
- 29. Jo, I., Experimental investigation of thermal transport in graphene and hexagonal boron nitride. 2012.
- 30. Qiu, J. and Z. Zhao, *Graphene: Synthesis, Properties, and Applications*, in *Nanomaterials Handbook, Second Edition*. 2017, CRC Press. p. 1-46.
- 31. Xavior, M.A. and H.P. Kumar, *Processing and characterization techniques of Graphene Reinforced Metal Matrix Composites (GRMMC); a review.* Materials Today: Proceedings, 2017. **4**(2): p. 3334-3341.
- 32. Torres, J.A. and R.B. Kaner, *Graphene synthesis: Graphene closer to fruition*. Nature materials, 2014. **13**(4): p. 328.
- 33. Du, X., R. Chen, and F. Liu, *Investigation of graphene nanosheets reinforced aluminum matrix composites*. Dig J Nanomater Bios, 2017. **12**(1): p. 37-45.
- 34. Wahab, I.F., et al., *Electrospun Graphene Oxide-Based Nanofibres*, in *Advances in Carbon Nanostructures*. 2016, InTech.
- 35. O'Masta, M., B. Russell, and V. Deshpande, *An exploration of the ballistic resistance of multilayer graphene polymer composites.* Extreme Mechanics Letters, 2017. **11**: p. 49-58.
- 36. Sur, U.K., *Graphene: A rising star on the horizon of materials science*. International Journal of Electrochemistry, 2012. **2012**.
- 37. Yi, M. and Z. Shen, *A review on mechanical exfoliation for the scalable production of graphene.* Journal of Materials Chemistry A, 2015. **3**(22): p. 11700-11715.
- 38. Lee, H., et al., Solution plasma exfoliation of graphene flakes from graphite electrodes. RSC Advances, 2014. **4**(93): p. 51758-51765.
- 39. Eigler, S., et al., *Wet chemical synthesis of graphene*. Advanced materials, 2013. **25**(26): p. 3583-3587.

- 40. Zhang, Y., L. Zhang, and C. Zhou, *Review of chemical vapor deposition of graphene and related applications.* Accounts of chemical research, 2013. **46**(10): p. 2329-2339.
- 41. Wong, C.H.A., et al., *Microwave exfoliation of graphite oxides in H2S plasma for the synthesis of sulfur-doped graphenes as oxygen reduction catalysts.* ACS applied materials & interfaces, 2016. **8**(46): p. 31849-31855.
- 42. Zhang, Y., et al., *Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices.* Applied Physics Letters, 2005. **86**(7): p. 073104.
- 43. Singh, K., A. Ohlan, and S. Dhawan, *Polymer-graphene nanocomposites:* preparation, characterization, properties, and applications, in *Nanocomposites-New Trends and Developments*. 2012, IntechOpen.
- 44. Ciesielski, A. and P. Samorì, *Graphene via sonication assisted liquid-phase exfoliation*. Chemical Society Reviews, 2014. **43**(1): p. 381-398.
- 45. Sattler, K.D., Carbon Nanomaterials Sourcebook: Graphene, Fullerenes, Nanotubes, and Nanodiamonds. Vol. 1. 2016: CRC Press.
- 46. Xu, Y., et al., *Liquid-Phase exfoliation of graphene: An overview on exfoliation media, techniques, and challenges.* Nanomaterials, 2018. **8**(11): p. 942.
- 47. Paton, K.R., et al., *Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids*. Nature materials, 2014. **13**(6): p. 624.
- 48. Mori, F., M. Kubouchi, and Y. Arao, *Effect of graphite structures on the productivity and quality of few-layer graphene in liquid-phase exfoliation*. Journal of materials science, 2018. **53**(18): p. 12807-12815.
- 49. Nicolosi, V., et al., *Liquid exfoliation of layered materials.* Science, 2013. **340**(6139): p. 1226419.
- 50. Park, S. and R.S. Ruoff, *Chemical methods for the production of graphenes*. Nature nanotechnology, 2009. **4**(4): p. 217.
- 51. Randviir, E.P., D.A. Brownson, and C.E. Banks, *A decade of graphene research: production, applications and outlook.* Materials Today, 2014. **17**(9): p. 426-432.
- 52. Hernandez, Y., et al., *High-yield production of graphene by liquid-phase exfoliation of graphite.* Nature nanotechnology, 2008. **3**(9): p. 563.

- 54. Hernandez, Y., et al., *Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery*. Langmuir, 2009. **26**(5): p. 3208-3213.
- 55. Srivastava, P.K., P. Yadav, and S. Ghosh, *Dielectric environment as a factor to enhance the production yield of solvent exfoliated graphene*. RSC Advances, 2015. **5**(79): p. 64395-64403.
- 56. Yi, M., et al., A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite. Journal of Nanoparticle Research, 2012.
 14(8): p. 1003.
- 57. Zhou, X., et al., *Dispersion of graphene sheets in ionic liquid [bmim][PF6] stabilized by an ionic liquid polymer.* Chemical Communications, 2010. **46**(3): p. 386-388.
- 58. Lotya, M., et al., *Measuring the lateral size of liquid-exfoliated nanosheets with dynamic light scattering.* Nanotechnology, 2013. **24**(26): p. 265703.
- 59. Yi, M. and Z. Shen, *Fluid dynamics: an emerging route for the scalable production of graphene in the last five years.* RSC Advances, 2016. **6**(76): p. 72525-72536.
- 60. Chong, K.Y., et al., Simplified production of graphene oxide assisted by high shear exfoliation of graphite with controlled oxidation. New Journal of Chemistry, 2018.
 42(6): p. 4507-4512.
- 61. Hendrix, J., et al., *Evaluation of exfoliated graphite to graphene in polyamide 66 using novel high shear elongational flow.* Polymers, 2018. **10**(12): p. 1399.
- 62. Tran, T.S., et al., *High shear-induced exfoliation of graphite into high quality graphene by Taylor–Couette flow.* RSC Advances, 2016. **6**(15): p. 12003-12008.
- 63. Liu, L., et al., *A green, rapid and size-controlled production of high-quality graphene sheets by hydrodynamic forces.* Rsc Advances, 2014. **4**(69): p. 36464-36470.
- 64. Phiri, J., P. Gane, and T.C. Maloney, *High-concentration shear-exfoliated colloidal dispersion of surfactant–polymer-stabilized few-layer graphene sheets.* Journal of materials science, 2017. **52**(13): p. 8321-8337.
- 65. Hod, O., *Graphite and hexagonal boron-nitride have the same interlayer distance. Why?* Journal of chemical theory and computation, 2012. **8**(4): p. 1360-1369.

- 66. Wang, J., F. Ma, and M. Sun, *Graphene, hexagonal boron nitride, and their heterostructures: properties and applications.* RSC Advances, 2017. **7**(27): p. 16801-16822.
- 67. Wang, X., et al. Boron nitride nanosheets: novel syntheses and applications in polymeric composites. in Journal of Physics: Conference Series. 2013. IOP Publishing.
- 68. Ouyang, T., et al., *Thermal transport in hexagonal boron nitride nanoribbons*. Nanotechnology, 2010. **21**(24): p. 245701.
- 69. Li, L.H., et al., *Strong oxidation resistance of atomically thin boron nitride nanosheets*. ACS nano, 2014. **8**(2): p. 1457-1462.
- 70. Qi, Y. and L.G. Hector Jr, *Planar stacking effect on elastic stability of hexagonal boron nitride.* Applied physics letters, 2007. **90**(8): p. 081922.
- 71. Topsakal, M., E. Aktürk, and S. Ciraci, *First-principles study of two-and one-dimensional honeycomb structures of boron nitride.* Physical Review B, 2009. **79**(11): p. 115442.
- 72. Taylor, R. and C. Coulson, *Studies in Graphite and Related Compounds III: Electronic Band Structure in Boron Nitride.* Proceedings of the Physical Society. Section A, 1952. **65**(10): p. 834.
- 73. Lopatin, V. and V. Shcherbina, *Nature of the interlayer interaction in hexagonal boron nitride.* Journal of Structural Chemistry, 1988. **29**(3): p. 466-469.
- 74. Zhang, K., et al., *Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications.* Journal of Materials Chemistry C, 2017. **5**(46): p. 11992-12022.
- 75. Engler, M., et al. *Hexagonal boron nitride (hBN): applications from metallurgy to cosmetics*. in *CFI. Ceramic forum international*. 2007. Göller.
- 76. Jan, R., et al., *Enhancing the mechanical properties of BN nanosheet–polymer composites by uniaxial drawing*. Nanoscale, 2014. **6**(9): p. 4889-4895.
- 77. Jan, R., M. Sadiq, and A. Hussain. *Boron nitride-polymer composites: Mechanical properties evaluation at various strain ratios*. in 2017 14th International Bhurban Conference on Applied Sciences and Technology (IBCAST). 2017. IEEE.
- 78. Baekeland, L.H., *The Synthesis, Constitution, and Uses of Bakelite.* Industrial & Engineering Chemistry, 1909. **1**(3): p. 149-161.

- 79. Salavagione, H.J., G. Martínez, and G. Ellis, *Graphene-based polymer nanocomposites*, in *Physics and Applications of Graphene-Experiments*. 2011, InTech.
- 80. Carter, L., J. Hendricks, and D. Bolley, *United States Patent No. 2531396*. Assigned to National Lead Company, 1950.
- 81. Mohammed, L., et al., *A review on natural fiber reinforced polymer composite and its applications.* International Journal of Polymer Science, 2015. **2015**.
- 82. Marquis, D.M., E. Guillaume, and C. Chivas-Joly, *Properties of nanofillers in polymer*, in *Nanocomposites and polymers with analytical methods*. 2011, InTech.
- 83. ISO, C., *TS 27687: 2008–Nanotechnologies–Terminology and definitions for nanoobjects–Nanoparticle, nanofibre and nanoplate (ISO/TS 27687: 2008).* German version: Vornorm DIN CEN ISO/TS, 2008. **27687**.
- 84. Khan, W.S., N. Hamadneh, and W.A. Khan, *Polymer nanocomposites–synthesis techniques, classification and properties.* Science and applications of Tailored Nanostructures: One Central Press (OCP), 2016.
- Camargo, P.H.C., K.G. Satyanarayana, and F. Wypych, *Nanocomposites: synthesis, structure, properties and new application opportunities.* Materials Research, 2009.
 12(1): p. 1-39.
- 86. Kaur, G., et al., *Electrically conductive polymers and composites for biomedical applications*. Rsc Advances, 2015. **5**(47): p. 37553-37567.
- 87. Ji, G., Nanoclay reinforced polymer composite and its application to hybrid composite structures. 2008.
- 88. Alexandre, M. and P. Dubois, *Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials.* Materials Science and Engineering: R: Reports, 2000. **28**(1-2): p. 1-63.
- 89. Bhowmick, A., et al., Morphology–property relationship in rubber-based nanocomposites: some recent developments, in Advanced Rubber Composites. 2010, Springer. p. 1-83.
- 90. Anandhan, S. and S. Bandyopadhyay, *Polymer nanocomposites: from synthesis to applications.* Nanocomposites and polymers with analytical methods, 2011. **1**: p. 1-28.

- 92. Li, W., et al., Understanding the role of different conductive polymers in improving the nanostructured sulfur cathode performance. Nano letters, 2013. **13**(11): p. 5534-5540.
- 93. Ding, K., et al., Octagonal prism shaped lithium iron phosphate composite particles as positive electrode materials for rechargeable lithium-ion battery. Electrochimica Acta, 2014. **146**: p. 585-590.
- 94. Shukla, A. and T. Prem Kumar, *Nanostructured electrode materials for electrochemical energy storage and conversion.* Wiley Interdisciplinary Reviews: Energy and Environment, 2013. **2**(1): p. 14-30.
- 95. Liu, W., et al., *Enhancing ionic conductivity in composite polymer electrolytes with well-aligned ceramic nanowires.* Nature energy, 2017. **2**(5): p. 17035.
- 96. Feldman, D., *Polymer nanocomposites in building, construction.* Journal of Macromolecular Science, Part A, 2014. **51**(3): p. 203-209.
- 97. Ferrara, M. and M. Bengisu, *Materials that change color*, in *Materials that Change Color*. 2014, Springer. p. 9-60.
- 98. Kamalisarvestani, M., et al., *Performance, materials and coating technologies of thermochromic thin films on smart windows.* Renewable and Sustainable Energy Reviews, 2013. **26**: p. 353-364.
- 99. Harvey, L.D., A handbook on low-energy buildings and district-energy systems: fundamentals, techniques and examples. 2012: Routledge.
- 100. Espinal, L., et al., *Measurement, standards, and data needs for CO2 capture materials: a critical review.* Environmental science & technology, 2013. **47**(21): p. 11960-11975.
- 101. Darwish, A.M., et al. Polymer nanocomposite luminescent films for solar energy harvesting made by concurrent multi-beam multi-target pulsed laser deposition. in Photonic Fiber and Crystal Devices: Advances in Materials and Innovations in Device Applications XII. 2018. International Society for Optics and Photonics.
- 102. Figueira, R., C.J. Silva, and E. Pereira, Organic-inorganic hybrid sol-gel coatings for metal corrosion protection: a review of recent progress. Journal of Coatings Technology and Research, 2015. 12(1): p. 1-35.

- 103. Hu, R.-G., et al., *Recent progress in corrosion protection of magnesium alloys by organic coatings*. Progress in Organic Coatings, 2012. **73**(2-3): p. 129-141.
- 104. Knudsen, O.Ø. and A. Forsgren, *Corrosion control through organic coatings*. 2017: CRC Press.
- 105. Chang, K., et al., Advanced anticorrosive coatings prepared from electroactive polyimide/graphene nanocomposites with synergistic effects of redox catalytic capability and gas barrier properties. Express Polymer Letters, 2014. **8**(4).
- Milani, A., et al., Raman spectroscopy as a tool to investigate the structure and electronic properties of carbon-atom wires. Beilstein journal of nanotechnology, 2015. 6: p. 480.
- 107. Hong, H., Unconfined flame synthesis of mono-layer graphene and other nanostructured materials. 2017, Rutgers University-School of Graduate Studies.
- 108. Clark, R.J., *Raman microscopy in the identification of pigments on manuscripts and other artwork.* The Scientific Examination of Art. National Academies of Science, Washington DC, 2005: p. 162-185.
- 109. Ferrari, A.C., *Raman spectroscopy of graphene and graphite: disorder, electron– phonon coupling, doping and nonadiabatic effects.* Solid state communications, 2007. **143**(1-2): p. 47-57.
- 110. Díez-Pascual, A.M., et al., *Rheological and tribological properties of carbon nanotube/thermoplastic nanocomposites incorporating inorganic fullerene-like WS2 nanoparticles.* The Journal of Physical Chemistry B, 2012. **116**(27): p. 7959-7969.
- 111. Gupta, R.K., Polymer and composite rheology. 2000: CRC Press.
- 112. Groisman, A. and V. Steinberg, *Elastic turbulence in curvilinear flows of polymer solutions.* New Journal of Physics, 2004. **6**(1): p. 29.
- 113. King, W.E., et al., *Ultrafast electron microscopy in materials science, biology, and chemistry.* Journal of Applied Physics, 2005. **97**(11): p. 8.
- 114. KARAN, S., et al. Shape Based Characterization of Nanoparticles–A Fuzzy Mathematical Approach. in Proc Indian Natn Sci Acad. 2015.
- Bliznyuk, V.N., D. LaJeunesse, and A. Boseman, Application of helium ion microscopy to nanostructured polymer materials. Nanotechnology Reviews, 2014.
 3(4): p. 361-387.

- 117. Sun, J., et al., *Quasi-static and dynamic nanoindentation of some selected biomaterials.* Journal of Bionic Engineering, 2014. **11**(1): p. 144-150.
- 118. Ray, S.S., *Environmentally friendly polymer nanocomposites: types, processing and properties.* 2013: Elsevier.
- 119. Liu, K., et al., *Nano-dynamic mechanical analysis (nano-DMA) of creep behavior of shales: Bakken case study.* Journal of Materials Science, 2018. **53**(6): p. 4417-4432.
- 120. Carfagni, M., E. Lenzi, and M. Pierini. *The loss factor as a measure of mechanical damping*. in *Proceedings-spie the international society for optical engineering*. 1998. SPIE INTERNATIONAL SOCIETY FOR OPTICAL.
- 121. Shuib, R.K., *Development of elastomeric composites from iron sand and natural rubber for vibration damping*. 2015, University of Waikato.
- 122. Cohen, S.R. and E. Kalfon-Cohen, *Dynamic nanoindentation by instrumented nanoindentation and force microscopy: A comparative review.* Beilstein journal of nanotechnology, 2013. **4**: p. 815.
- 123. Zheng, W., X. Lu, and S.C. Wong, *Electrical and mechanical properties of expanded graphite reinforced high density polyethylene*. Journal of Applied Polymer Science, 2004. **91**(5): p. 2781-2788.
- 124. Atif, R., I. Shyha, and F. Inam, *Mechanical, thermal, and electrical properties of graphene-epoxy nanocomposites—A review.* Polymers, 2016. **8**(8): p. 281.
- 125. Dang, Z.-M., et al., Fundamentals, processes and applications of high-permittivity polymer–matrix composites. Progress in materials science, 2012. **57**(4): p. 660-723.
- 126. Peplow, M., *The plastics revolution: how chemists are pushing polymers to new limits.* Nature News, 2016. **536**(7616): p. 266.
- 127. Hussain, F., M. Okamoto, and R. Gorga, *Review article: polymer–matrix nanocomposites.* Journal of Composite Material, 2006. **40**(17): p. 1511-1575.
- 128. Hernandez, Y., et al., *High-yield production of graphene by liquid-phase exfoliation of graphite.* Nature nanotechnology, 2008. **3**(9): p. 563-568.

- 129. Chen, X., J.F. Dobson, and C.L. Raston, *Vortex fluidic exfoliation of graphite and boron nitride.* Chemical Communications, 2012. **48**(31): p. 3703-3705.
- 130. Paton, K.R., et al., *Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids*. Nature materials, 2014. **13**(6): p. 624-630.
- 131. Kim, H., A.A. Abdala, and C.W. Macosko, *Graphene/polymer nanocomposites*. Macromolecules, 2010. **43**(16): p. 6515-6530.
- 132. Porwal, H., S. Grasso, and M. Reece, *Review of graphene–ceramic matrix composites*. Advances in Applied Ceramics, 2013. **112**(8): p. 443-454.
- 133. Nosker, T., et al., In Situ Exfoliation Method to Fabricate a Graphene-Reinforced Polymer Matrix Composite. 2019, Google Patents.
- 134. Lynch, J., et al. Lightweight, high performance polymer composites for modern engineering applications. in 11th Annual TechConnect World Innovation Conference and Expo, Held Jointly with the 20th Annual Nanotech Conference and Expo, the 2018 SBIR/STTR Spring Innovation Conference, and the Defense TechConnect DTC Spring Conference. 2018. TechConnect.
- Nusser, K., G.J. Schneider, and D. Richter, *Rheology and anomalous flow properties* of poly (ethylene-alt-propylene)–silica nanocomposites. Macromolecules, 2013.
 46(15): p. 6263-6272.
- Ferrari, A.C., Raman spectroscopy of graphene and graphite: disorder, electron– phonon coupling, doping and nonadiabatic effects. Solid state communications, 2007. 143(1): p. 47-57.
- 137. Gayathri, S., et al., *Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study*. Aip Advances, 2014. **4**(2): p. 027116.
- 138. Li, C., et al., *Preparation of single-and few-layer graphene sheets using Co deposition on SiC substrate.* Journal of Nanomaterials, 2011. **2011**: p. 44.
- 139. Papageorgiou, D.G., I.A. Kinloch, and R.J. Young, *Mechanical properties of graphene and graphene-based nanocomposites.* Progress in Materials Science, 2017. **90**: p. 75-127.
- 140. Beams, R., L.G. Cançado, and L. Novotny, *Raman characterization of defects and dopants in graphene.* Journal of Physics: Condensed Matter, 2015. **27**(8): p. 083002.

- Biswas, B., A. Chowdhury, and B. Mallik, Tuning of electrical conductivity and hysteresis effect in poly (methyl methacrylate)–carbon nanotube composite films. RSC Advances, 2013. 3(10): p. 3325-3332.
- 142. Tölle, F.J., M. Fabritius, and R. Mülhaupt, *Emulsifier Free Graphene Dispersions* with High Graphene Content for Printed Electronics and Freestanding Graphene Films. Advanced Functional Materials, 2012. **22**(6): p. 1136-1144.
- 143. Su, R., et al., *Study on the absorption coefficient of reduced graphene oxide dispersion.* The Journal of Physical Chemistry C, 2014. **118**(23): p. 12520-12525.
- 144. Hossain, M.M., J.R. Hahn, and B.-C. Ku, *Synthesis of Highly Dispersed and Conductive Graphene Sheets by Exfoliation of Preheated Graphite in a Sealed Bath and its Applications to Polyimide Nanocomposites.* Bulletin of the Korean Chemical Society, 2014. **35**(7): p. 2049-2056.
- 145. Chakraborty, H., et al., *Exfoliated graphite reinforced PMMA composite: a study on nanoindentation and scratch behavior.* Journal of Nanotechnology, 2012. **2012**.
- 146. Starr, F.W., T. Schroder, and S.C. Glotzer, *Molecular dynamics simulation of a polymer melt with a nanoscopic particle*. Macromolecules, 2002. **35**: p. 4481.
- Smith, G.D., et al., A molecular dynamics simulation study of the viscoelastic properties of polymer nanocomposites. The Journal of chemical physics, 2002.
 117(20): p. 9478-9489.
- 148. Das, B., et al., *Nano-indentation studies on polymer matrix composites reinforced by few-layer graphene.* Nanotechnology, 2009. **20**(12): p. 125705.
- Schniepp, H.C., et al., Functionalized single graphene sheets derived from splitting graphite oxide. Journal of Physical Chemistry B-Condensed Phase, 2006. 110(17): p. 8535-8539.
- 150. Ramanathan, T., et al., *Functionalized graphene sheets for polymer nanocomposites*. Nature nanotechnology, 2008. **3**(6): p. 327-331.
- 151. Vallés, C., et al., *Few layer graphene–polypropylene nanocomposites: the role of flake diameter.* Faraday discussions, 2014. **173**: p. 379-390.
- 152. Hornberger, L. and K. Devries, *The effects of residual stress on the mechanical properties of glassy polymers.* Polymer Engineering & Science, 1987. **27**(19): p. 1473-1478.

- 153. Bora, M.Ö., The influence of heat treatment on scratch behavior of polymethylmethacrylate (PMMA). Tribology International, 2014. **78**: p. 75-83.
- 154. Wang, C., et al. Formation and the effects of the thermo-residual stress on mechanical properties of the thermoplastic composites. in 2016 4th International Conference on Sensors, Mechatronics and Automation (ICSMA 2016). 2016. Atlantis Press.
- 155. Huber, D.L., *Controlling anisotropy in stereolithographically printed polymers.* Journal of Materials Science, 2019. **54**(4): p. 2763-2765.
- 156. Grubb, D.T., *Elastic properties of crystalline polymers*. Materials Science and Technology, 2006.
- 157. Gedde, U., *Polymer physics*. 1995: Springer Science & Business Media.
- 158. Nosker, T., et al., *In situ exfoliation method to fabricate a graphene-reinforced polymer matrix composite (G-PMC)*. 2018, Google Patents.
- 159. Martin-Gallego, M., et al., *Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites.* European Polymer Journal, 2013. **49**(6): p. 1347-1353.
- 160. Einstein, A., *A new determination of molecular dimensions.* Ann. Phys., 1906. **19**: p. 289-306.
- 161. Makarova, V.V., et al., *Rheology–Structure Interrelationships of Hydroxypropylcellulose Liquid Crystal Solutions and Their Nanocomposites under Flow.* Macromolecules, 2013. **46**(3): p. 1144-1157.
- Vega, J., et al., *Rheology, processing, tensile properties, and crystallization of polyethylene/carbon nanotube nanocomposites.* Macromolecules, 2009. 42(13): p. 4719-4727.
- 163. Jiang, Z., et al., *Percolation model of reinforcement efficiency for carbon nanotubes dispersed in thermoplastics.* Composites Part A: Applied Science and Manufacturing, 2016. **86**: p. 49-56.
- 164. Abraham, J., et al., *Rheological percolation in thermoplastic polymer nanocomposites*. Rheology: Open access, 2017. **1**(1): p. 1-15.
- 165. Meyer, J.C., et al., *The structure of suspended graphene sheets*. Nature, 2007. 446(7131): p. 60-63.

- 167. Harito, C., et al., *Polymer nanocomposites having a high filler content: synthesis, structures, properties, and applications.* Nanoscale, 2019. **11**(11): p. 4653-4682.
- 168. Al Sheheri, S.Z., et al., *The preparation of carbon nanofillers and their role on the performance of variable polymer nanocomposites.* Designed monomers and polymers, 2019. **22**(1): p. 8-53.
- 169. Asif, S.S., K. Wahl, and R. Colton, *Nanoindentation and contact stiffness measurement using force modulation with a capacitive load-displacement transducer.* Review of scientific instruments, 1999. **70**(5): p. 2408-2413.
- 170. Wai, S.W., Rapid assessment of paint coatings by micro and nano indentation methods. 2013.
- 171. Quadrini, F., E.A. Squeo, and A. Guglielmotti, *Indentation creep of polymers. I. Experimental.* Polymer Engineering & Science, 2010. **50**(12): p. 2431-2439.
- 172. Choi, W., et al., *Influence of removing PMMA residues on surface of CVD graphene using a contact-mode atomic force microscope*. RSC Advances, 2017. **7**(12): p. 6943-6949.
- 173. Liu, J., R.G. Kutty, and Z. Liu, *Controlled synthesis of atomically layered hexagonal boron nitride via chemical vapor deposition.* Molecules, 2016. **21**(12): p. 1636.
- 174. Le, H.D., et al., Synthesis of multi-layer graphene films on copper tape by atmospheric pressure chemical vapor deposition method. Advances in Natural Sciences: Nanoscience and Nanotechnology, 2013. **4**(3): p. 035012.
- 175. Gorbachev, R.V., et al., *Hunting for monolayer boron nitride: optical and Raman signatures.* Small, 2011. **7**(4): p. 465-468.
- 176. Chen, J., et al., Enhancement of mechanical and wear resistance performance in *hexagonal boron nitride reinforced epoxy nanocomposites*. Polymer International, 2017. **66**(5): p. 659-664.
- 177. Yang, Y., et al., Judicious selection of bifunctional molecules to chemically modify graphene for improving nanomechanical and thermal properties of polymer composites. Journal of Materials Chemistry A, 2014. **2**(47): p. 20038-20047.
- 178. Schniepp, H.C., et al., *Functionalized single graphene sheets derived from splitting graphite oxide.* The Journal of Physical Chemistry B, 2006. **110**(17): p. 8535-8539.

- 179. Ramanathan, T., et al., *Functionalized graphene sheets for polymer nanocomposites*. Nature nanotechnology, 2008. **3**(6): p. 327.
- 180. Oommen, Z., G. Groeninckx, and S. Thomas, Dynamic mechanical and thermal properties of physically compatibilized natural rubber/poly (methyl methacrylate) blends by the addition of natural rubber graft poly (methyl methacrylate). Journal of Polymer Science Part B: Polymer Physics, 2000. 38(4): p. 525-536.
- Varela-Rizo, H., et al., Analysis of the electrical and rheological behavior of different processed CNF/PMMA nanocomposites. Composites Science and Technology, 2012. 72(2): p. 218-224.
- Singh, P. and A.K. Ghosh, Torsional, tensile and structural properties of acrylonitrile-butadiene-styrene clay nanocomposites. Materials & Design, 2014.
 55: p. 137-145.
- Tripathi, S.N., R.S. Malik, and V. Choudhary, *Melt rheology and thermomechanical behavior of poly (methyl methacrylate)/reduced graphene oxide nanocomposites.* Polymers for Advanced Technologies, 2015. 26(12): p. 1558-1566.
- 184. Du, F., et al., *Nanotube networks in polymer nanocomposites: rheology and electrical conductivity.* Macromolecules, 2004. **37**(24): p. 9048-9055.
- 185. Wei, W., et al., *Improving the Damping Properties of Nanocomposites by Monodispersed Hybrid POSS Nanoparticles: Preparation and Mechanisms.* Polymers, 2019. **11**(4): p. 647.
- 186. Her, S.-C. and K.-Y. Lin, Dynamic Mechanical Analysis of Carbon Nanotube-Reinforced Nanocomposites. Journal of applied biomaterials & functional materials, 2017. 15(1_suppl): p. 13-18.
- 187. Meena, A., et al., *Effect of adding nanoalumina and marble dust powder on the physical, mechanical, and thermo mechanical characterization of dental composite.* Polymer Composites, 2018. **39**: p. E321-E331.
- 188. Zhang, L.-Y. and Y.-F. Zhang. *Microstructure and viscoelastic behaviors of graphene/PMMA nanocomposites*. in *Electronic Packaging Technology (ICEPT), 2015 16th International Conference on*. 2015. IEEE.
- Teodorescu, M. and M. Bercea, Poly (vinylpyrrolidone)-a versatile polymer for biomedical and beyond medical applications. Polymer-Plastics Technology and Engineering, 2015. 54(9): p. 923-943.

- El Achaby, M., et al., Graphene oxide reinforced chitosan/polyvinylpyrrolidone polymer bio - nanocomposites. Journal of Applied Polymer Science, 2014. 131(22).
- 191. He, S., et al., *Growth of low-threading-dislocation-density GaN on graphene by hydride vapor phase epitaxy.* Japanese Journal of Applied Physics, 2017. **56**(3): p. 030308.
- Saini, P., R. Sharma, and N. Chadha, Determination of defect density, crystallite size and number of graphene layers in graphene analogues using X-ray diffraction and Raman spectroscopy. Indian Journal of Pure & Applied Physics (IJPAP), 2017. 55(9): p. 625-629.
- 193. Childres, I., et al., *Raman spectroscopy of graphene and related materials*. New developments in photon and materials research, 2013. **1**.
- 194. Verdejo, R., et al., *Graphene filled polymer nanocomposites*. Journal of Materials Chemistry, 2011. **21**(10): p. 3301-3310.
- 195. Tomczak, N., N.F. van Hulst, and G.J. Vancso, *Beaded electrospun fibers for photonic applications*. Macromolecules, 2005. **38**(18): p. 7863-7866.
- 196. Guerrini, L.M., et al., *Electrospinning and characterization of polyamide 66 nanofibers with different molecular weights.* Materials Research, 2009. **12**(2): p. 181-190.
- 197. Sharma, J., et al., *Multifunctional nanofibers towards active biomedical therapeutics.* Polymers, 2015. **7**(2): p. 186-219.
- Huang, Z.-M., et al., A review on polymer nanofibers by electrospinning and their applications in nanocomposites. Composites science and technology, 2003.
 63(15): p. 2223-2253.
- 199. Garg, K. and G.L. Bowlin, *Electrospinning jets and nanofibrous structures*. Biomicrofluidics, 2011. **5**(1): p. 013403.
- Yarin, A.L., S. Koombhongse, and D.H. Reneker, *Taylor cone and jetting from liquid droplets in electrospinning of nanofibers*. Journal of applied physics, 2001. **90**(9): p. 4836-4846.
- 201. Subbiah, T., et al., *Electrospinning of nanofibers*. Journal of applied polymer science, 2005. **96**(2): p. 557-569.

- 202. Fridrikh, S.V., et al., *Controlling the fiber diameter during electrospinning*. Physical review letters, 2003. **90**(14): p. 144502.
- 203. Chen, M., *Mechanical behavior of metallic glasses: microscopic understanding of strength and ductility.* Annu. Rev. Mater. Res., 2008. **38**: p. 445-469.
- 204. Echlin, P., Handbook of sample preparation for scanning electron microscopy and *X*-ray microanalysis. 2011: Springer Science & Business Media.
- 205. Chen, Y., et al., *Preparation and characterization of electrospinning PLA/curcumin composite membranes.* Fibers and Polymers, 2010. **11**(8): p. 1128-1131.
- Cheng, W.-D., et al., *Microstructural changes of graphene/PLA/PBC nanofibers by electrospinning during tensile tests.* Chinese Physics Letters, 2017. 34(3): p. 036101.
- 207. Abbasi, A., et al., *Electrospinning of nylon-6, 6 solutions into nanofibers: rheology and morphology relationships.* Chinese Journal of Polymer Science, 2014. **32**(6): p. 793-804.
- 208. Wang, L., et al., Wrinkled surface topographies of electrospun polymer fibers. Applied Physics Letters, 2009. **94**(15): p. 151916.
- 209. Monticelli, O., et al., *On the use of TEM in the characterization of nanocomposites.* Materials Letters, 2007. **61**(16): p. 3446-3450.
- 210. Kim, S.M., et al., *Synthesis of patched or stacked graphene and hBN flakes: a route to hybrid structure discovery.* Nano letters, 2013. **13**(3): p. 933-941.
- De Faria, A.F., et al., Antimicrobial electrospun biopolymer nanofiber mats functionalized with graphene oxide—silver nanocomposites. ACS applied materials & interfaces, 2015. 7(23): p. 12751-12759.