2015

Fabrication of Multifunctional Graphenebased Polymer Composite Materials Using Different Fillers

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Recommended Citation

Chakraborty, Indrani, "Fabrication of Multifunctional Graphenebased Polymer Composite Materials Using Different Fillers" (2015). *Open Access Dissertations.* Paper 335.
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FABRICATION OF MULTIFUNCTIONAL GRAPHENE-BASED POLYMER COMPOSITE MATERIALS USING DIFFERENT FILLERS

BY

INDRANI CHAKRABORTY

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMICAL ENGINEERING

UNIVERSITY OF RHODE ISLAND

2015

DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

OF

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2015

ABSTRACT

Multi-functional polymer composite materials are of great interest in the field of fabrication of composites owing to their high volume of applications. Different nano and micron sized filler materials are embedded into the matrix to achieve desirable functionalities. Graphene, a sheet of a single atom thick, sp^2 bonded carbon atoms arranged in honeycomb structures is one of the most extensively used filler because of its several exceptional features such as high electrical and thermal conductivities, mechanical and gas barrier properties. Few layer and multilayer graphene sheets are also very promising alternatives of single layer graphene sheet. The biggest challenge in working with graphene is to keep them well dispersed as they always tend to agglomerated due to strong van der Waals force. In this thesis, graphene based polymer composite materials are fabricated and their various engineering properties have been studied. The primary goal of the thesis is to find out different strategies to disperse graphene sheets uniformly in the matrix. A non-conductive, second filler is added to the matrix as a dispersion aid to prevent restacking of graphene sheets. The electrical conductivity of the composites is studied. Several orders of magnitude increase in the electrical conductivity is observed with the addition of non-conductive filler. Different multi-functional polymer composite materials using appropriate fillers are fabricated. Incorporating some fillers can deteriorate the mechanical properties of the system. Suitably selected fillers can act as dispersion aid as well as can enhance the toughness of the composites. Quasi-static compression test and three-point flexural test are performed on these materials. X-ray diffraction and scanning electron microscope are used to study the dispersion of graphene sheets in the matrix. Also

Instron Universal testing machine and two-point probe technique are used to examine the electrical and mechanical properties of the composites. The effect of the size of the second filler on the electrical conductivity of the composites is also studied using silica nanoparticles (200 nm) and alumino-silicate ceramic microspheres (12 microns). Smaller particles are found to be more effective in improving the dispersion of graphene compared to the bigger particles.

ACKNOWLEDGMENTS

First of all, I would like to thank my advisor Dr. Arijit Bose, professor of Chemical Engineering Department, University of Rhode Island for his tremendous support throughout my graduate school. He always encouraged me to not only grow as a chemical engineer, research scientist and an experimentalist but also as an independent thinker. I would also like to thank him for being very supportive and patient with me and having faith in me when I was struggling to achieve my goal. I am sincerely grateful to him for all his valuable advice, guidance and encouragement without those I would not have been able to complete my thesis.

I would also like to thank Dr. Richard Brown, professor of Chemical Engineering, University of Rhode Island and Dr. Arun Shukla, professor of Mechanical Engineering, University of Rhode Island for their constructive, insightful discussions.

I would like to thank all my friends here for their support, help and making my stay at URI so special.

I would like to thank all my labmates for providing me their invaluable suggestions and support.

I would also like to thank Sheryl Girard, Brenda Moyer and Dr. Crisman for their tremendous help throughout my time at graduate school. A very special thanks is given to Abayomi Yussuf, an undergraduate student of department of Mechanical Engineering, University of Rhode Island for his time and incredible help for my experiments.

Finally, I am very much grateful to my wonderful parents who are always immensely

supportive for me. I would like to thank them for believing in me especially while I decided to come to United States and staying thousands miles apart from them for my graduate study to accomplish my goal. Their prayer for me was what sustained me this far.

PREFACE

This thesis is written in manuscript format. The first chapter is an introduction about polymer based composite materials using graphene as filler. The second chapter entitled " Massive Electrical Conductivity Enhancement of Multilayer Graphene/ Polystyrene Composites Using a Nonconductive Filler" was published in ACS Applied Materials and Interfaces in September 2014 (ACS appl. Mater. Interfaces 2014, 6, 16472-16475). The third chapter entitled " The Multi-functional Graphene Based Polymer Composite Materials using Rubber particles as Toughening Agent" is in preparation for Langmuir. The fourth chapter entitled" Effectiveness of the size of the Second Filler on the Electrical Conductivity of the Graphene based Polymer Composite Materials" is in preparation for Langmuir. The fifth chapter entitled " Recommended Future Works" presents different aspects of extending the ongoing work.

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CHAPTER 1

INTRODUCTION

1.1Background:

Polymer based composite materials possess enormous possibilities in a wide range of fields including antistatic floor mats, antistatic plastic materials, electrodes for batteries, sensors, electromagnetic interference (EMI) shielding materials, flexible displays, thin film transistors, photovoltaic, liquid crystal devices[1-8]. Different nano-sized filler materials are embedded into the matrix to tailor the properties of the composites. Polymers are very extensively used as matrix in the field of fabrication of composite materials due to some useful properties such as light-weight, high-strength and the ability to be injection molded into complex shapes with tight tolerances. Academic and industrial research on developing nanocomposite materials started to increase significantly after a report published by researchers of Toyota Motor Corporation where a remarkable enhancement in mechanical property was observed when montmorillonite was added as a filler in the nylon-6 matrix[9]. Three conventional methods used to fabricate polymer composite materials are solvent casting, in-situ polymerization and melt extrusion[1, 5]. Carbon black, layered silicates, carbon nanotubes are embedded in the polymer matrix as filler to improve electrical, thermal, mechanical and gas barrier properties of the composites while keeping all the other intrinsic properties of polymers. The selection of appropriate filler materials is very essential in order to achieve the desired properties of the composites. Graphene is a single atom thick, two dimensional sheet comprising sp^2 bonded carbon atoms arranged in honeycomb structures as shown in figure 1. They display remarkable properties including exceptional in-plane electrical and thermal conductivity, high stiffness and tensile strength, optical transparency, negligible permeability to gases, and van der Waals transparency[10-14].

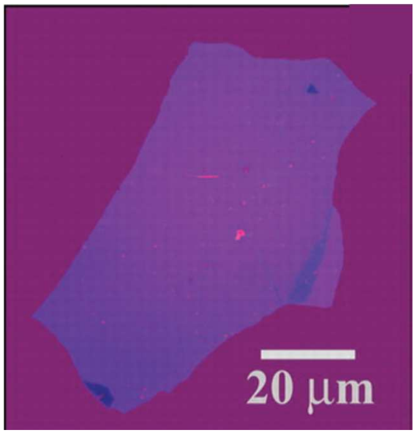

Figure 1: Graphene is a two dimensional, single atom thick sheet of sp^2 bonded carbon atoms, arranged in honeycomb structures. (Chem. Rev. 2010, 110, 132-145)

Since the award of the 2010 Nobel Prize in Physics for *"groundbreaking experiments regarding the two-dimensional material graphene"*, extensive efforts have been initiated worldwide to take advantage of some of these unusual functionalities of graphene in a variety of applications. The academic and industrial interest in graphene is not only confined to the pristine monolayer, but other 2D materials that include few-layer graphene (FLG), multilayer graphene (MLG), graphite nanoplates (GNP, ultrathin 3D crystalline flakes with thickness < 100 nm), and chemically modified forms such as graphene oxide (GO) are very promising alternatives of single layer graphene sheet[15]. Following recent recommendations, we designate these together as graphene based materials (GBM). Graphene has been widely accepted as a filler material in the polymer matrix to impart desired functionalities in the final composites.

The number of publications on graphene and graphene based composite materials is increasing remarkably owing some exceptional properties of graphene. The evidence is shown in figure (2) while searching in three most popular database such as Institute for Scientific Information (ISI)-Web of Science, Science Direct and SciFinder with "Graphene" or "Graphene Composites" as keywords results in numerous publications[1].

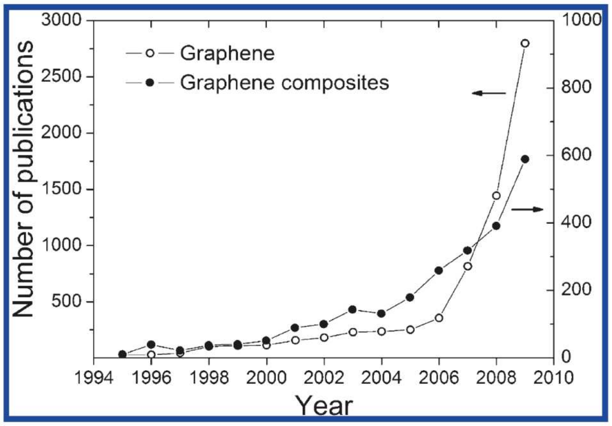

Figure 2: The increasing number of publications on graphene and graphene based composite materials in the last several years. (Macromolecules, 2010, 43, 6515-6530)

1.2 Thesis Objectives:

The one of the goal of this project is to fabricate the electrically conductive polymer composites. The main principle behind developing these composites is to add conductive filler in an insulating polymer matrix. These conductive fillers would make a connected network which would result in significant increase in the electrical conductivity. The minimum amount of the filler at which the conductivity starts to increase is defined as the percolation threshold of the composites. We use graphene nanoplatelets (GNP) as filler and polystyrene as matrix. Since graphene is essentially a two-dimensional structure, the 'volume' swept by it is equivalent to that of a sphere of diameter corresponding to the lateral dimensions of the graphene sheets, giving a theoretical volume loading at percolation which is significantly lower than that of spheres[16]. If graphene-based sheets are modeled as disks of aspect ratio AR (AR = disk diameter/thickness), the percolation threshold φ_c is inversely proportional to AR, and is given by

$$\varphi_c = 1.5\ (\varphi_{sphere}/AR). \tag{1}$$

Here, φ_{sphere} is the percolation threshold for spheres, i.e., $\varphi_{sphere} = 0.29$. The pre factor is 1.5 for disks, and depends on the geometry of the sheets. Since AR can take on values of the order of 10^4, the advantage of using high aspect ratio conducting sheets in lowering the percolation threshold becomes apparent. In practice, φ_c as low as 0.001 has been reported[2], while for spheres the percolation thresholds reported have been closer to 0.15[2, 5, 6, 17]. Achieving percolation at such a low loading also is also extremely beneficial for mechanical properties, particularly under impact loading conditions, as filler materials can act as nucleation sites for crack growth[18].

The objectives of this project are to develop strategies for distributing graphene nano platelets (GNP) in a polymer to significantly enhance its functionality. Specific property targets are electrical conductivity, mechanical properties. The combination of the high aspect ratio graphene nano platelets (GNP) and traditional dispersion techniques such as melt extrusion, that are both highly directional, inherently produce composites with the sheets aligned in the flow direction, either in a parallel or perpendicular orientation. In addition, agglomeration of these sheets during processing is a key problem. A key goal of this project is to fabricate graphene-polymer composite materials with enhanced electrical and mechanical properties by developing good dispersion techniques for graphene sheets. But one of the biggest challenge with the processing of these composites is to disperse graphene uniformly in the polymer matrix. Due to its inherent sheet-like two-dimensional structure, graphene sheets always tend to get agglomerated or restacked because of strong van der Waals force[19]. This is very crucial as long as different properties of multifunctional composite materials are concerned. It is very difficult to exploit all interesting, inherent properties of graphene sheets, if they always tend to get agglomerated. As a result of this, keeping graphene sheets dispersed uniformly throughout the matrix is paramount importance to all researchers working with graphene as an electrically conductive additive in the composites. To facilitate the dispersion of graphene in polymer matrix, silica nanoparticles are added in the matrix where they randomly occupy some space of the matrix where graphene sheets are not allowed to enter. These second, non-conductive fillers can act as posts in the matrix. So the graphene sheets then move around these particles and can make a conductive network in these composites at lower loading. Solvent casting method is used to make these composite materials[17]. Also it is not very convenient to process a large amount of graphene sheets to get desired amount of electrical conductivity as these sheets always get restacked and make the processing condition extremely difficult and as a result of that the effectiveness of using graphene as an electrically conductive additive disappears. So this technique can serve the purpose of utilizing graphene in the polymer composites and helps to keep them dispersed in the matrix without compromising exceptional electrical properties of graphene.

The mechanical properties of GNP-siica/rubber-polystyrene composites are also studied. As we are expecting some significant improvement in the electrical property of the composites after incorporating silica in it, the ductility of the composites would be deteriorated making them more brittle because of the presence of silica in it. So another way to overcome this issue is to replace silica particles with rubber spheres as second filler. In this way, the final composites would be electrically conductive and ductility of the composites would be improved. Finally an interesting study is to do comparative analysis of mechanical properties between GNP -polystyrene composites containing silica particles and rubber particles. Static compression tests and three-point flexural tests will be performed on these composites and an effort will be made to fabricate a multi-functional polymer composites possessing significant electrical and mechanical properties.

1.3 References:

1. Kim, H.; Abdala, A.; Macosko, C. W., Graphene/Polymer Nanocomposites. *Macromolecules (Washington, DC, United States)* **2010,** 43, 6515-6530.

2. Kuilla, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H., Recent advances in graphene based polymer composites. *Progress in Polymer Science* **2010,** 35, (11), 1350-1375.

3. Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A., Graphene Filled Polymer Nanocomposites. *Journal of Materials Chemistry* **2011,** 21, 3301-3310.

4. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-based composite materials. *Nature (London, United Kingdom)* **2006,** 442, (7100), 282-286.

5. Potts, J. R.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S., Graphene-based polymer nanocomposites. *Polymer* **2011,** 52, (1), 5-25.

6. Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S., Graphene based materials: Past, present and future. *Progress in Materials Science* **2011,** 56, (8), 1178-1271.

7. Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C., Graphene Photonics and Optoelectronics. *Nature Photonics* **2010,** 4, 611-622.

8. Chiacchiarelli, L. M.; Rallini, M.; Monti, M.; Puglia, D.; Kenny, J. M.; Torre, L., The role of irreversible and reversible phenomena in the piezoresistive behavior of graphene epoxy nanocomposites applied to structural health monitoring. *Composites Science and Technology* **2013,** 80, 73-79.

9. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O., Synthesis of nylon 6-clay hybrid. *Journal of Materials Research* **1993,** 8, (5), 1179-84.

10. Geim, A. K., Graphene: status and prospects. *arXiv.org, e-Print Archive, Condensed Matter* **2009**, 1-8, arXiv:0906 3799v1 [cond-mat mes-hall].

11. Rao, C. N. R.; Sood, A. K.; Voggu, R.; Subrahmanyam, K. S., Some Novel Attributes of Graphene. *Journal of Physical Chemistry Letters* **2010,** 1, (2), 572-580.

12. Allen, M. J.; Tung, V. C.; Kaner, R. B., Honeycomb Carbon: A Review of Graphene. *Chemical Reviews (Washington, DC, United States)* **2010,** 110, (1), 132-145.

13. Sun, X.; Sun, H.; Li, H.; Peng, H., Developing Polymer Composite Materials: Carbon Nanotubes or Graphene? *Advanced Materials (Weinheim, Germany)* **2013,** 25, (37), 5153-5176.

14. Geim, A. K.; Novoselov, K. S., The Rise of Graphene. *Nat. Mater.* **2007,** 6, 183-191.

15. Bianco, A.; Cheng, H.-M.; Enoki, T.; Gogotsi, Y.; Hurt, R. H.; Koratkar, N.; Kyotani, T.; Monthioux, M.; Park, C. R.; Tascon, J. M. D.; Zhang, J., All in the graphene family â€“ A recommended nomenclature for two-dimensional carbon materials. *Carbon* **2013,** 65, (0), 1-6.

16. Jing LI, P. C. M., Chow Wing SZE, To Chi KAI, Ben Zhong TANG, Jang-Kyo KIM, Percolation threshold of polymer nanocomposites containing graphite nanoplatelets and carbon nanotubes. In *16th International Conference on Composite Materials*.

17. Qi, X.-Y.; Yan, D.; Jiang, Z.-G.; Cao, Y.-K.; Yu, Z.-Z.; Yavari, F.; Koratkar, N., Enhanced Electrical Conductivity in Polystyrene Nanocomposites at Ultra-Low Graphene Content. *ACS Applied Materials & Interfaces* **2011,** 3, (8), 3130-3133.

18. Evora, V. M. F.; Shukla, A., Fabrication, Characterization, and Dynamic Behavior of Polyester/TiO2 Nanocomposites. *Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing* **2003,** A361, 358-366.

19. Tang, L.-C.; Wan, Y.-J.; Yan, D.; Pei, Y.-B.; Zhao, L.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q., The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* **2013,** 60, 16-27.

CHAPTER 2

Massive Electrical Conductivity Enhancement of Multilayer Graphene/ Polystyrene Composites Using a Non-Conductive Filler

published in ACS Applied Materials and Interfaces, 2014, 6, 16472-16475

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2. 1 Abstract:

Graphene is as an attractive filler material for polymers because of its excellent electrical, mechanical and thermal properties. In this paper, we report a massive increase in the electrical conductivity of a multilayer graphene (MLG)/polystyrene composite following the addition of <u>non-conducting</u> silica particles. The non-conducting filler acts as a highly effective dispersion aid, preventing the sheet-like MLG from restacking or agglomerating during the solvent casting process used to fabricate the composite. The enhanced dispersion of the MLG leads to orders of magnitude enhancement in electrical conductivity compared to samples without this filler.

2.2 Introduction:

Defect-free single layer graphene sheets consist of single-atom-thick ,sp^2-bonded, hexagonally arranged carbon atoms. They display remarkable properties including exceptional in-plane electrical and thermal conductivity, high stiffness and tensile strength, optical transparency, negligible permeability to gases, and van der Waals transparency.[1-8] The scientific and commercial interest in graphene is not restricted to the pristine monolayer, but includes related 2D materials that include few-layer graphene (FLG), multilayer graphene (MLG) and chemically modified forms such as graphene oxide (GO).[2] The essentially 2-dimensional nature of these materials along with their excellent properties makes them important as fillers, imparting useful functionalities into matrices. Polymers that display high conductivity have a variety of uses ranging from bulk applications such as anti-static mats and fuel lines,[9-15] to specialty applications such as radiation shields, sensors and electrodes for batteries.[16-

[24] While single layer graphene remains expensive and best suited for high-value applications in electronic devices, opto-electronics, and supercapacitors,[1, 25] the much lower cost MLG is a more promising material for applications that seek to impart electrical conductivity to polymers. Therefore, we target MLG/polymer composites in an effort to provide electrical conductivity to the insulating polymer. In this paper, we report an unexpected result, where we observe a massive enhancement in the electrical conductivity of a MLG/polystyrene composite upon the addition of a second, non-conducting filler.

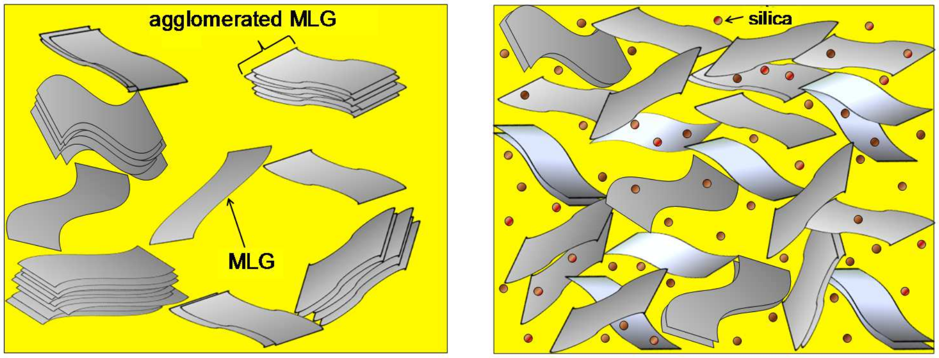
To achieve practical levels of electrical conductivity in an insulating material, a conducting filler must be loaded to a volume fraction beyond the percolation threshold.[16, 17] MLG are two-dimensional structures, which if allowed to rotate freely in a matrix, sweep a 'volume' that is a sphere of diameter corresponding to the lateral dimensions of the MLG, giving a theoretical volume loading at percolation that is well below that of spheres.[17] If MLG are modeled as ideally dispersed and randomly rotated disks of aspect ratio AR (AR = disk diameter/thickness), the percolation threshold ϕ_c is given by[26]

$$\phi_c = 1.5\ (\phi_{sphere}/AR). \qquad (1)$$

In Equation (1), ϕ_{sphere} is the percolation threshold for spheres, i.e., $\phi_{sphere} = 0.29$ ($\phi_{sphere} = 0.29$ is for monodispersed spheres; that number is lower if there is polydispersity, but remains of the same order of magnitude). Since AR can take on values of the order of 10^4 for MLG, the advantage of using these high aspect ratio conducting particles in lowering the volume loading at percolation becomes apparent.

Providing such a low loading at percolation also has a significant benefit for mechanical properties, particularly under impact conditions, as filler materials can act as nucleation sites for crack growth.[27-29]

While the volume loading at percolation is small for sheet like materials, van der Waals attraction between these sheets causes rapid agglomeration, degrades dispersion, and enhances restacking. The restacking reduces the aspect ratio and typically prevents achieving the performance predicted by Equation (1). Thus dispersing these high aspect ratio sheets in a polymer remains a major challenge. We hypothesized that the addition of a second filler could overcome this issue, because this filler would act as spacers and prevent agglomeration of MLG during processing. In addition, if the second fillers were dispersed homogeneously throughout the polymer, they would guide the sheet-like MLG into a more random orientation in the polymer, enhancing the probability of MLG percolation at low loadings as shown in **figure 1**.



MLG+PS: low conductivity

silica + MLG+PS: high conductivity

Figure 1. Schematic showing the improved dispersion MLG using silica particles as dispersion aids.

2. 3 Materials:

MLG are purchased from XG Sciences, USA. The lateral dimension of these nanoplatelets is 25µm and thickness is approximately 6nm. 200nm silica nanoparticles are purchased from Nyacol, USA. Polystyrene (MW 121,000) pellets are purchased from Styrolution, USA.

2. 4 Fabrication of Composites:

7g of the polystyrene pellets are dissolved in 42ml of N,N- dimethylformamide (DMF) and the solution is stirred magnetically for 12 hours.[30] The silica particles are then added and the mixture sonicated for 1.5 hrs. MLG at a concentration of 0.001gm/ml are dispersed in DMF and sonicated for 1.5hrs. Both particle-containing suspensions are then mixed in a 1:1 ratio and magnetically stirred for 2hrs. This mixed suspension is then poured into methanol, an antisolvent for PS. The PS precipitates rapidly, creating the composite. The excess methanol is withdrawn, and the composite is dried in an oven for 18 hr at 90ºC. The sample is then hot pressed at 120ºC to get rid of all entrapped air bubbles, and to create a sample with a disk-like shape that is amenable for electrical conductivity measurements. All reported loadings are based upon the volume percent in the final composite.

2.5 Characterization and Electrical Conductivity Measurement Technique:

The surfaces of specimens are coated with silver paint to reduce contact resistance. A standard two-point probe using a constant current source (Keithley Instruments Model 6221) is used to obtain bulk volumetric electrical conductivity. The voltage drop across the specimen is recorded, and the resistance of the sample calculated from this measurement. This is normalized with the dimensions of the sample to produce the electrical conductivity. The surface morphology of the composites is observed using scanning electron microscopy (Zeiss SIGMA VP FE-SEM) in backscatter mode. A Rigaku Ultima IV diffractometer with Cu Kα radiation is used for the X-ray diffraction (XRD) measurements.

2. 6 Results and Discussions:

We added 200nm diameter spherical silica particles to MLG-containing polystyrene, and show results for 2.5 vol% loading of MLG in **Figure 2**. The electrical conductivity of MLG-silica-polystyrene composites increases by several orders of magnitude as the loading of the non-conductive silica is increased. We rationalize this surprising observation by imaging the samples at various silica concentrations using scanning electron microscopy, and complementing those results with X-ray diffraction.

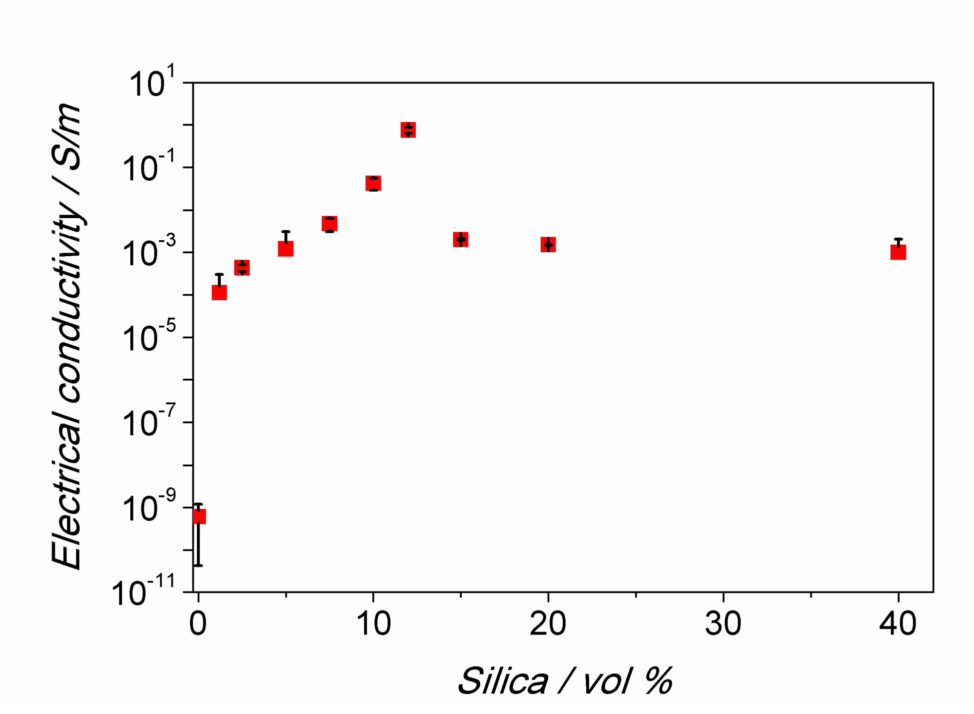


Figure 2. Electrical conductivity of MLG-silica-polystyrene composites at 2.5 vol% MLG. The conductivity increases by several orders of magnitude as 200nm silica particles are added.

Figure 3(a) is a back-scattered SEM image of the sample with no silica. The MLG are agglomerated rather than well dispersed in the polystyrene (PS), and the conductivity is 10^{-9} S/m. At 2.5 vol% silica, the conductivity of the composite rises dramatically to 10^{-4} S/m. **Figure 3(b)** shows better dispersion of the MLG at this silica concentration.. As the silica loading is increased to 12 vol%, the conductivity rises further to 1S/m, and the MLG are dispersed more uniformly throughout the sample (**Figure 3(c)**). Beyond 12 vol% silica, there is a decrease in electrical conductivity of the composite, which is then nearly constant over the remaining range of feasible silica loadings. The excessive silica particles at these concentrations starts to break the connectivity of the MLG network, as seen in **Figure 3(d)** at 20 vol% silica.

We measure the full width at half maximum of the graphite (0 0 2) diffraction peaks (**Figure 3(e)**), and use Scherrer's analysis to determine an average 'crystallite' size for the MLG as an indicator of restacking (**Figure 3(f))**. The average crystallite size decreases as the silica loading goes to 12 vol%, and then rises again. This indicates a suppression of restacking and also suggests improved dispersion of the MLG at concentrations up to 12 vol% silica, followed by increased MLG agglomeration as the silica content is increased further.

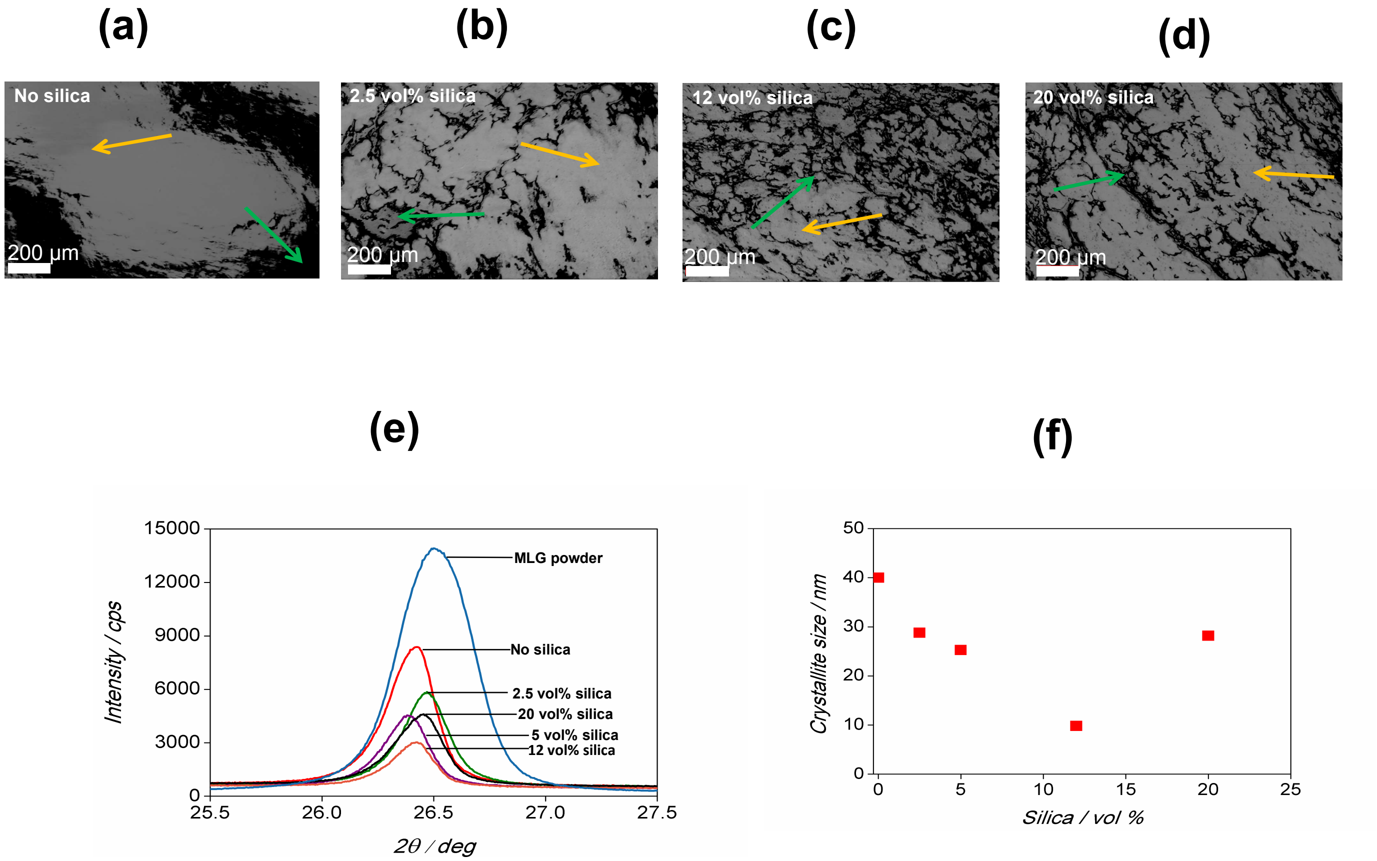


Figure 3. Backscattered SEM images showing the distribution of graphene in polystyrene matrix.(a) 0 vol % silica. The dark regions show agglomerated MLG sheets. (b) 2.5 vol% silica. The MLG dispersion is improved. (c) 12 vol% silica. The dispersion of MLG is improved over cases (a) and (b). (d) 20 vol% silica. The dispersion of MLG deteriorates because of the presence of excess non-conducting silica. Yellow arrows - polystyrene, green arrows - MLG. The silica particles are not visible at this magnification. Scale bars are 200□m. (e) XRD plots around the graphite peaks for all samples. (f) Average crystal dimension of MLG agglomerates obtained using Scherrer's equation. The crystal dimension decreases as silica is added, indicating improved dispersion and reduced restacking of MLG during processing. At silica loading above 12 vol%, the crystal dimension increases again, indicating enhanced agglomeration or restacking.

We use 10^{-6} S/m as a threshold value for determining if a sample is conducting, and summarize our data for a range of MLG and silica loadings in **Figure 4**. We show that adding a non-conducting (silica) filler can initiate conductivity in an otherwise non-conducting MLG/PS composite.

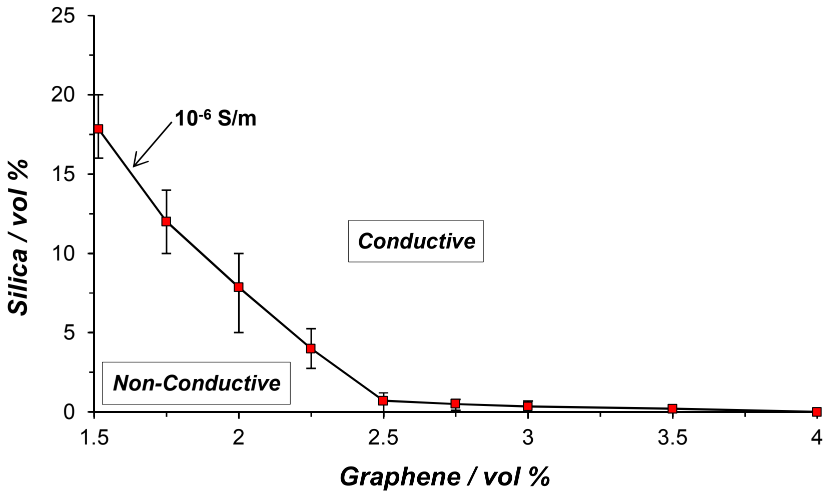


Figure 4. Partition between non-conductive and conductive regions of the MLG-silica–PS ternary composites at different loadings of MLG and silica nanoparticles. The data marks a (arbitrary) transition point from non-conductive to conductive at 10^{-6}S/m, and the line is drawn to guide the eye.

2.7 Conclusions:

We see that addition of a non-conductive filler can significantly reduce the loading of MLG required for percolation. While we have used 200nm silica particles as dispersion aids in this work, we recognize that there is a range of materials, morphologies and sizes of fillers that can be exploited to impart desirable properties to a composite. Optimization of this novel second-filler concept will be the subject of future work.

2.8 Acknowledgements:

This work was supported by a grant from the Rhode Island Science and Technology Advisory Council.

2.9 References:

1. Geim, A. K., Graphene: Status and Prospects. *Science (Washington, DC, United States)* **2009,** *324*, 1530-1534.

2. Bianco, A.; Cheng, H.-M.; Enoki, T.; Gogotsi, Y.; Hurt, R. H.; Koratkar, N.; Kyotani, T.; Monthioux, M.; Park, C. R.; Tascon, J. M. D.; Zhang, J., All in the Graphene Family-A Recommended Nomenclature for Two-Dimensional Carbon Materials. *Carbon* **2013,** *65*, 1-6.

3. Rao, C. N. R.; Sood, A. K.; Voggu, R.; Subrahmanyam, K. S., Some Novel Attributes of Graphene. *J. Phys. Chem. Lett.* **2010,** *1*, 572-580.

4. Allen, M. J.; Tung, V. C.; Kaner, R. B., Honeycomb Carbon: A Review of Graphene. *Chem. Rev. (Washington, DC, U. S.)* **2010,** *110*, 132-145.

5. Geim, A. K.; Novoselov, K. S., The Rise of Graphene. *Nat. Mater.* **2007,** *6*, 183-191.

6. Soldano, C.; Mahmood, A.; Dujardin, E., Production, Properties and Potential of Graphene. *Carbon* **2010,** *48*, 2127-2150.

7. Choi, W.; Lahiri, I.; Seelaboyina, R.; Kang, Y. S., Synthesis of Graphene and its Applications: a Review. *Crit. Rev. Solid State Mater. Sci.* **2010,** *35*, 52-71.

8. Compton, O. C.; Nguyen, S. T., Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials. *Small* **2010,** *6*, 711-723.

9. Kim, H.; Miura, Y.; Macosko, C. W., Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity. *Chem. Mater.* **2010,** *22*, 3441-3450.

10. Huang, X.; Qi, X.; Boey, F.; Zhang, H., Graphene-Based Composites. *Chem. Soc. Rev.* **2012,** *41*, 666-686.

11. Cai, D.-Y.; Song, M., Recent Advance in Functionalized Graphene/Polymer Nanocomposites. *J. Mater. Chem.* **2010,** *20*, 7906-7915.

12. Du, J.; Cheng, H.-M., The Fabrication, Properties, and Uses of Graphene/Polymer Composites. *Macromol. Chem. Phys.* **2012,** *213*, 1060-1077.

13. Vadukumpully, S.; Paul, J.; Mahanta, N.; Valiyaveettil, S., Flexible Conductive Graphene/Poly(vinyl chloride) Composite Thin Films with High Mechanical Strength and Thermal Stability. *Carbon* **2011,** *49*, 198-205.

14. Terrones, M.; Martin, O.; Gonzalez, M.; Pozuelo, J.; Serrano, B.; Cabanelas, J. C.; Vega-Diaz, S. M.; Baselga, J., Interphases in Graphene Polymer-Based Nanocomposites: Achievements and Challenges. *Adv. Mater. (Weinheim, Ger.)* **2011,** *23*, 5302-5310.

15. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-Based Composite Materials. *Nature (London, U. K.)* **2006,** *442*, 282-286.

16. Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A., Graphene Filled Polymer Nanocomposites. *J. Mater. Chem.* **2011,** *21*, 3301-3310.

17. Jing LI, P. C. M., Chow Wing SZE, To Chi KAI, Ben Zhong TANG, Jang-Kyo KIM, Percolation Threshold of Polymer Nanocomposites Containing Graphite Nanoplatelets and Carbon Nanotubes. In *16th International Conference on Composite Materials*, **2007**.

18. Liang, J.; Wang, Y.; Huang, Y.; Ma, Y.; Liu, Z.; Cai, J.; Zhang, C.; Gao, H.; Chen, Y., Electromagnetic Interference Shielding of Graphene/Epoxy Composites. *Carbon* **2009,** *47*, 922-925.

19. Zhu, X.; Zhu, Y.; Murali, S.; Stoller, M. D.; Ruoff, R. S., Nanostructured Reduced Graphene Oxide/Fe2O3 Composite As a High-Performance Anode Material for Lithium Ion Batteries. *ACS Nano* **2011,** *5*, 3333-3338.

20. Song, Z.; Xu, T.; Gordin, M. L.; Jiang, Y.-B.; Bae, I.-T.; Xiao, Q.; Zhan, H.; Liu, J.; Wang, D., Polymer-Graphene Nanocomposites as Ultrafast-Charge and -Discharge Cathodes for Rechargeable Lithium Batteries. *Nano Lett.* **2012,** *12*, 2205-2211.

21. Yang, N.; Zhai, J.; Wang, D.; Chen, Y.; Jiang, L., Two-Dimensional Graphene Bridges Enhanced Photoinduced Charge Transport in Dye-Sensitized Solar Cells. *ACS Nano* **2010,** *4*, 887-894.

22. Jang, B. Z.; Zhamu, A., Processing of Nanographene Platelets (NGPs) and NGP Nanocomposites: a Review. *J. Mater. Sci.* **2008,** *43*, 5092-5101.

23. Wang, X.; Zhi, L.; Muellen, K., Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells. *Nano Lett.* **2008,** *8*, 323-327.

24. Ramanathan, T.; Abdala, A. A.; Stankovich, S.; Dikin, D. A.; Herrera-Alonso, M.; Piner, R. D.; Adamson, D. H.; Schniepp, H. C.; Chen, X.; Ruoff, R. S.; Nguyen, S. T.; Aksay, I. A.; Prud'Homme, R. K.; Brinson, L. C., Functionalized Graphene Sheets for Polymer Nanocomposites. *Nat. Nanotechnol.* **2008,** *3*, 327-331.

25. Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C., Graphene Photonics and Optoelectronics. *Nat. Photonics* **2010,** *4*, 611-622.

26. Kim, H., Abdala, A.A., Macosko, C.W., Graphene/polymer nanocomposites. *Macromolecules* **2010,** *43*, 6515-6530.

27. Rafiee, M. A.; Rafiee, J.; Wang, Z.; Song, H.; Yu, Z.-Z.; Koratkar, N., Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content. *ACS Nano* **2009,** *3*, 3884-3890.

28. Evora, V. M. F.; Shukla, A., Fabrication, Characterization, and Dynamic Behavior of Polyester/TiO2 Nanocomposites. *Mater. Sci. Eng., A* **2003,** *A361*, 358-366.

29. Rafiee, M. A.; Rafiee, J.; Srivastava, I.; Wang, Z.; Song, H.; Yu, Z.-Z.; Koratkar, N., Fracture and Fatigue in Graphene Nanocomposites. *Small* **2010,** *6*, 179-183.

30. Qi, X.-Y.; Yan, D.; Jiang, Z.-G.; Cao, Y.-K.; Yu, Z.-Z.; Yavari, F.; Koratkar, N., Enhanced Electrical Conductivity in Polystyrene Nanocomposites at Ultra-Low Graphene Content. *ACS Appl. Mater. Interfaces* **2011,** *3*, 3130-3133.

CHAPTER 3

Multifunctional Graphene based Polymer Composite Materials Using Rubber Particles as Toughening Agent

In preparation for Langmuir

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3.1 Abstract:

We fabricate multi-functional polymer composite materials with graphene nanoplatelets (GNP),core-shell rubber particles and silica nanoparticles. The shell structures of rubber particles lead to enhanced dispersion in the matrix which results in improved electrical and mechanical properties of the composites. Rubber particles can induce percolation in the system at lower loading compared to silica particles. We also study the quasi-static compression test and three-point flexural test in order to compare the mechanical properties of the composites comprising rubber and silica particles. We find that rubber particles can increase the toughness of the composites preventing the mechanical failure of the samples. Also the flexural strength of the composites filled with rubber gets improved compared to samples with silica in them.

3.2 Introduction:

Graphene Nanoplatelets (GNP) have attracted the attention of many researchers due to its exceptional electrical, thermal , mechanical and barrier properties[1-3]. GNP is considered to be one of the most widely used filler materials in the polymser composites for various applications ranging from antistatic plastic materials, electrode for batteries, electromagnetic interference (EMI) shielding materials, field effect transistors (FET), solar cells, photovoltaics to various weight-sensitive aerospace and automotive applications[4-10]. Multiple fillers are usually incorporated to impart desired electrical/ mechanical properties on the finished products. These fillers are carefully selected based on the desired performance target. The final properties of the composites are highly dependent on the type of filler selected, polymer-filler interactions and processing conditions. One of the biggest challenge of working with

GNP is that they always tend to get agglomerated due to favorable van der Waals interactions. So keeping them dispersed in the matrix remains major challenge in the field of fabrication of composites. In our previous work, we have successfully shown that incorporating a second filler in the polymer matrix is always beneficial in terms of dispersing GNP in the matrix[11]. The second filler can act as dispersion aid and prevent the restacking of GNP sheets. The electrical conductivity increases remarkably on the addition of second, non-conductive filler because of well connected GNP network throughout the matrix. But there is always a trade-off between good electrical and mechanical property of the composites depending on the type of filler used in the system[12-27]. We have already shown good electrical property with silica particles as dispersion aid. But silica deteriorates the mechanical property of the composites significantly making them extremely brittle. Also poor interaction between silica and polystyrene matrix limits its scope as a filler to fabricate multi-functional polymer composite materials. To overcome this issue, we use core-shell rubber particles as second filler in order to substitute silica. The main goal of this work is to fabricate multi-functional polymer composite materials comprising significant electrical and mechanical properties so that having second filler as dispersion aid does not allow to compromise the mechanical properties of the composites. In this work, we use core-shell rubber particles dispersed in the matrix. The rubber particles gets dispersed uniformly in the matrix due to the shell structures surrounding them which prevent the fusion of rubber particles together. As shown in figure 1,we find that rubber particles act more efficiently in keeping the GNP dispersed in the matrix which results in increasing the electrical conductivity of the composites at very low content of GNP and rubber particles.

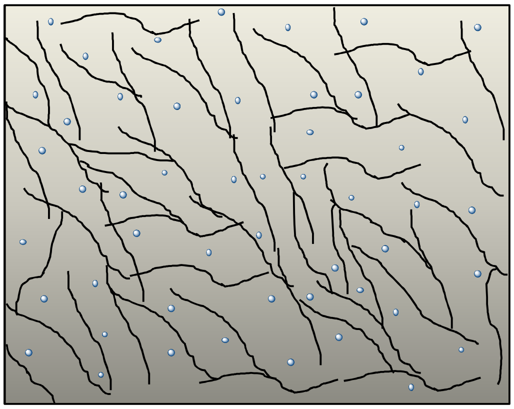


Figure 1. Schematic showing graphene nanoplatelets are uniformly dispersed in the matrix using rubber spheres as dispersion aid.

At the same time, these composites are mechanically tougher due to their ductility, preventing the mechanical failure/fracture of the samples under the quasi-static loading condition. Rubber particles act as toughening agents to increase the toughness of the composites. We perform quasi-static compression test and three-point flexural test and compare the maximum compressive strength and flexural strength of the composites comprising silica and rubber particles. Enhanced compatibility between rubber particles and polystyrene matrix plays a significant role on the electrical as well as mechanical properties of the composites. These multi-functional composite materials create a platform of opportunities for enormous applications.

3.3 Materials:

GNP are purchased from XG Sciences, USA. The lateral dimension of these nanoplatelets is 25 μm and thickness is approximately 6 nm. 200 nm silica nanoparticles are purchased from Nyacol, USA. Core-shell rubber particles are obtained from Dow Chemical. The core is composed of polybutadiene and shell is made of methylmethacrylate/styrene/ acrylate. The size of the rubber particles is 200nm with a shell thickness of 4nm. Polystyrene (MW 121,000) pellets are purchased from Styrolution, USA. N,N-dimethylformamide (DMF) and methanol are purchased from Fisher Scientific, USA.

3.4 Fabrication of Composites:

7 g of the polystyrene pellets are dissolved in 42 ml of N,N- dimethylformamide (DMF) and the solution is stirred magnetically for 12 hours[28]. The rubber/silica particles are then added and the mixture is sonicated for 1.5 hours. GNP at a concentration of 0.001 gm/ml are dispersed in DMF and sonicated for 1.5 hours. Both particle-containing suspensions are then mixed in a 1:1 ratio and magnetically stirred for 2 hours. This mixed suspension is then poured into methanol, an antisolvent for PS. The PS precipitates rapidly, creating the composite. The excess methanol is withdrawn, and the composite is dried in an oven for 18 hours at 90ºC. The sample is then hot pressed at 120ºC to get rid of all entrapped air bubbles, and to create a sample with a disk-like shape that is amenable for electrical conductivity measurements. All reported loadings are based upon the volume percent in the final composite. The surfaces of specimens are coated with silver paint to reduce contact resistance.

3.5 Characterization and Electrical Conductivity and Mechanical Properties Measurement:

A standard two-point probe using a constant current source (Keithley Instruments Model 6221) is used to obtain bulk volumetric electrical conductivity. The voltage drop across the specimen is recorded, and the resistance of the sample calculated from this measurement. This is normalized with the dimensions of the sample to produce the electrical conductivity. The compressive strength of the samples are measured using Instron Universal Testing Machine of Model 5585. Six cylindrical samples are made for each composition. The flexural strength of the composites are measured using Instron Universal Testing Machine .The surface morphology of the composites is observed using scanning electron microscopy (Zeiss SIGMA VP FE-SEM).

3.6 Results and Discussions:

Core-shell rubber particles induce percolation in the matrix by maintaining a well connected network of GNP. Figure 2(a) and (b) show TEM images of rubber particles and silica particles respectively.

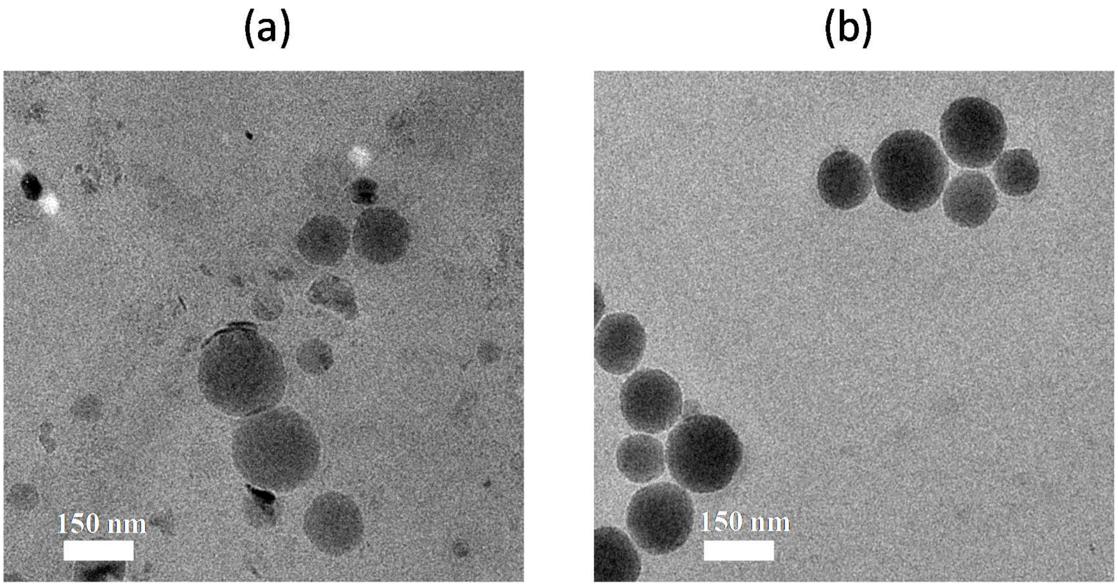


Figure 2: TEM images of (a) rubber and (b) silica particles.

In the Figure 3, we can see that rubber particles are very effective as dispersion aids which can significantly lower down the percolation threshold of GNP-rubber-polystyrene composites. Even very small amount of rubber particles can trigger the percolation using only at 1.5 vol% GNP. So it is very much evident from the figure that rubber particles are more efficient in keeping GNP dispersed uniformly compared to silica particles. This is due to the fact that having a shell structures surrounding the rubber particles which are more compatible with the matrix results in enhanced dispersion of rubber particles compared to those silica particles.

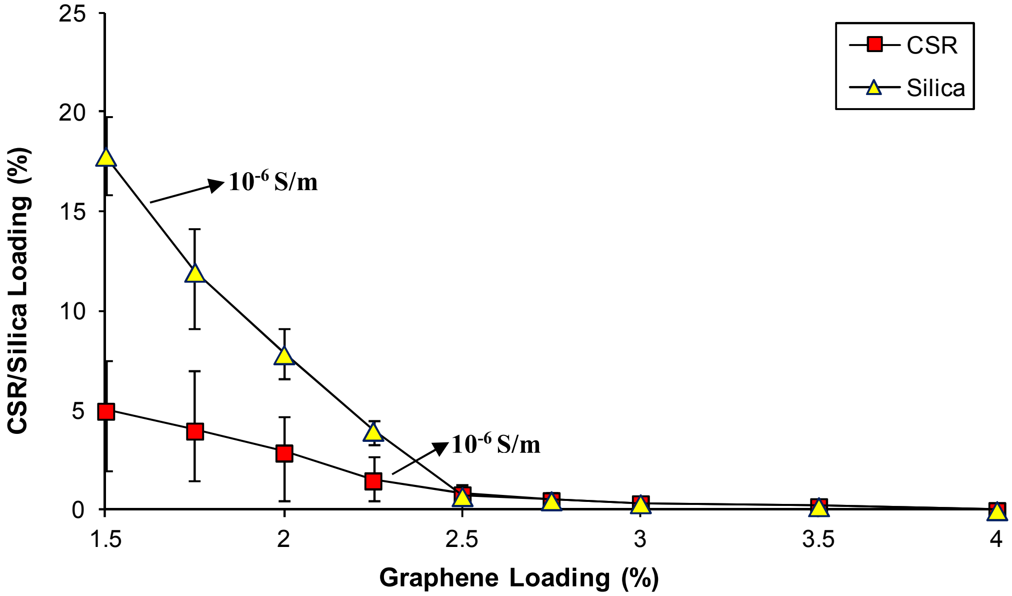


Figure 3. The electrical conductivities of GNP/rubber/polystyrene and GNP/silica/polystyrene composites. The rubber particles induce percolation at much lower loading compared to the samples with silica. The data marks a (arbitrary) transition point from non-conductive to conductive at 10^{-6}S/m, and the line is drawn to guide the eye.

Figure 4 (a) shows an SEM image of rubber particles in the matrix and 4 (b) shows the agglomeration of silica particles which demonstrate the better dispersion of rubber particles in the matrix. This explains a lot about the improved electrical conductivity of the composites at lower loading of rubber particles.

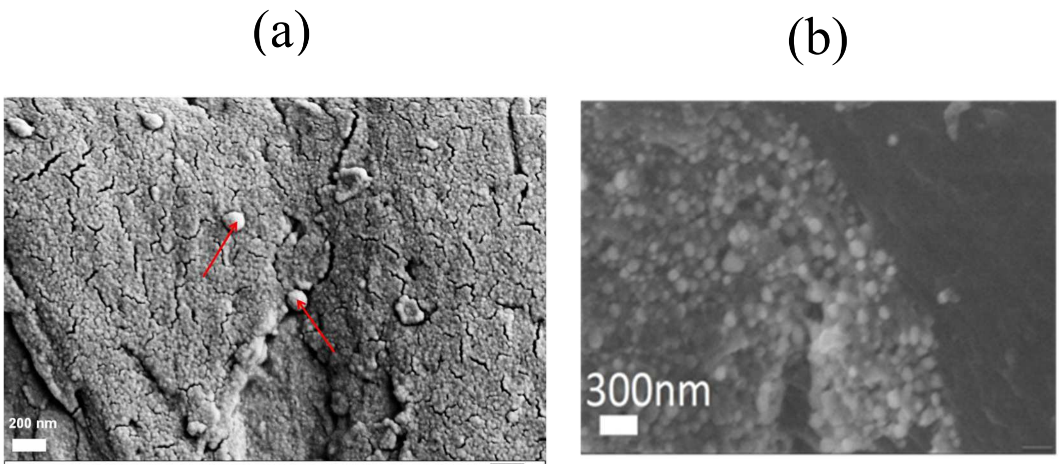


Figure 4: (a) SEM image shows the dispersion of rubber particles in the polystyrene matrix. (b) SEM image shows the agglomeration of silica particles in the matrix. The content of both particles is 20 vol%. Clearly the enhanced dispersion of rubber particles leads to improved properties of the composites.

X-ray diffraction (XRD) analysis is done on rubber-GNP-polystyrene composites. Figure 5 shows the diffraction peaks of the composites at different loading of rubber particles. By using Scherrer's equation, the size of the crystallites are calculated and it has been found that the crystallite size decrease with increasing rubber content in the composites which confirms the better dispersion of GNP sheets in the matrix. Another important insight of the study is that the size of the crystallites with 5 vol% rubber filler is smaller compared to the samples containing same amount of silica. So lesser amount of rubber particles can induce percolation in the composites with better dispersion of GNP sheets in comparison to the silica particles where more amount of silica needs to be incorporated in order to achieve percolation.

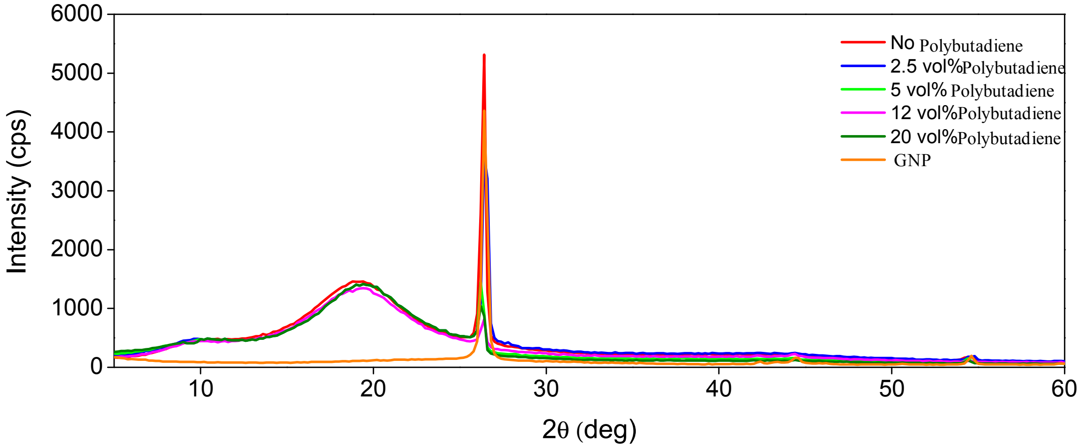
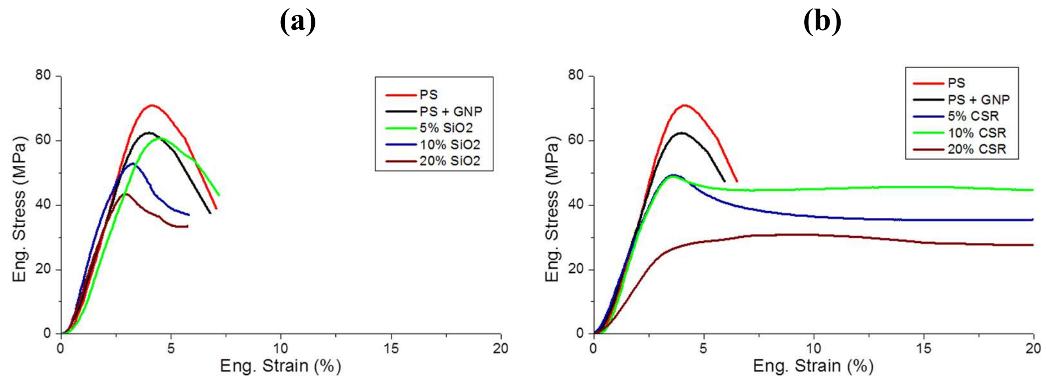


Figure 5. The X-Ray Diffraction peaks of rubber/GNP/ Polystyrene composites with different content of rubber.

We study quasi-static compression stress-strain behavior of GNP-rubber/silica-polystyrene composites under static compression loading. Figure 6 shows the stress-strain behavior of GNP-silica/rubber-polystyrene composites. In figure 6(a), composites with varying loading of silica particles fail under compression. Also the maximum strengths of the composites decrease gradually with the increase in the amount of silica loading. Incorporating a filler such as GNP alone or GNP along with the different silica loading deteriorate the capability of maximum compressive strength of a composite before it fails compared to the pristine polystyrene. In figure 6 (b), GNP-rubber-polystyrene composites with different loading of rubber particles do not fail under the compressive loading. Also the maximum compressive strength of the composites with rubber decreases compared to the composites with silica particles. This behavior is expected as the ductile materials can be compressed more in comparison with brittle materials. So there is a loss in maximum compressive strength in case of rubber filler. But on the other hand, composites with rubber filler get deformed without any mechanical failure under compressive loading. By substituting silica particles with rubber particles increases the toughness of the composites significantly. Silica particles make the composites extremely brittle as a result of which mechanical failure is observed for all samples containing silica.


(a)

(b)

Figure 6. (a) The stress-strain curves of GNP/ silica/polystyrene composites with different loading of silica particles. All the samples fail under quasi-static compression loading. (b) The stress-strain curves of GNP/rubber/polystyrene composites with different loading of rubber. The toughness of the composites increases significantly with rubber in them preventing the mechanical failure of the samples.

We also perform three-point flexural test on the composites with silica and rubber particles along with GNP. We see in figure 7 that the flexural strength of the composites with rubber filler is lower at lower content of the second filler (till 10 vol%) compared to the composites with silica. But at higher content of second filler, the flexural strength of rubber composites increases remarkably compared to the silica containing composites. This is due to the fact that at higher content, silica particles get agglomerated in the matrix which results in lowering the flexural strength under static loading. Agglomerated silica particles can act as nucleation sites for crack initiation

But having compatible shell structures surrounding the rubber particles help in improved dispersion in the matrix which increases the flexural strength.

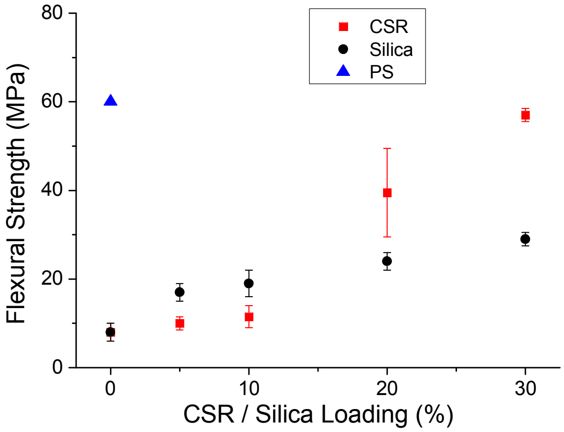


Figure 7. The flexural strength of the composites is shown with silica and rubber in them using three-point flexural test. The flexural strength of the composites filled with rubber increases several orders in magnitude compared to the samples with silica in them.

The agglomeration of the filler in the matrix can deteriorate the mechanical property as we can see here. The inherent flexural strength of the polystyrene can be restored efficiently with the addition of rubber particles. This is the most promising result in terms of fabricating multi-functional polymer composites where they possess good electrical conductivity without compromising the mechanical properties of the matrix. To exploit the best possible inherent properties of the filler, uniform dispersion of the filler is very essential which on the other hand can affect the electrical and mechanical properties significantly[29]. In our study, we see that rubber particles can perform better as filler materials due to better interaction of shell structures of rubber particles with the polystyrene matrix. For electrical property of the composites, lesser amount of rubber particle is necessary to induce percolation in the system compared to the silica particles. Also the flexural strength of the composites increases with rubber fillers due to better compatibility between the shell structure and the polystyrene matrix which leads to the improved dispersion of the second filler in the system. Under static compressive loading, the composites with rubber filler do not break which results in enhanced toughness of the composites. So the properties of the composites are very easily tunable by selecting appropriate filler depending on the final applications.

3.7 Conclusion:

We see that incorporating appropriate filler materials into the polymer matrix enables us to fabricate composites with desirable functionalities. While having silica particles along with GNP induces percolation in the system, it makes the composites extremely brittle. Rubber particles on the other hand, increase the toughness and flexural strength of the composites along with pertaining electrical conductivity in the system. Dispersion of the second filler plays a key role in controlling the properties of the final composites. Rubber particles get dispersed more uniformly in the matrix due to the good compatibility of the rubber particles and polystyrene leading to develop composites with enhanced electrical and mechanical properties.

3.8 Acknowledgements:

I would like to thank department of chemical engineering, University of Rhode Island for supporting my work. We thank Dr. Arun Shukla for several insightful discussions.

3. 9 References:

1. Geim, A. K., Graphene: Status and Prospects. *Science (Washington, DC, United States)* **2009,** 324, 1530-1534.

2. Geim, A. K.; Novoselov, K. S., The Rise of Graphene. *Nat. Mater.* **2007,** 6, 183-191.

3. Rao, C. N. R.; Sood, A. K.; Voggu, R.; Subrahmanyam, K. S., Some Novel Attributes of Graphene. *Journal of Physical Chemistry Letters* **2010,** 1, (2), 572-580.

4. Kim, H.; Abdala, A.; Macosko, C. W., Graphene/Polymer Nanocomposites. *Macromolecules (Washington, DC, United States)* **2010,** 43, 6515-6530.

5. Kuilla, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H., Recent advances in graphene based polymer composites. *Progress in Polymer Science* **2010,** 35, (11), 1350-1375.

6. Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A., Graphene Filled Polymer Nanocomposites. *Journal of Materials Chemistry* **2011,** 21, 3301-3310.

7. Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S., Graphene based materials: Past, present and future. *Progress in Materials Science* **2011,** 56, (8), 1178-1271.

8. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-based composite materials. *Nature (London, United Kingdom)* **2006,** 442, (7100), 282-286.

9. Potts, J. R.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S., Graphene-based polymer nanocomposites. *Polymer* **2011,** 52, (1), 5-25.

10. Wang, Z. P.; Nelson, J. K.; Miao, J. J.; Linhardt, R. J.; Schadler, L. S.; Hillborg, H.; Zhao, S., Effect of High Aspect Ratio Filler on Dielectric Properties of Polymer Composites: A Study on Barium Titanate Fibers and Graphene Platelets. *Ieee Transactions on Dielectrics and Electrical Insulation* **2012,** 19, (3), 960-967.

11. Chakraborty, I.; Bodurtha, K. J.; Heeder, N. J.; Godfrin, M. P.; Tripathi, A.; Hurt, R. H.; Shukla, A.; Bose, A., Massive Electrical Conductivity Enhancement of Multilayer Graphene/Polystyrene Composites Using a Nonconductive Filler. *ACS Applied Materials & Interfaces* **2014,** 6, (19), 16472-16475.

12. Rafiee, M. A.; Rafiee, J.; Wang, Z.; Song, H.; Yu, Z.-Z.; Koratkar, N., Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content. *ACS Nano* **2009,** 3, 3884-3890.

13. Zaeri, M. M.; Ziaei-Rad, S.; Vahedi, A.; Karimzadeh, F., Mechanical modelling of carbon nanomaterials from nanotubes to buckypaper. *Carbon* **2010,** 48, (13), 3916-3930.

14. Rahman, R., The role of graphene in enhancing the stiffness of polymeric material: A molecular modeling approach. *Journal of Applied Physics* **2013,** 113, (24).

15. Martin-Gallego, M.; Bernal, M. M.; Hernandez, M.; Verdejo, R.; Lopez-Manchado, M. A., Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites. *European Polymer Journal* **2013,** 49, (6), 1347-1353.

16. Li, W. K.; Dichiara, A.; Bai, J. B., Carbon nanotube-graphene nanoplatelet hybrids as high-performance multifunctional reinforcements in epoxy composites. *Composites Science and Technology* **2013,** 74, 221-227.

17. Kuvardina, E. V.; Novokshonova, L. A.; Lomakin, S. M.; Timan, S. A.; Tchmutin, I. A., Effect of the graphite nanoplatelet size on the mechanical, thermal, and electrical properties of polypropylene/exfoliated graphite nanocomposites. *Journal of Applied Polymer Science* **2013,** 128, (3), 1417-1424.

18. Khan, U.; O'Connor, I.; Gun'ko, Y. K.; Coleman, J. N., The preparation of hybrid films of carbon nanotubes and nano-graphite/graphene with excellent mechanical and electrical properties. *Carbon* **2010,** 48, (10), 2825-2830.

19. Chen, P.; Wang, Y.; Wei, T.; Meng, Z.; Jia, X.; Xi, K., Greatly enhanced mechanical properties and heat distortion resistance of poly(l-lactic acid) upon compositing with functionalized reduced graphene oxide. *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2013,** 1, (32), 9028-9032.

20. Satti, A.; Larpent, P.; Gun'ko, Y., Improvement of mechanical properties of graphene oxide/poly(allylamine) composites by chemical crosslinking. *Carbon* **2010,** 48, (12), 3376-3381.

21. Sengupta, R.; Bhattacharya, M.; Bandyopadhyay, S.; Bhowmick, A. K., A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. *Progress in Polymer Science* **2011,** 36, (5), 638-670.

22. Ruoff, R. S., Graphene-based materials. *Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009* **2009**, PMSE-011.

23. Gouda, P. S. S.; Kulkarni, R.; Kurbet, S. N.; Jawali, D., Effects of multi walled carbon nanotubes and graphene on the mechanical properties of hybrid polymer composites. *Advanced Materials Letters* **2013,** 4, (4), 261-270, 10 pp.

24. Dai, J.; Lang, M., Preparation and mechanical properties of graphene oxide/PMMA and surface-functionalized graphene/PMMA composites. *Huaxue Xuebao* **2012,** 70, (11), 1237-1244.

25. Layek, R. K.; Das, A. K.; Park, M. J.; Kim, N. H.; Lee, J. H., Enhancement of physical, mechanical, and gas barrier properties in noncovalently functionalized graphene oxide/poly(vinylidene fluoride) composites. *Carbon* **2015,** 81, 329-338.

26. Kuila, T.; Khanra, P.; Mishra, A. K.; Kim, N. H.; Lee, J. H., Functionalized-graphene/ethylene vinyl acetate co-polymer composites for improved mechanical and thermal properties. *Polymer Testing* **2012,** 31, (2), 282-289.

27. Yan, N.; Buonocore, G.; Lavorgna, M.; Kaciulis, S.; Balijepalli, S. K.; Zhan, Y.; Xia, H.; Ambrosio, L., The role of reduced graphene oxide on chemical, mechanical and barrier properties of natural rubber composites. *Composites Science and Technology* **2014,** 102, 74-81.

28. Qi, X.-Y.; Yan, D.; Jiang, Z.-G.; Cao, Y.-K.; Yu, Z.-Z.; Yavari, F.; Koratkar, N., Enhanced Electrical Conductivity in Polystyrene Nanocomposites at Ultra-Low Graphene Content. *ACS Applied Materials & Interfaces* **2011,** 3, (8), 3130-3133.

29. Tang, L.-C.; Wan, Y.-J.; Yan, D.; Pei, Y.-B.; Zhao, L.; Li, Y.-B.; Wu, L.-B.; Jiang, J.-X.; Lai, G.-Q., The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites. *Carbon* **2013,** 60, 16-27.

CHAPTER 4

Effectiveness of the Size of the Second Filler on the Electrical Conductivity of Graphene based Polymer Composite Materials

In preparation for Langmuir

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4.1 Abstract:

The size of the second, non-conductive filler plays a significant role in order to enhance the electrical conductivity of the system. Two different sized second fillers are chosen to compare the effectiveness of the particles in increasing the conductivity of the composites. In the work, it has been found that smaller particles can act as better dispersion aids in preventing the restacking of GNP sheets in compared to bigger particles. The distribution of GNP networks is studied using back-scattered scanning electron microscope (SEM) and the orientation of the non-conductive filler along with GNP sheets is analyzed using charge-contrast scanning electron microscope (SEM).

4.2 Introduction:

Graphene nanoplatelets (GNP) are considered to be one of the most widely used filler in the field of fabrication of composite materials[1-4]. Electrically conductive polymer composites have been accepted for numerous applications in a broad range of areas from specialty uses such as electromagnetic interference (EMI) shielding materials, electrodes for batteries,sensors to bulk applications which include anti-static plastic mats, fuel lines[5-17]. Electrically conductive fillers are added into non-conductive matrix to impart conductivity in the system. In order to achieve the conductivity, a minimum amount of conductive filler needs to be present which is called the percolation threshold of the system[18-20]. In our previous work we have shown that incorporating a second, non-conductive filler can induce percolation with improved dispersion of GNP[21]. One of the biggest problem in working with GNP is that they always tend to get agglomerated due to strong van der Waals force. Introducing a second filler can remarkably prevent restacking of GNP sheets resulting in increase in electrical conductivity at lower loading of GNP. Several properties of the second filler such as size, shape, interaction of the filler with the matrix can significantly affect the electrical conductivity of the final composites[22-24]. The effect of the size of the second filler is one of the most interesting area to study. We have used two different sized second fillers in our work which are silica nanoparticles and alumino-silicate ceramic sphere. Silica particles are 200 nm in size whereas the ceramic particles are 12 micron in size. The lateral dimension of GNP is 25 micron. Two fillers are chosen in such a way that the size ratios of the second filler to the GNP are very different from each other. Silica nanoparticles are several orders magnitude smaller in size in compared to GNP sheets. Ceramic spheres are in the same order in size with GNP. The wide variation in the size of the second filler plays a significant role in the formation of GNP network in the matrix which in turn would affect the electrical conductivity.

4. 3 Materials:

MLG are purchased from XG Sciences, USA. The lateral dimension of these nanoplatelets is 25μm and thickness is approximately 6nm. 200nm silica nanoparticles are purchased from Nyacol, USA. Polystyrene (MW 121,000) pellets are purchased from Styrolution, USA. The alumino-silicate-ceramic microspheres are purchased from 3M, USA.

4. 4 Fabrication of Composites:

7g of the polystyrene pellets are dissolved in 42ml of N,N- dimethylformamide (DMF) and the solution is stirred magnetically for 12 hours.[25] The silica particles/alumino-silicate ceramic microspheres are then added and the mixture sonicated for 1.5 hrs. GNP at a concentration of 0.001gm/ml are dispersed in DMF and sonicated for 1.5hrs. Both particle-containing suspensions are then mixed in a 1:1 ratio and magnetically stirred for 2hrs. This mixed suspension is then poured into methanol, an antisolvent for PS. The PS precipitates rapidly, creating the composite. The excess methanol is withdrawn, and the composite is dried in an oven for 18 hr at 90ºC. The sample is then hot pressed at 120ºC to get rid of all entrapped air bubbles, and to create a sample with a disk-like shape that is amenable for electrical conductivity measurements. All reported loadings are based upon the volume percent in the final composite.

4.5 Characterization and Electrical Conductivity Measurement Technique:

The surfaces of specimens are coated with silver paint to reduce contact resistance. A standard two-point probe using a constant current source (Keithley Instruments Model 6221) is used to obtain bulk volumetric electrical conductivity. The voltage drop across the specimen is recorded, and the resistance of the sample calculated from this measurement. This is normalized with the dimensions of the sample to produce the electrical conductivity. The surface morphology of the composites is observed using scanning electron microscopy (Zeiss SIGMA VP FE-SEM) in backscatter mode. A Rigaku Ultima IV diffractometer with Cu Kα radiation is used for the X-ray diffraction (XRD) measurements.

4.6 Results and Discussions:

Electrical Conductivity of graphene/ alkali alumino silicate ceramic/ polystyrene composites:

We have investigated the effect of the size of the non- conductive filler on the electrical conductivity of the composites. These alumino silicate ceramics (12 micron in size) act as posts in the matrix, preventing agglomeration of graphene sheets which in turn helps in building the connected pathways of graphene sheets which will increase the electrical conductivity.

The electrical conductivity of these composites is lower than the electrical conductivity of graphene/ silica particles/ polystyrene composites at the same loading of graphene and the non-conductive filler. These results are summarized in figure 1.

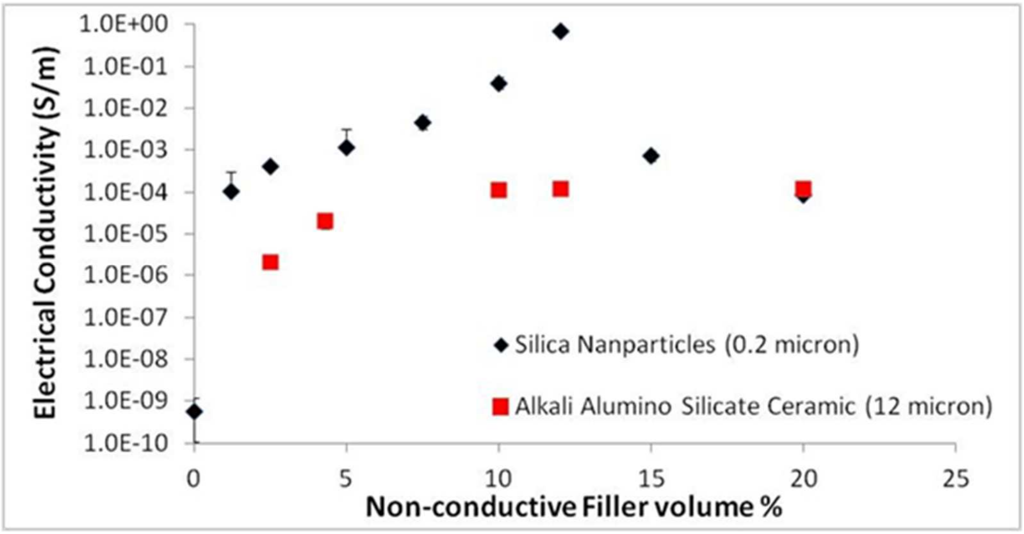

Figure 1: Electrical conductivity of graphene-silica-polystyrene composites and graphene-alumino silicate ceramic-polystyrene composites.

Smaller particles get distributed more evenly These results can be explained by the fact that the smaller particles get dispersed more easily and randomly in the matrix during processing whereas it is more challenging to keep these bigger ceramic microspheres dispersed due to their larger size as they always have a tendency to settle down. So smaller silica particles are more effective in dispersing graphene uniformly throughout the matrix compared to bigger ceramic microspheres. Another important fact is that at a certain volume of a second, non-conductive filler, there are more number of particles in case of small silica particles in comparison to bigger alumino-silicate-ceramic where we can have lesser number of particles as we can see in the figure 2. So in this way, we can have more number of posts in the matrix with small silica particles compared to the bigger particles. As a result of which, graphene sheets can get dispersed more homogeneously with the help of smaller particles as compared

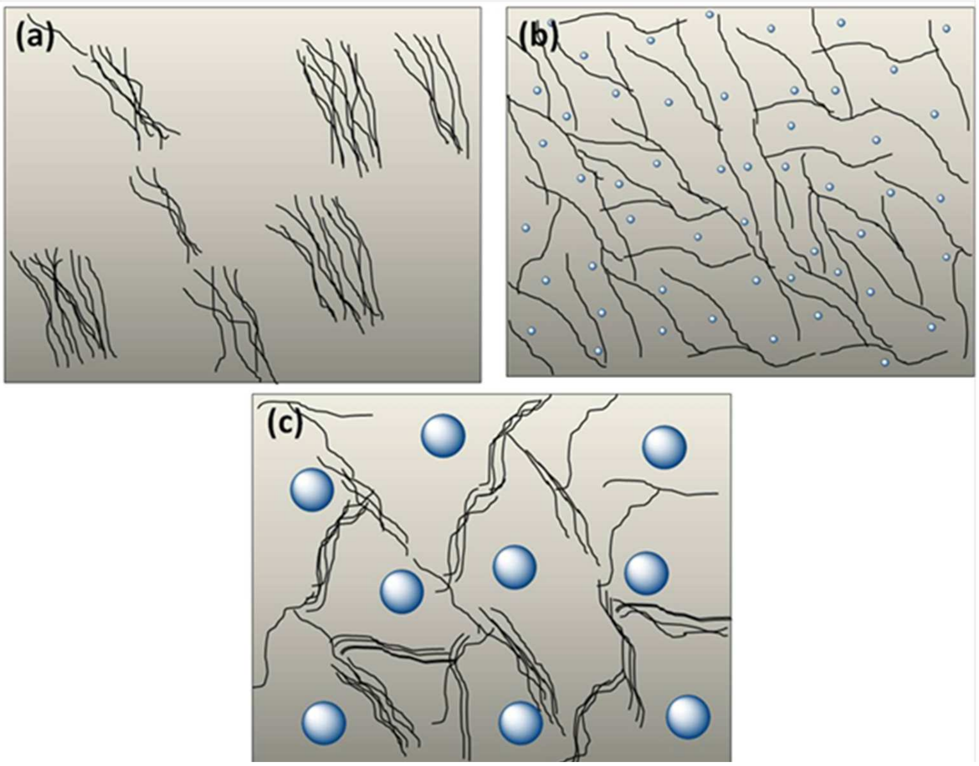

Figure 2. (a) Schematic shows the agglomerations of GBM present in the matrix. (b) More uniform dispersion of GBM in the presence of more number of smaller silica particles. (c) Less homogeneous dispersion of GBM in the presence of fewer number of larger alumino-silicate-ceramic particles.

to bigger particles. Having more number of posts in the matrix is advantageous in terms of guiding graphene in the matrix as observed in figure 2.(b) and 2.(c)Therefore, smaller silica particles are more effective in increasing the electrical conductivity of the composites in comparison to the bigger alumino-silicate-ceramic.

The distribution of GBM and alumino silicate ceramic particles in the polystyrene phase is studied under SEM with varying loading of alumino silicate particles. Figure 3 (a) shows the large agglomeration of GNP sheets in absence of a second filler. In figure 3.(b) at 2.5 vol%, few network formation of GBM is observed along with large agglomertion of GBM which is consistent with the case of small silica/GBM/ polystyrene composite. The electrical conductivity reaches 2×10^{-6} S/m. At 5 vol%, more network formation of GBM is visible and the conductivity goes to 2×10^{-5} S/m . Large agglomeration of GBM is not present here in figure 3.(c). At 12 vol%, more homogeneous distribution of GBM is observed with almost negligible number of GBM agglomeration as seen in figure 3.(d). The electrical conductivity increase to 1.23×10^{-4} S/m.

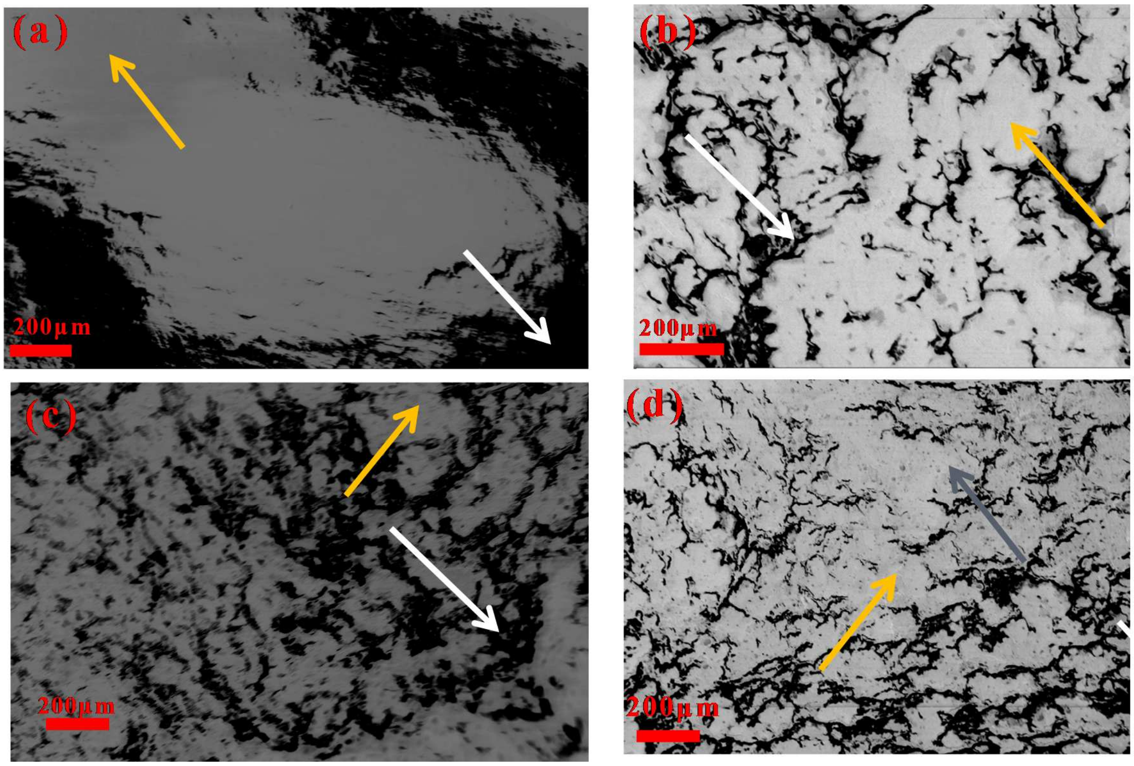

Figure 3. Backscattered SEM images showing the distribution of GNP and alkali-alumino-silicate-ceramic particles in the polystyrene phase. (a) Large agglomerations of GBM are observed in the absence of second filler. (b)At 2.5 vol% of alkali-alumino-silicate-ceramic, few networks of GBM are started to form along with some agglomerations of GBM . (c) More networks of GBM are visible at 5vol% of alkali-alumio-silicate-ceramic. (d) Uniform dispersion of GBM is observed with more connectivity in the matrix at 12 vol% of ceramic particles. All yellow arrows show polystyrene phase and all white arrow shows GNP sheets.

The morphology of these composites are also studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM)Figure 4(a)-(c) are higher magnification, charge-contrast SEM images of graphene/alkali-alumino-silicate-ceramic/polystyrene composites at different loading of alkali-alumino-silicate-ceramic from 2.5vol% to 12vol%., Here we can see that graphene sheets move around the larger filler which is the evidence of improving the electrical conductivity of these composites by preventing the agglomeration of graphene sheets where these particles can stay in between graphene sheets. In figure 4.(d) we see that ceramic microspheres are dispersed in the matrix. The rough surface indicates the presence of graphene sheets in the polystyrene.These sheets are not allowed to go to certain regions of the matrix due to the presence of these spheres. So they try to arrange themselves by moving around the ceramic microspheres which results in forming a network of connected pathways of graphene sheets

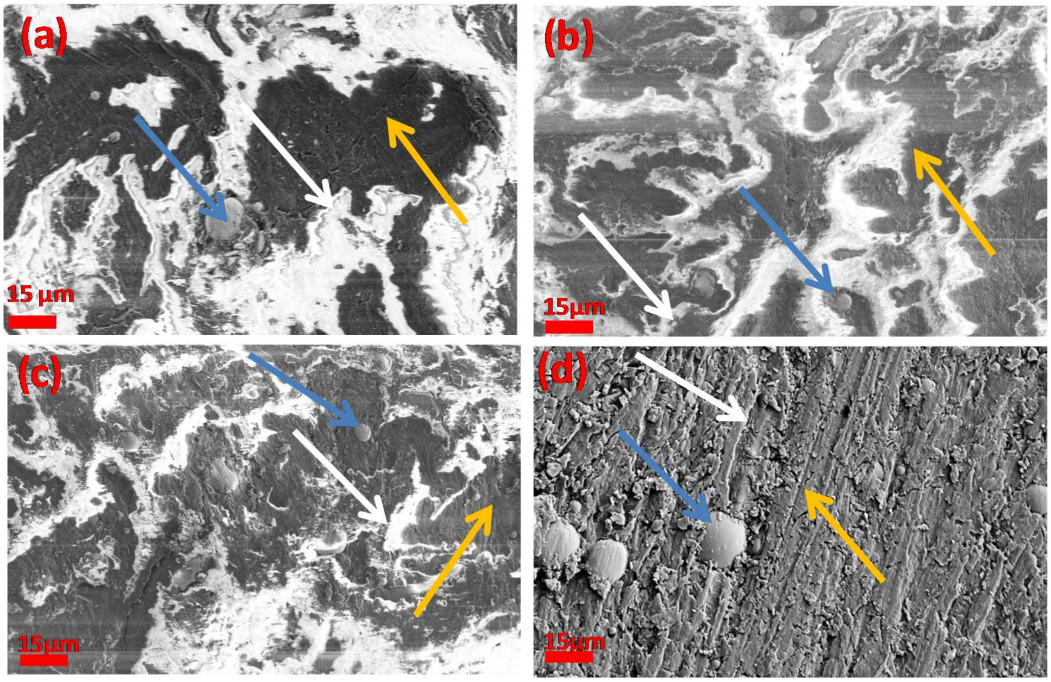

Figure 4. Higher magnification charge-contrast SEM images show the morphology of graphene/alkali-alumino-silicate-ceramic/ polystyrene composites. (a) at 2.5 vol% fewer number of sphere is visible with GNP sheets moving around it. (b) at 5 vol% more number of spheres are present along with GNP sheets, (c) at 12 vol%, uniform dispersion of GNP is observed with ceramic spheres in between them, (d) gold-coated SEM image where spheres are randomly distributed in the matrix. The rough surface confirms the presence of GNP.

In figure 5, the TEM images of GNP-polystyrene composites show the orientation of silica/ alumino-silicate-ceramic spheres and graphene sheets in the matrix. Figure 9.(a) shows the distribution of silica nanoparticles and graphene sheets in the matrix. Energy dispersive X-ray spectroscopy (EDS) shows the presence of silicon peak which confirms the presence of silica nanoparticles in figure 9.(b). Figure 9.(c) shows the arrangement of alkali-alumino-silicate-ceramic spheres and graphene sheets in the matrix. EDS analysis in figure 9.(d) shows the peaks of aluminum and silicon confirming the presence of alumino-silicate ceramic spheres in the polystyrene.

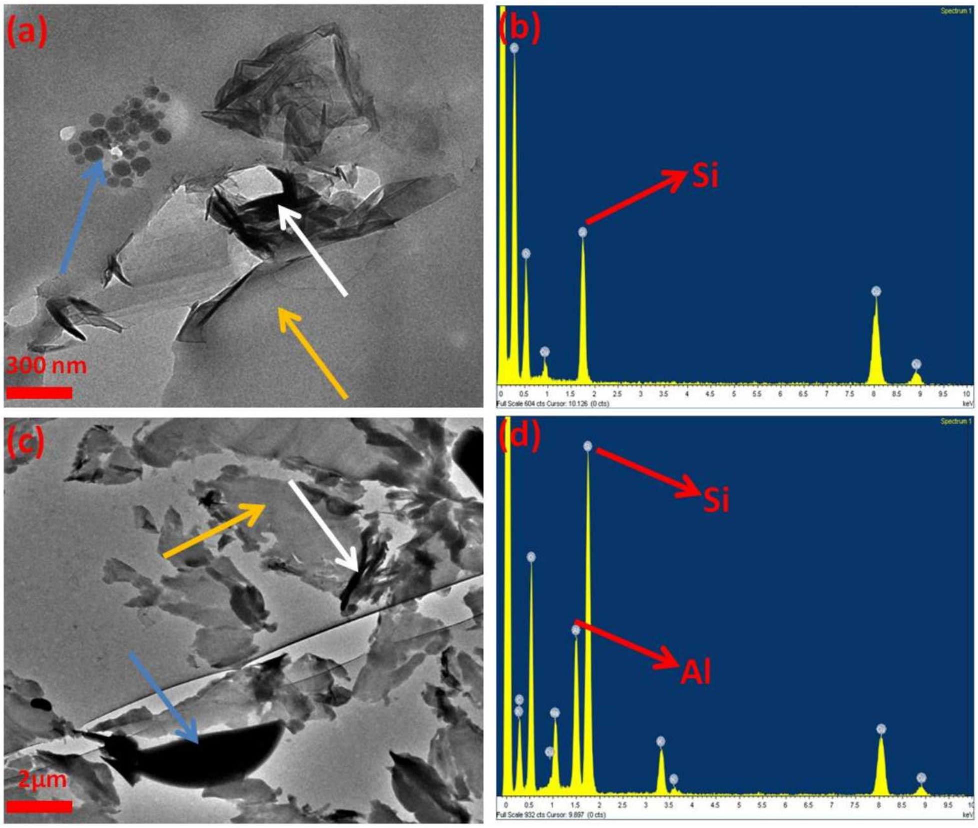

Figure 5. Thin-section Transmission electrom microscope images of graphene-polystyrene composites (a) at 12 vol% of silica particles, the orientation of silica and graphene sheets is observed, (b) EDX result shows silicon peak confirming the presence of silica nanoparticles, (c) the distribution of alumino-silicate-ceramic sphere and graphene sheets in the polystyrene matrix at 12vol% is studied and (d) EDX result shows silicon and aluminum

peaks, confirming the presence of alumino-silicate-ceramic spheres. All yellow arrows show polystyrene, all blue arrows show silica/alumino-silicate-ceramic spheres and all white arrows show graphene sheets.

4.7 Conclusions:

The presence of a second filler is always beneficial in enhancing the electrical conductivity of the composites. Both smaller and bigger sized particles improve the dispersion of GNP by preventing the agglomeration of sheets. Smaller sized silica particles are more effective as dispersion aids in comparison to the bigger ceramic microspheres because of the higher number concentration of smaller particles compared to the bigger one at the same loading of second filler. This phenomenon can be extended to different sized non-conductive fillers featuring mechanical/thermal/barrier properties so that these multifunctional composites may find numerous applications in various fields.

4. 8 References

1. Geim, A. K., Graphene: Status and Prospects. *Science (Washington, DC, United States)* **2009,** 324, 1530-1534.

2. Geim, A. K.; Novoselov, K. S., The Rise of Graphene. *Nat. Mater.* **2007,** 6, 183-191.

3. Rao, C. N. R.; Sood, A. K.; Voggu, R.; Subrahmanyam, K. S., Some Novel Attributes of Graphene. *Journal of Physical Chemistry Letters* **2010,** 1, 572-580.

4. Allen, M. J.; Tung, V. C.; Kaner, R. B., Honeycomb Carbon: A Review of Graphene. *Chem. Rev. (Washington, DC, U. S.)* **2010,** 110, 132-145.

5. Eda, G.; Chhowalla, M., Graphene-based Composite Thin Films for Electronics. *Nano Letters* **2009,** 9, (2), 814-818.

6. Kim, H.; Abdala, A.; Macosko, C. W., Graphene/Polymer Nanocomposites. *Macromolecules (Washington, DC, United States)* **2010,** 43, 6515-6530.

7. Kuilla, T.; Bhadra, S.; Yao, D.; Kim, N. H.; Bose, S.; Lee, J. H., Recent advances in graphene based polymer composites. *Progress in Polymer Science* **2010,** 35, (11), 1350-1375.

8. Singh, V.; Joung, D.; Zhai, L.; Das, S.; Khondaker, S. I.; Seal, S., Graphene based materials: Past, present and future. *Progress in Materials Science* **2011,** 56, (8), 1178-1271.

9. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S., Graphene-based composite materials. *Nature (London, United Kingdom)* **2006,** 442, (7100), 282-286.

10. Verdejo, R.; Bernal, M. M.; Romasanta, L. J.; Lopez-Manchado, M. A., Graphene Filled Polymer Nanocomposites. *Journal of Materials Chemistry* **2011,** 21, 3301-3310.

11. Potts, J. R.; Dreyer, D. R.; Bielawski, C. W.; Ruoff, R. S., Graphene-based polymer nanocomposites. *Polymer* **2011,** 52, (1), 5-25.

12. Araby, S.; Zhang, L. Q.; Kuan, H. C.; Dai, J. B.; Majewski, P.; Ma, J., A novel approach to electrically and thermally conductive elastomers using graphene. *Polymer* **2013,** 54, (14), 3663-3670.

13. Bose, S.; Kuila, T.; Uddin, M. E.; Kim, N. H.; Lau, A. K. T.; Lee, J. H., In-situ synthesis and characterization of electrically conductive polypyrrole/graphene nanocomposites. *Polymer* **2010,** 51, (25), 5921-5928.

14. Fan, W.; Zhang, C.; Tjiu, W. W.; Liu, T. X., Fabrication of electrically conductive graphene/polystyrene composites via a combination of latex and layer-by-layer assembly approaches. *Journal of Materials Research* **2013,** 28, (4), 611-619.

15. Kim, B. J.; Jang, H.; Lee, S. K.; Hong, B. H.; Ahn, J. H.; Cho, J. H., High-Performance Flexible Graphene Field Effect Transistors with Ion Gel Gate Dielectrics. *Nano Letters* **2010,** 10, (9), 3464-3466.

16. Maiti, S.; Shrivastava, N. K.; Suin, S.; Khatua, B. B., Polystyrene/MWCNT/Graphite Nanoplate Nanocomposites: Efficient Electromagnetic Interference Shielding Material through Graphite Nanoplate-MWCNT-Graphite Nanoplate Networking. *ACS Applied Materials & Interfaces* **2013,** 5, (11), 4712-4724.

17. Nasibulin, A. G.; Koltsova, T.; Nasibulina, L. I.; Anoshkin, I. V.; Semencha, A.; Tolochko, O. V.; Kauppinen, E. I., A novel approach to composite preparation by direct synthesis of carbon nanomaterial on matrix or filler particles. *Acta Materialia* **2013,** 61, (6), 1862-1871.

18. Martin-Gallego, M.; Bernal, M. M.; Hernandez, M.; Verdejo, R.; Lopez-Manchado, M. A., Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites. *European Polymer Journal* **2013,** 49, (6), 1347-1353.

19. Jing LI, P. C. M., Chow Wing SZE, To Chi KAI, Ben Zhong TANG, Jang-Kyo KIM, Percolation Threshold of Polymer Nanocomposites Containing Graphite Nanoplatelets and Carbon Nanotubes. In *16th International Conference on Composite Materials*, 2007.

20. Pang, H.; Chen, T.; Zhang, G. M.; Zeng, B. Q.; Li, Z. M., An electrically conducting polymer/graphene composite with a very low percolation threshold. *Materials Letters* **2010,** 64, (20), 2226-2229.

21. Chakraborty, I.; Bodurtha, K. J.; Heeder, N. J.; Godfrin, M. P.; Tripathi, A.; Hurt, R. H.; Shukla, A.; Bose, A., Massive Electrical Conductivity Enhancement of Multilayer Graphene/Polystyrene Composites Using a Nonconductive Filler. *ACS Applied Materials & Interfaces* **2014,** 6, (19), 16472-16475.

22. Wang, Z. P.; Nelson, J. K.; Miao, J. J.; Linhardt, R. J.; Schadler, L. S.; Hillborg, H.; Zhao, S., Effect of High Aspect Ratio Filler on Dielectric Properties of Polymer Composites: A Study on Barium Titanate Fibers and Graphene Platelets. *Ieee Transactions on Dielectrics and Electrical Insulation* **2012,** 19, (3), 960-967.

23. Kuvardina, E. V.; Novokshonova, L. A.; Lomakin, S. M.; Timan, S. A.; Tchmutin, I. A., Effect of the graphite nanoplatelet size on the mechanical, thermal, and electrical properties of polypropylene/exfoliated graphite nanocomposites. *Journal of Applied Polymer Science* **2013,** 128, (3), 1417-1424.

24. Knauert, S. T.; Douglas, J. F.; Starr, F. W., The effect of nanoparticle shape on polymer-nanocomposite rheology and tensile strength. *Journal of Polymer Science Part B-Polymer Physics* **2007,** 45, (14), 1882-1897.

25. Qi, X.-Y.; Yan, D.; Jiang, Z.-G.; Cao, Y.-K.; Yu, Z.-Z.; Yavari, F.; Koratkar, N., Enhanced Electrical Conductivity in Polystyrene Nanocomposites at Ultra-Low Graphene Content. *ACS Appl. Mater. Interfaces* **2011,** 3, 3130-3133.

CHAPTER 5

RECOMMENDED FUTURE WORKS

Graphene is one of the most widely used filler for fabrication of polymer composite materials due to its high electrical, thermal, mechanical, barrier properties. The agglomeration of graphene sheets can be inhibited with the use of a second filler in the matrix which can act as very effective dispersion aid. Several orders increase in the electrical conductivity is observed with the addition of non-conductive filler by achieving improved dispersion of graphene. Silica nanoparticles and polybutadiene spheres are found to induce percolation in the system at very low loading of graphene. Polybutadiene spheres increase toughness and flexural strength of the composites. While incorporating a second filler is always beneficial in improving the dispersion of graphene, it always brings numerous possibilities of developing multi-functional polymer composite materials. The appropriate fillers are selected to impart desired functionalities in the final system depending on the target applications. Although there are countless prospects of fabricating composite materials by incorporating different types of second filler with specific properties, some of the most significant future works are mentioned below.

1) Polystyrene latex spheres are one of the most promising second filler. They can act as dispersion aids as well as improve the strength of the composites with the help of stronger interface between filler and the matrix.

2) The electro-mechanical response of these multi-functional composite materials can be studied. This feature is very useful for various sensors applications.

3) Composites with improved electrical and thermal properties can be developed with graphene and good thermally conductive second fillers such as gold, silver, aluminum nanoparticles. Electronic devices, thermal pastes, heat-actuated, shape-memory polymers have enormous demands for these type of composites.

4) The stress-strain response of these multi-functional composites can be studied under dynamic loading condition. The dynamic responses of these composites have many applications in blast loading, impact during crash and impulse loading.

5) The combination of two conductive fillers such as graphene with carbon nanotube might be very promising area to work on. These electrically conductive polymer composites can be used as anti-static mat, anti-static coating, conducting paint, electromagnetic interference (EMI) shielding materials.

6) The effect of the shape of the second filler can significantly affect the electrical conductivity of the composites. Different shaped second filler can alter the network of graphene network which will result in variation in the conductivity. Investigating the best possible shape of the second filler in terms of improving the electrical conductivity would be a very interesting topic.

7) Varying the type of polymer for the matrix can help in fabricating a completely different type of composites where incorporating graphene with any second filler will impart remarkable electrical and mechanical properties in the final composites. For example, graphene and polyisobutylene spheres can be used as fillers in the polybutadiene matrix to make a very flexible, electrically conductive polymer composites which can be used as automobile fuel line injector applications.

8) A novel composites can be developed with graphene and silica or silver nanoparticles as second filler. These electrically conductive, optically transparent composites are very promising materials for touch screen devices.

9) Developing a mathematical model would be very useful for predicting the effect of the presence of second filler causing a several orders rise in the electrical conductivity of the composites. Quantification of the dispersion of graphene in the matrix in the presence of second filler should be an important parameter of that novel model.