STUDIES ON GRAPHENE BASED POLY(METHYL METHACRYLATE) NANOCOMPOSITES

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APRIL 2015

STUDIES ON GRAPHENE BASED POLY(METHYL METHACRYLATE) NANOCOMPOSITES

by

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submitted

in fulfilment of requirements of the degree of

Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2015

Dedicated to my parents

Shri Haridwar Nath Tripathi

&

Smt. Ramrati Devi

CERTIFICATE

This is to certify that thesis entitled **"Studies on Graphene Based Poly(methyl methacrylate) Nanocomposites"** being submitted by **Mr. Sandeep Nath Tripathi** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research carried out by him. **Mr. Sandeep Nath Tripathi** has worked under my supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ACKNOWLEDGEMENTS

This thesis could have not been completed without the generosity and support of many. First of all I wish to express my heartiest gratitude to my supervisor, Prof (Mrs) Veena Choudhary for her invaluable guidance and constant encouragement. Her caring attitude like mother and co-operation has been monumental throughout my research. Through her wealth of knowledge, direction and leadership I have been able to expand my knowledge in many areas of polymer science.

I express my sincere thanks to Prof S.N. Maiti, Prof A.K. Ghosh, Dr Josemon Jacob, Dr B.K. Satapathy and Prof Manjeet Jassal for their constant encouragement, advice and support throughout my research work.

My special thanks to Mr Surender Kumar Sharma, Mr Shivkant, Mr Ashok Kapoor, Mr Virender Kumar Sharma (from glass blowing workshop), Mr Keshav Dev and Mr Alok Yadav (from NMR lab), Mr D.C. Sharma and Mr Kuldeep Sharma (from SEM lab) and office staff Ms Shalini, Sudhir, Raj and Pramod for their immediate help whenever needed.

I express my thanks to Prof B.D. Gupta from Physics Department, IIT Delhi, Dr S.K. Dhawan and Dr R.B Mathur of National Physical Laboratory Delhi, India for providing facilities to carry out experiments in their lab.

Nothing could have been accomplished without my family support. I would like to extend my special gratitude to my family for their love, support and encouragement. I am extremely thankful to my brothers Mr Dilip Nath Tripathi and Mr Amrendra Nath Tripathi for their constant encouragement and emotional support throughout my career.

I am extremely thankful to all my friends and colleagues Mr. Rajender Singh Malik, Mr Harjeet Singh Jaggi, Mrs Meenakshi Verma, Mr Pawan Verma, Ms Bhavna Sharma, Mrs Shilpi Sharma, Mrs Savita Meena, Mrs Bindu Manchanda, Mrs Achla Tripathi, Mr Debanga Konwar, Mr Sampat S. Chauhan, Mr Vishwa Pratap Singh, Ms Banpreet Kaur, Ms Pragati,

Mrs Priyanka Singh, Mrs Manisha Tomar, Dr Hemlata, Mr Rajendra Singla, Mr Abhishek Kumar, Mr Tahir Zafar and Mr Devendra Mogha and also my seniors Dr Bhanu P. Singh, Dr Parveen Saini, Dr Deeksha Gupta, Dr Anju Gupta, Dr Pravin Kumar Srivastav, Dr Shveta Mahajan and Dr Prabhat Garg.

I am also thankful to friends from other departments Dr Deepak Tripathi, Dr Navin Kumar Dwivedi, Dr Gaurav Kumar Singh (IAS), Dr Udit Kumar Soni, Dr Vinod Kumar, Mr Satyendra Kumar Mishra, Mr Manu Dalela, Mr Dinesh Shukla, Mr Abhishek Gandhi and Mr Vineet Chaudhary.

My dear friends Dr Anupam Gupta, Mr Narendra Kumar Mishra, Mr Alok Agrahari, Mr Ashwani Kumar Singh, Dr Deepak Kumar Yadav, Mr Upendra Pratap Singh and Mr Parvej Alam are greatly thanked for being an incredible support system and their encouraging words throughout my PhD.

I gratefully acknowledge University Grant Commission (UGC), India for providing Junior and Senior Research Fellowships.

Finally, I thank the 'ALMIGHTY GOD' for his blessings and further seek him to provide me blessings, patience and strength to accomplish newer goals.

Sandeep Nath Tripathi

ABSTRACT

Over the last two decades polymer nanocomposites have been the subject of intense research interest in academia and industry which is spawned by advances such as the discovery of spherical fullerenes and carbon nanotubes. Graphene has been incorporated into various types of polymer matrices due to the exceptionally unique combination of properties such as high electrical and thermal conductivity, high surface area, strength toughness and stiffness. It was therefore expected that the incorporation of graphene into the polymer matrices will improve its mechanical, electrical, thermal and gas barrier properties. A number of thermosetting and thermoplastics have been used as matrix for the preparation of graphene/polymer nanocomposites and poly(methyl methacrylate) [PMMA] is one of them. It is used because of its some specific advantages such as low cost, optical clarity, ease of melt processibilty, mould-ability mostly into any shape, good weather-ability and good physico-chemical properties. The present study was carried out to investigate the effect of reduced graphene oxide (RGO)/graphene-carbon nanotubes (GCNT) content and its method of incorporation on the properties of PMMA. These composites were characterized for thermal, electrical, mechanical, rheological, morphological properties and evaluated as gas sensor based on surface plasmon resonance utilizing fiber optic probe.

The thesis has been divided into six chapters. **Chapter 1** deals with the brief introduction of polymer nanocomposites and various nanofillers of carbon family along with detailed study of graphene followed by comprehensive literature review on the synthesis, characterization and applications of graphene in the field of polymer composites. It also reviews the different processing techniques used to fabricate polymer nanocomposites and their characterization [thermal, mechanical and electrical properties]. The basics of gas

sensors based on surface plasmon resonance utilizing fiber optic probe, the role of graphene and PMMA have also been included in this chapter.

The detailed experimental methods used for the preparation of reduced graphene oxide (RGO)/graphene-carbon nanotube (GCNT) hybrids and PMMA/RGO or PMMA/GCNT composites are given in **chapter 2** of thesis. The different techniques used for characterization and evaluation of the properties of PMMA/RGO or PMMA/GCNT composites are also described in this chapter.

The effect of reduced graphene oxide content and its method of incorporation by three methods on the properties of PMMA in PMMA/RGO composites are given in **chapter 3**. The interaction of RGO with PMMA matrix was investigated using FT-IR, Raman spectroscopy and also by X-ray diffraction analysis. The effect of RGO content on thermal, mechanical and electrical properties of PMMA/RGO nanocomposites fabricated by three different techniques, i.e. (i) *in situ* polymerization of MMA in presence of RGO (ii) *in situ* polymerization of MMA in presence of RGO and commercial PMMA beads and (iii) *in situ* polymerization of MMA in presence of RGO followed by sheet casting; up to 2.0 wt% RGO loading was investigated and the results are summarized in this chapter. Thermal stability of PMMA enhances upon incorporation of RGO in PMMA matrix irrespective of the methods. However, the mass loss in first step, which may be due to the weak linkages such as head to head linkages decreased in case of sheet casting method as compared to other two methods. It was found that for a given RGO content, all three samples give different electrical conductivity highlighting the importance of compounding method. It was found that, conductivity of composites at 0.5 wt% RGO was 3.8×10^{-6} S/cm (for in situ polymerized), 4.1×10^{-6} S/cm (for in situ polymerized in presence of PMMA beads) which is ~ 5-order higher than neat PMMA (2.4×10^{-11} S/cm) and 9.5×10^{-5} S/cm (for samples prepared by sheet

casting method) i.e. 6-orders higher of magnitude than PMMA. The mechanical properties of PMMA/RGO showed that addition of RGO leads to improvement of modulus which indicates the increase in stiffness of the composite. Further, the tensile strength of composites show that addition beyond 1 wt% loading of RGO, leads to deterioration of mechanical strength that can be attributed to the filler agglomeration effect and poor stress transfer characteristics. The elongation decreased with increasing RGO content indicating brittle fracture of composites. These studies clearly show that all the properties were better in case of sheet casting method and hence for further studies (i.e. for melt rheology and gas sensing behaviour) all the samples were prepared using sheet casting technique.

Chapter 4 includes the preparation and characterization of graphene-CNT (GCNT) hybrid filler via chemical method for nanocomposite application by varying the weight ratio of graphene and CNT i.e. 1:2, 1:1 and 2:1 and designated as GCNT-1, GCNT-2 and GCNT-3 respectively. The composites based on these fillers at fixed concentration (1 wt%) were prepared to investigate the effect of hybrid filler nature on the properties. On the basis of thermal and electrical properties, composites based on GCNT-2 filler showed better properties as compared to composites prepared using GCNT-1 and GCNT-3. Therefore for further studies GCNT-2 have been used to prepare PMMA/GCNT nanocomposites using varying amounts of GCNT-2 and evaluated as gas sensor.

Chapter 5 describes the evaluation of PMMA nanocomposites based on RGO/GCNT as gas sensors using surface plasmon resonance technique utilizing fiber optic probe. For the study of sensing performance of PMMA composites based on RGO/GCNT, chapter 5 was divided into two subchapters. In **chapter 5A,** we investigated the effect of RGO content on sensing behaviour. The probe was fabricated using a 24 cm length of plastic clad silica optical fibre of core diameter 600 μm and numerical aperture 0.4. About 1 cm length of

cladding was removed from the middle portion of the fibre followed by washing with acetone and then a Cu layer of 40 nm was coated using thermal evaporation technique. The sensing layer was then deposited over the Cu layer by dip coating method. In the first part PMMA/RGO nanocomposites were evaluated for gases like NH_3, H_2S, Cl_2, H_2 and N_2 where the composites show selectivity mainly for NH_3 gas. It was also found that as RGO loading increased in PMMA/RGO composite, shift in the resonance wavelength increases and a maximum shift of 35 nm at 5 wt% RGO loading in PMMA was observed. The second part of this chapter (**chapter 5B**) deals with the sensing performance of PMMA/GCNT nanocomposites for CH_4, NH_3, H_2S, CO_2, Cl_2, H_2 and N_2 where nanocomposite showed selectivity for methane gas. The maximum shift of 30 nm was observed at 5 wt% GCNT loading for PMMA/GCNT nanocomposite.

The final summary and conclusions of the thesis are given in **chapter 6**. Suggestions for future work are also included in this chapter.

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