STUDIES ON MULTIWALLED CARBON NANOTUBES REINFORCED POLY(TRIMETHYLENE TEREPHTHALATE) COMPOSITES

by

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submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology Delhi

DECEMBER, 2011

CERTIFICATE

This is to certify that thesis entitled **"Studies on multiwalled carbon nanotubes reinforced poly(trimethylene terephthalate) composites"** being submitted by **Ms. Anju Devi Gupta** 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 her. **Ms. Anju Devi Gupta** has worked under my guidance and 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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ACKNOWLEDGEMENT

I wish to express my heartiest gratitude to my supervisor, Prof. (Mrs.) Veena Choudhary for her invaluable guidance and constant encouragement. Her caring attitude and co-operation have 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 am thankful to Prof. S.N.Maiti, Prof. A.K.Ghosh, Prof. B.L Deopura, Dr. Josemon Jacob, Dr. B.K. Sathpathy and Prof. A.K.Gupta for their constant encouragement and help throughout my research work.

My special thanks to Mr. Surrender Kumar, Mr. Shivkant, Mr. Ashok Kapoor and Mrs. Rama for their immediate help whenever needed.

I express my thanks to Dr. L. M. Manocha from Sardar Patel University, Gujarat, 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.

Many thanks are due to my husband Ranjan. His support, encouragement and patience enable me to pursue my career, while at the same time enjoying a lifetime of happiness with him.

I am extremely thankful to all my seniors Dr. Dipti Singh, Dr. Pooja Chhabra, Dr. Sujata Mishra, Dr. Geeta Saini, Piyush Anant, Pravin Srivastav, Pravin Saini, Bhanu Pratap Singh, Shveta, Saikat Banerjee, Satpal Singh and friends & colleagues Monu, Manisha, Meenakshi, Deeksha, Jina, Suneel, Renchu, Sneha, Priyanka, Khushboo and Naresh for their constant encouragement.

The financial assistance provided by UGC is highly acknowledged.

Last but not the least I am thankful to the Almighty God in helping me to accomplish this task.

Anju Devi Gupta

ABSTRACT

Polymeric nanocomposites have been the subject of intense research interest over the past two decades in academia and industry, spawned by advances such as the discovery of spherical fullerenes and carbon nanotubes. As nano fillers are projected to provide advanced performance capabilities for engineering polymer applications, imparting the high strength and modulus obtained with traditional fillers without their negative side effects, such as reduced processability and impact strength. As compared to other nanofillers, carbon nanotubes (CNTs) have emerged as the most promising nanofiller for polymer composites due to its remarkable thermal/mechanical and electrical properties. Incorporation of CNTs in polymer matrices provides materials that could be used for many high performance engineering applications.

Therefore, present study was carried out to investigate the effect of untreated and acid-treated multiwalled carbon nanotubes [MWCNTs] on the properties of poly(trimethylene terephthalate) [PTT] having viscosity average molecular weight (M_v) 44,000 and 80,000. MWCNTs were synthesized using chemical vapor deposition (CVD) method. Modified CNT's were prepared by acid-treatment using a mixture of nitric acid: sulphuric acid (3:1) to prepare modified CNTs. PTT composites based on untreated and acid-treated MWCNTs were prepared using melt blending and their thermal, electrical, mechanical, rheological and morphological properties were evaluated.

The thesis has been divided into seven chapters. Chapter 1 deals with the brief introduction of polymer nanocomposites followed by comprehensive literature review on the synthesis, characterization, modification and applications of carbon nanotubes 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 detailed methods used for the preparation of MWCNTs and PTT/MWCNTs composites are given in chapter 2 of thesis. The techniques used for characterization and evaluation of the properties of PTT(l/h)/MWCNT composites are also described in this chapter.

The details of morphological and thermal behavior of PTT(l/h)/MWCNT composites are reported in chapter 3. TEM micrographs showed uniform dispersion of nanotubes in the PTT(l/h) matrix. Individual nanotubes were found to be highly curved and randomly coiled because of the intrinsic van der Waals attractions, in combination with high aspect ratio and large surface area. SEM images also showed uniform dispersion of MWCNTs and some pulled out MWCNT bundles from PTT(l/h) matrix. Presence of pulled out nanotubes on the surface of composites suggest poor interaction between MWCNTs and polymer matrix.

The effect of carbon nanotubes on the crystallization behavior of PTT(l/h) was investigated by recording DSC scans under isothermal and non isothermal conditions. Incorporation of CNTs enhanced the rate of crystallization of l-PTT whereas it didn't show any significant effect on the crystallization behavior of h-PTT. Percent crystallinity and melting temperature of PTT(l/h) were found to be independent of MWCNT content. Effect of MWCNTs on the crystal morphology of PTT(l/h) and PTT(l/h)/MWCNT composites was investigated using polarizing light microscope [PLM] and XRD. PLM micrographs of PTT(l/h) and PTT(l/h)/MWCNT composites supported the results obtained from the isothermal and non-isothermal crystallization studies. PLM images of l-PTT/MWCNT composites showed formation of smaller spherulites as compared to neat l-PTT, which indicated that MWCNTs increased the number of nucleating sites in l-PTT matrix. However, bigger and perfect crystals were seen in case of h-PTT/MWCNT composites. XRD results also showed that presence of MWCNTs affected the crystal structure of PTT(l/h). The thermal stability of PTT(l/h) remained unaffected upon incorporation of varying amounts of MWCNTs.

Chapter 4 describes the effect of MWCNTs on the electrical properties of PTT(l/h)/MWCNT composites and also investigates the potential of these composites as an effective light weight electromagnetic interference (EMI) shielding material in the frequency range of 8.2-18 GHz. The electrical conductivity (σ) of PTT(l/h)/MWCNT composites increased upon incorporation of MWCNTs and percolation threshold concentration was obtained at a loading of MWCNTs in the range of 1-1.5 wt%. The maximum shielding effectiveness (SE) obtained for l-PTT/MWCNT and h-PTT/MWCNT composites were 42 and 29 dB respectively, at 10 wt% MWCNT loading. Shielding mechanism was studied by resolving the total SE into absorption (SE_A) and reflection loss (SE_R). PTT(l/h)/MWCNT composites showed absorption dominated shielding; thus these composites can be used as microwave, radar absorbing and stealth material. The effect of MWCNT loadings on electrical conductivity and dielectric properties of PTT(l/h) and the correlation among conductivity, tan δ, absorption loss and reflection loss were also studied.

Chapter 5 describes the rheological and mechanical properties of melt compounded PTT(l/h)/MWCNT composites. Significant increase in melt viscosity, storage modulus (G') and loss modulus (G'') of PTT(l/h) matrix was observed on MWCNT addition. A dramatic increase in the melt viscosity of PTT was observed when MWCNT content was in the range of 0.5 and 2 wt %. This could be due to the formation of interconnected network of MWCNT in polymer matrix and thus it can be regarded as rheological percolation threshold concentration. The significant increase in viscosity can be attributed to the significant increase in G' as compared to moderate increase in G'' upon MWCNT addition. Cole-Cole plot showed change in slope and also shift in the G' vs G'' plot which suggested micro-structural change on MWCNT addition. Dynamic mechanical characterization of composites showed an increase in storage modulus of PTT upon incorporation of MWCNTs.

Chapter 6 discusses the effect of modification of MWCNTs on thermal, mechanical, electrical, rheological and morphological properties of PTT(l/h). Modification of MWCNTs (by introducing carboxylic acid groups) was performed to enhance intermolecular interactions between MWCNT and PTT(l/h) matrix through hydrogen bonding. Morphological observations revealed that the modified MWCNTs were uniformly dispersed in the PTT(l/h) matrix and increased interfacial adhesion between modified nanotubes and PTT(l/h) as compared to the unmodified MWCNTs. Furthermore, a very small quantity of modified MWCNTs substantially enhanced the crystallization temperature and tensile strength/modulus of PTT(l/h). Surface functionalization of MWCNTs showed significant effect on the rheological properties of PTT matrix as functionalization leads to enhancement of storage modulus, loss modulus and viscosity. The increase in rheological properties can be attributed to increase in interfacial interaction between acid-treated MWCNTs and PTT(l/h) matrix. The effect of surface functionalization was also evident on the mechanical properties of PTT(l/h)/MWCNT composites. The untreated MWCNT showed only increase in modulus of PTT(l/h) matrix whereas after functionalization, both tensile strength and modulus of PTT(l/h) matrix showed improvement. This study demonstrates that the thermal, mechanical and rheological properties of PTT(l/h)/MWCNT composites are strongly dependent on the dispersion of MWCNT and their interactions with polymer matrix [enhanced by slight chemical modification of MWCNTs], providing a design guide of CNT-reinforced PTT(l/h)/MWCNT composites with a great potential for industrial uses. The final summary and conclusion are given in Chapter 7 of thesis. Suggestions for future work are also made. References are given at the end of thesis.

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