

**STUDIES ON GRAPHENE BASED THERMOPLASTIC  
POLYURETHANE NANOCOMPOSITES FOR  
ELECTROMAGNETIC INTERFERENCE SHIELDING  
APPLICATIONS**

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APPLICATIONS**

by

**MEENAKSHI VERMA**

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Submitted

*in fulfillment of the requirements of the degree of Doctor of Philosophy*

to the



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***Dedicated to my  
parents  
and my lovely  
daughter KUHU***

## CERTIFICATE

This is to certify that the thesis entitled, “**Studies on graphene based thermoplastic polyurethane nanocomposites for electromagnetic interference shielding applications**” being submitted by **Mrs. Meenakshi Verma** to the Indian Institute of Technology Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Mrs. Meenakshi Verma** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our 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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## ABSTRACT

Electromagnetic pollution is the overabundance of electromagnetic radiations emitted by electronic devices like cell phones, cordless phones, WiFi routers or bluetooth-enabled equipment and our relationship with these devices has become more and more intimate. The potential effects of electromagnetic pollution, both in terms of its interaction with electronic devices as well as biological species are serious concerns for research community. Therefore, protection from such harmful radiations must be acquired by either blocking or shielding these unavoidable severe electromagnetic radiations. Metals have been typically used as the material of choice for shielding applications but heavy weight, corrosion susceptibility and cumbersome processing methods makes them unsuitable for both the researchers and users. Alternatively, polymer nanocomposites have gained significant popularity as electromagnetic interference (EMI) shielding materials because of their low cost, facile synthesis and ease of processing.

Different thermoplastic and thermoset polymer matrices have been explored for development of lightweight composite material for EMI shielding applications. Among the thermoplastic polymers, thermoplastic polyurethanes (TPU) have attracted a great deal of attention due to their combination of properties such as flexibility, stretchability, transparency, good abrasion and chemical resistance, good wear and weather resistance and good mechanical properties. Although graphene and carbon nanotubes have been explored as conducting fillers in polyurethane matrix for the development of EMI shields, however no reports are available using a combination of these fillers along with magnetic nanoparticles in thermoplastic polyurethane matrix. Therefore, it was of great interest to investigate graphene and graphene based hybrid fillers and their composites with TPU matrix as efficient EMI shielding material. In addition to the EMI shielding, thermal, mechanical and electrical properties have also been discussed.

The thesis has been divided into six chapters. **Chapter 1** deals with the brief introduction of electromagnetic radiation and interference along with the method used and materials required for EMI shielding. Graphene is discussed briefly including structure, properties, synthesis techniques and integration to hybrid filler. Different processing techniques used to fabricate polymer composites are described. It also summarizes the literature reports based on the thermal and mechanical properties, electrical conductivity and EMI shielding performance of graphene/TPU nanocomposites.

The detailed methods used for the synthesis of reduced graphene oxide (RGO), graphene-carbon nanotubes hybrid,  $\text{BaFe}_{12}\text{O}_{19}$ @RGO and  $\text{BaFe}_{12}\text{O}_{19}$ @GCNT hybrid fillers and also illustrations of different techniques and underlying principles for their detailed characterization are given in **Chapter 2** of thesis. Fabrication of nanocomposites of TPU with above mentioned fillers and their detailed characterization is also a part of this chapter.

The effect of reduced graphene oxide on the morphological, thermal, mechanical and electrical properties of thermoplastic polyurethane is discussed in **Chapter 3**. The polymer shows uniform adherence with the filler nanosheets and this adhesion is indicative of strong interactions between filler and matrix. A marginal enhancement in the thermal stability and tensile modulus of TPU was observed with the addition of RGO. The developed PUG nanocomposites exhibited an EMI shielding value of -21 dB in the X-band (8.2–12.4 GHz) and -38 dB in the Ku-band (12.4–18 GHz) for 10 wt.% RGO loading at sample thickness of 3 mm. These composites show a low percolation threshold of 0.81 wt.% which is mainly attributed to the formation of first continuous network of conducting interconnected graphene nanosheets in the insulating polyurethane matrix.

Adding hybrid fillers to a polymer matrix has proven to be a favorable way to improve the physical properties of polymer nanocomposites. In this regard, graphene and carbon nanotubes are integrated into a hybrid structure (GCNT) and their synergistic effect on the thermal, mechanical, morphological and electrical properties of thermoplastic polyurethane was investigated and discussed in **Chapter 4**. Morphological studies reveal the formation of hybrid nanostructure with CNTs adsorbed on the graphene sheets. Raman and FTIR spectroscopic techniques were employed to characterize the structural changes occurring in the hybrid filler based nanocomposites. The tensile modulus of nanocomposites increased upon incorporation of GCNT filler. The developed PUGCNT nanocomposites exhibited an EMI shielding value of -34 dB in the X-band and -47 dB in the Ku-band at 10 wt.% GCNT loading which was much better than the RGO/TPU composites.

Since, some strategic applications requires to reduce the contribution of shielding effectiveness due to reflection, magnetic filler barium hexaferrite has been introduced along with the above mentioned conducting fillers in the last part of the thesis. **Chapter 5** focuses on the EMI shielding performance of barium ferrite decorated reduced graphene oxide /or barium ferrite decorated graphene-carbon nanotubes hybrid/polyurethane nanocomposites. The presence of different phases has been confirmed by XRD, TEM/HRTEM, FTIR and Raman spectroscopic analysis. The total EMI shielding effectiveness of barium ferrite decorated reduced graphene oxide hybrid and barium ferrite decorated graphene-carbon nanotubes hybrid is achieved upto -32 dB and -84 dB in the Ku band. Composites of polyurethane as matrix and the above mentioned hybrids as filled inclusions crossed the required limit of the EMI shielding value for commercial applications and suggest the suitability of these nanocomposites as capable aspirants to make futuristic radar absorbers.

**Chapter 6** summarizes the key findings of the study, gives major conclusions and offers the need to demonstrate the practical utility and commercial viability of these nanocomposites as EMI shields. Suggestions for the future work are also included.

## सारांश

विद्युतीय उपकरणों जैसे सेल फोन, ताररहित फोन, वाईफाई राउटर्स या ब्लूटूथ-सक्षम उपकरण से विद्युत चुम्बकीय विकिरण का अधिक मात्रा में उत्सर्जित होना विद्युत चुम्बकीय प्रदूषण कहलाता है और इन उपकरणों के साथ हमारा संबंध बहुत घनिष्ठ हो गया है। विद्युत चुम्बकीय प्रदूषण के दोनों, इलेक्ट्रॉनिक उपकरणों और जैविक प्रजातियों पर गंभीर प्रभाव, अनुसंधान समुदाय के लिए गहन चिंता का विषय है। इसलिए, ऐसे अनिवार्य परन्तु हानिकारक विद्युत चुम्बकीय विकिरणों से सुरक्षा या तो इनको अवरुद्ध पैदा करके या परिरक्षित करके की जानी चाहिए। आमतौर पर परिरक्षण के लिए धातुएं, एक पसंदीदा पदार्थ के रूप में इस्तेमाल की जाती हैं, लेकिन इनका भारी वजन, संक्षारण के प्रति संवेदनशीलता और बोझिल प्रसंस्करण विधियां इन्हे शोधकर्ताओं और उपयोगकर्ताओं दोनों के लिए अनुपयुक्त बनाते हैं। वैकल्पिक रूप से, बहुलक नैनोकंपोजिट्स उनकी कम कीमत, सहज संश्लेषण और आसान प्रसंस्करण की वजह से विद्युत चुम्बकीय हस्तक्षेप (ईएमआई) परिरक्षण पदार्थ के रूप में काफी लोकप्रियता प्राप्त कर चुके हैं।

ईएमआई परिरक्षण अनुप्रयोगों के लिए, हल्के मिश्रित पदार्थों, के विकास के लिए विभिन्न थर्मोप्लास्टिक तथा थर्मोसेट बहुलक मैट्रिक्स की खोज की गयी है। थर्मोप्लास्टिक पॉलिमर्स के बीच, थर्मोप्लास्टिक पॉलीयूरेथेंस (टीपीयू) ने उनके लचीलेपन, विस्तारण, पारदर्शिता, अच्छे घर्षण, रासायनिक प्रतिरोध, वियर प्रतिरोध, मौसम प्रतिरोध और अच्छे यांत्रिक गुण जैसे कई गुणों के कारण बहुत अधिक ध्यान आकर्षित किया है। यद्यपि ईएमआई परिरक्षण के विकास के लिए, ग्रेफ़ीन और कार्बन नैनोट्यूब को पॉलीयूरेथेन मैट्रिक्स में चालक फिलर्स के रूप में इस्तेमाल किया गया है, फिर भी थर्मोप्लास्टिक पॉलीयूरेथेन मैट्रिक्स में चुंबकीय नैनोकणों के साथ इन फिलर्स के संयोजन के इस्तेमाल पर कोई रिपोर्ट उपलब्ध नहीं है। इसलिए ग्रेफ़ीन तथा ग्रेफ़ीन आधारित हाइब्रिड फिलर्स तथा उनके टीपीयू मैट्रिक्स के साथ संयोजन का एक कुशल ईएमआई

परिरक्षण पदार्थ के रूप में जांच बहुत ही रुचि का विषय था। ईएमआई परिरक्षण के साथ साथ ऊष्मीय, यान्त्रिकी और विद्युतीय गुणों की भी चर्चा की गयी है।

इस थीसिस को छह अध्यायों में विभाजित किया गया है। **अध्याय 1** में विद्युत चुम्बकीय विकिरण और हस्तक्षेप के संक्षिप्त परिचय के साथ साथ ईएमआई परिरक्षण के लिए आवश्यक पदार्थों तथा उसके लिए प्रयोग की जाने वाली विधियों के बारे में बताया गया है। ग्रेफ़ीन की संरचना, गुण, संश्लेषण विधि और हाइब्रिड फिलर के लिए एकीकरण की संक्षेप में चर्चा की गयी है। बहुलक कंपोजिट को प्रसंस्करण करने की विभिन्न तकनीकों का वर्णन किया गया है। इस अध्याय में ग्रेफ़ीन / टीपीयू नैनोकंपोजिट्स के ऊष्मीय और यान्त्रिकी गुणों, विद्युत चालकता और ईएमआई परिरक्षण प्रदर्शन पर मौजूद साहित्य का सारांश भी दिया गया है।

रिड्यूस्ड ग्रेफ़ीन ऑक्साइड (आरजीओ), ग्रेफ़ीन -कार्बन नैनोट्यूब हाइब्रिड, बेरियम फेराइट द्वारा सजाए गए रिड्यूस्ड ग्रेफ़ीन ऑक्साइड हाइब्रिड और बेरियम फेराइट द्वारा सजाए गए ग्रेफ़ीन -कार्बन नैनोट्यूब हाइब्रिड फिलर्स के संश्लेषण में इस्तेमाल की गयी विस्तृत विधियों तथा उनके विस्तृत लक्षण वर्णन के लिए इस्तेमाल की गयी विभिन्न तकनीकों और अंतर्निहित सिद्धांतों का विस्तृत वर्णन थीसिस के **अध्याय 2** में किया गया है। उपर्युक्त फिलर के साथ टीपीयू के नैनोकंपोजिट्स का निर्माण और उनका विस्तृत लक्षण वर्णन भी इस अध्याय का एक हिस्सा है।

**अध्याय 3** में थर्मोप्लास्टिक पॉलीयूरेथेन के मॉर्फोलॉजिकल, ऊष्मीय, यांत्रिकीय और विद्युतीय गुणों पर आरजीओ के प्रभाव की चर्चा की गयी है। बहुलक नैनो शीट्स फिलर के साथ एकसमान चिपकाव दिखाता है और यह चिपकाव फिलर और मैट्रिक्स के बीच एक मजबूत आसंजन का संकेत है। आरजीओ के मिलाने से टीपीयू की ऊष्मीय स्थिरता और तन्य मापांक में एक अत्यल्प वृद्धि देखी गई है। 10 वेट% आरजीओ मिलाने पर 3 मिमी मोटे पीयूजी नैनोकंपोजिट्स नमूने ने एक्स-बैंड (8.2-12.4 गीगाहर्ट्ज) में - 21 डीबी एवं केयू-बैंड (12.4-18 गीगाहर्ट्ज) में - 38 डीबी ईएमआई परिरक्षण मूल्य को दर्शाया है। इन

कंपोजिट्स ने 0.81 वेट% की कम पर्कोलेशन थ्रेशोल्ड को दर्शाया है जो मुख्य रूप से कुचालक पॉलीयूरेथेन मैट्रिक्स में एक दूसरे से जुड़े हुए चालक ग्रेफ़ीन नैनोशीट के सतत नेटवर्क के गठन होने की वजह से होता है।

किसी बहुलक मैट्रिक्स के साथ एक हाइब्रिड फिलर्स का जोड़ना, बहुलक नैनोकंपोजिट्स के भौतिक गुणों को बेहतर बनाने के लिए एक अनुकूल तरीका साबित हुआ है। इस संबंध में, ग्रेफ़ीन और कार्बन नैनोट्यूब को हाइब्रिड संरचना (जीसीएनटी) में एकीकृत किया गया है और थर्मोप्लास्टिक पॉलीयूरेथेन के ऊष्मीय, यांत्रिकीय, मॉर्फोलॉजिकल और विद्युतीय गुणों पर उनके सहयोगी प्रभाव की जांच और चर्चा **अध्याय 4** में की गई है। मॉर्फोलॉजिकल अध्ययन से हाइब्रिड नैनोस्ट्रक्चर के गठन का पता चला है जिसमें कार्बन नैनोट्यूब्स ग्रेफ़ीन शीट्स पर अधिशोषित थीं। रमन और एफटीआईआर स्पेक्ट्रोस्कोपिक तकनीक हाइब्रिड फिलर आधारित नैनोकंपोजिट्स में होने वाले संरचनात्मक परिवर्तनों को चिह्नित करने के लिए नियोजित की गई है। जीसीएनटी फिलर के निगमन से नैनोकंपोजिट्स के तन्यता मापांक में बढ़ोतरी हुई है। विकसित पीयूजीसीएनटी नैनोकंपोजिट्स ने 10 वेट% जीसीएनटी मिलाने पर एक्स-बैंड में -34 डीबी और केयू-बैंड में -47 डीबी ईएमआई परिरक्षण का प्रदर्शन किया जोकि आरजीओ / टीपीयू कंपोजिट से काफी बेहतर था।

चूंकि, कुछ रणनीतिक अनुप्रयोगों में प्रतिबिंब के कारण परिरक्षण प्रभावशीलता के योगदान को कम करने की आवश्यकता होती है, इसलिए बेरियम हेग्ज़ाफेराइट चुंबकीय फिलर को थ्रीसिस के अंतिम भाग में उपरोक्त उल्लिखित चालक फिलर्स के साथ पेश किया गया है। **अध्याय 5** को बेरियम फेराइट द्वारा सजाए गए रिड्यूस्ड ग्रेफ़ीन ऑक्साइड हाइब्रिड तथा बेरियम फेराइट द्वारा सजाए गए ग्रेफ़ीन-कार्बन नैनोट्यूब हाइब्रिड/ पॉलीयूरेथेन नैनोकंपोजिट्स के ईएमआई परिरक्षण प्रदर्शन पर केंद्रित किया गया है। विभिन्न रूप की उपस्थिति की पुष्टि एक्सआरडी, टीईएम/ एचआरटीईएम, एफटीआईआर और रमन स्पेक्ट्रोस्कोपिक विश्लेषण द्वारा की गई है। बेरियम फेराइट द्वारा सजाए गए रिड्यूस्ड ग्रेफ़ीन ऑक्साइड हाइब्रिड और बेरियम

फेराइट द्वारा सजाए गए ग्राफीन-कार्बन नैनोट्यूब हाइब्रिड की कुल ईएमआई परिरक्षण प्रभावशीलता को केयू-बैंड में -32 डीबी और -84 डीबी तक हासिल किया गया है। मैट्रिक्स के रूप में पॉलीयुरेथेन और फिलर के रूप में उपर्युक्त हाइब्रिड के कंपोजिट्स ने वाणिज्यिक अनुप्रयोगों के लिए ईएमआई परिरक्षण की आवश्यक सीमा को पार कर दिया है और भविष्य में रडार अवशोषक बनाने के लिए सक्षम उम्मीदवारों के रूप में इन नैनोकंपोजिट्स की उपयुक्तता का सुझाव दिया है।

**अध्याय 6** में अध्ययन के मुख्य निष्कर्षों का सारांश तथा प्रमुख निष्कर्षों को दिया गया है तथा ईएमआई परिरक्षण के रूप में इन नैनोकंपोजिट्स की व्यावहारिक उपयोगिता और वाणिज्यिक व्यवहार्यता प्रदर्शित करने की आवश्यकता को बताया गया है। इस अध्याय में भविष्य में किए जाने वाले काम पर सुझावों को भी शामिल किया गए हैं।

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