

**STUDIES ON HYBRID 3D CARBONACEOUS  
NANOFILLERS BASED MULTIFUNCTIONAL  
THERMOPLASTIC POLYURETHANE COMPOSITES**

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*by*

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Submitted

in partial fulfillment of the requirements for the

Degree of **Doctor of Philosophy**

**to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**JULY, 2024**

*DEDICATED*  
*TO*  
*MY PARENTS*  
*SUPERVISORS*  
*WIFE, SON & DAUGHTER*

## CERTIFICATE

This is to certify that the thesis entitled “**Studies on hybrid 3D carbonaceous nanofillers based multifunctional thermoplastic polyurethane composites**” being submitted by **Mr. Subhash Mandal**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile & Fiber Engineering, is a record of bonafide research work carried out by him. Mr. Subhash Mandal has worked under our guidance and supervision and fulfilled all the requirements for the submission of the thesis. The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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## Abstract

Polymer nanocomposites containing carbon nanotubes (CNTs) and graphene are influenced by several factors, including the methods used for CNTs and graphene synthesis, functional group introduced, purification, geometrical and structural attributes, their alignment within the composite material, the dispersion techniques, and the manufacturing processes. Overcoming the challenge of graphene exfoliation is a significant issue. To address the dispersion and exfoliation challenges, hybrid 3D nanofillers have been developed by immobilizing the multiwall carbon nanotubes (MWCNTs) into few layer graphene (FLG) flakes and subsequently evaluating their performance. The dispersion of the developed nanofillers has been improved by the formation of cellular structure of polyurethane nanocomposites. The developed nanocomposites have also been evaluated for multifunctional properties. Further preparation and evaluation of the metal-decorated CNTs and graphene have also been investigated to increase the microwave absorption properties. The hybrid 3D nanofiller reinforced polyurethane nanocomposites have been found to enhance physical properties viz. gas barrier and microwave absorption properties.

The main challenge to develop flexible polymeric films based on polyurethane and hybrid 3D carbonaceous nanofillers for gas barrier properties is the dispersion of carbonaceous nanofillers viz. CNTs and graphene or graphite nanoflakes into the polymer matrix. To enhance the dispersion of carbonaceous nanofillers one of the most important things is that they need to be functionalized. Though the functionalization of nanofiller helps to enhance the dispersion still it can be improved further by adopting a novel concept by adapting a thermo-chemical technique with the combination of (i) formation of cellular structure by thermo-responsive gel formation method and (ii) compounding by melt mixing through twin screw extrusion (TSE) technique. The enhancement in dispersion leads to the increase of the length of tortuous path of helium gas which plays the main role to improve the gas barrier property.

The interfacial interactions and characteristics of a polyurethane nanocomposite with a cellular structure, utilizing carbonaceous nano-fillers have been investigated. The effect of carbonaceous nanofillers viz. multiwall carbon nanotube (MWCNTs), few layer graphene (FLG) flakes and carboxylated MWCNT immobilized into the hydroxylated FLG (FLG-OH) as 3D nanofillers in thermoplastic polyurethane (TPU) on the tensile properties of the fabricated cellular structures has been studied. The concentration of nanofillers was varied as 0.1, 1 and 5 wt%. The results have shown significant increase of the tensile strength and modulus for 2D and 3D nanofillers incorporated TPU cellular structures. The interfacial adhesion was calculated by using experimental tensile data and predictive models. The interfacial adhesion parameter ( $B_{\sigma}$ ) calculated using the Pukanszky equation was found significantly higher value for 2D ( $B_{\sigma 20} = 195.8$ ) and 3D ( $B_{\sigma 20} = 192.0$ ) fillers.

The large-scale dispersion of the hierarchical (1D, 2D & 3D) carbonaceous nanofillers in thermoplastic polyurethane has been carried out through two routes- (i) cellular structure formation using supramolecular self-assembly route (SSAR) followed by twin screw extrusion (TSE) and (ii) direct TSE technique. The hierarchical nanofillers viz. carboxylated multiwall carbon nanotubes (MWCNT-COOH), hydroxylated few layer graphene (FLG-OH) flakes, and hybrid 3D were dispersed into TPU by TSE. The concentration of nanofillers was varied as 0.25, 0.5, 1.0, 2.0 and 5 wt%. To increase the level of dispersion, hybrid 3D nanofillers were also incorporated into TPU by making cellular structures through SSAR followed by TSE. The large-scale uniform dispersion was observed at higher loading (2 wt%) by SSAR followed by TSE when compared with direct TSE. However, uniform dispersion was observed at 1 wt% loading by direct TSE.

The mechanism, measurement and mathematical models to validate experimental data have been carried out using hybrid 3D nanofiller incorporated polyurethane nanocomposite films with enhanced gas barrier properties. This study reported the potential of hybrid 3D nanofillers

for the improvement of helium gas barrier properties of segmented TPU film. Hybrid 3D nanofiller incorporated PU nanocomposite (PUNC) films were prepared by making cellular structure through SSAR followed by TSE and subsequent compression molding. The concentration of hybrid 3D nanofillers was varied within the range of 0 to 5 wt% to achieve uniform dispersion and higher exfoliation of graphene sheets in the PU matrix. Increasing the concentration of hybrid 3D nanofillers led to a gradual improvement in the gas barrier properties of nanocomposite films. Specifically, at a 2 wt% loading of hybrid 3D nanofillers, helium gas permeability decreased by around 63%. To validate these findings, well-established models such as the Nielsen, Bhardwaj, and Cussler-random array models were employed. Notably, the Cussler-random array model, with aspect ratios of 90 and 180, proved most effective (up to 2 wt% loading) for assessing the gas barrier properties of PU nanocomposite films. The strong hydrogen bonding interactions between PU and the hybrid 3D nanofiller played a pivotal role in achieving a high degree of nanofiller dispersion within the PU matrix, consequently enhancing the gas barrier properties of the PU nanocomposite films.

The infusion of magnetic characteristics by decorating metal nanoparticles, specifically iron (Fe) and nickel (Ni), onto the surface of hybrid 3D carbonaceous nanofillers has also been investigated. The impact of these metal nanoparticles on the microstructural and microwave absorption properties of hybrid 3D nanofillers, as well as their polyurethane (TPU) nanocomposites, have been explored at concentration varying from 5, 10, 15 and 20 wt% loading. Fe-3D and Ni-3D nanomaterials have demonstrated considerable potential for Electromagnetic Interference (EMI) shielding applications, particularly for microwave absorption where a 10 dB value is required. The highest EMI shielding effectiveness (EMI SE) attenuation is observed for Fe-3D nanomaterials, reaching 28 dB, attributed to their high conductivity ( $16 \text{ Sm}^{-1}$ ). In comparison, Ni-3D nanomaterials exhibit a lower EMI SE of 22 dB, owing to their relatively lower conductivity ( $8 \text{ Sm}^{-1}$ ). Morphological factors of the nanofillers,

such as aspect ratio, dispersion within the polymeric matrix, and nanofiller concentrations, significantly influence the shielding effectiveness of resulting TPU/Fe-3D and TPU/Ni-3D nanocomposites. The study highlights that TPU/Fe-3D and TPU/Ni-3D nanocomposites with almost uniform dispersion can be effectively prepared using a solution casting route upto 5 wt% loading. However, at higher loadings (10, 15, and 20 wt%), agglomeration, non-uniform dispersion, and restacking of few-layer graphene (FLG) flakes of metal-decorated hybrid 3D nanofillers have been observed in TPU nanocomposites. TPU/Fe-3D nanocomposites exhibit superior EMI SE compared to TPU/Ni-3D nanocomposites. Both TPU/Fe-3D and TPU/Ni-3D nanocomposites at a loading of 20 wt% showcase potential as effective EMI shielding materials, achieving a total shielding effectiveness higher than 10 dB like 28 dB and 22 dB for Fe-3D and Ni-3D respectively. The findings suggest that these nanocomposites can serve as effective solutions for EMI shielding applications.

## सार

कार्बन नैनोट्यूब (CNT) और ग्राफीन युक्त पॉलिमर नैनोकम्पोजिट कई कारकों से प्रभावित होते हैं, जिनमें CNT और ग्राफीन संश्लेषण के लिए उपयोग की जाने वाली विधियां, पेश किए गए कार्यात्मक समूह, शुद्धि, ज्यामितीय और संरचनात्मक विशेषताएं, समग्र सामग्री के भीतर उनका संरेखण, फैलाव तकनीक और विनिर्माण प्रक्रियाएँ शामिल हैं। ग्राफीन एक्सफोलिएशन की चुनौती पर काबू पाना एक महत्वपूर्ण मुद्दा है। फैलाव और एक्सफोलिएशन चुनौतियों का समाधान करने के लिए, मल्टीवॉल कार्बन नैनोट्यूब (MWCNT) को कुछ परत ग्राफीन (FLG) प्लेक्स में स्थिर करके और बाद में उनके प्रदर्शन का मूल्यांकन करके हाइब्रिड 3डी नैनोफिलर्स विकसित किया गया है। पॉलीयूरेथेन नैनोकम्पोजिट्स की सेलुलर संरचना के निर्माण से विकसित नैनोफिलर्स के फैलाव में सुधार हुआ है। विकसित नैनोकम्पोजिट का मूल्यांकन बहुकार्यात्मक गुणों के लिए भी किया गया है। माइक्रोवेव अवशोषण गुणों को बढ़ाने के लिए धातु से सजाए गए CNT और ग्राफीन की आगे की तैयारी और मूल्यांकन की भी जांच की गई है। हाइब्रिड 3डी नैनोफिलर प्रबलित पॉलीयूरेथेन नैनोकम्पोजिट्स को गैस अवरोध और माइक्रोवेव अवशोषण गुणों जैसे भौतिक गुणों को बढ़ाने के लिए पाया गया है।

गैस अवरोधक गुणों के लिए पॉलीयूरेथेन और हाइब्रिड 3डी कार्बोनेसियस नैनोफिलर्स पर आधारित लचीली पॉलिमरिक फिल्में विकसित करने की मुख्य चुनौती कार्बोनेसियस नैनोफिलर्स का फैलाव है। पॉलिमर मैट्रिक्स में CNT और ग्राफीन या ग्रेफाइट नैनोप्लेक्स। कार्बोनेसियस नैनोफिलर्स के फैलाव को बढ़ाने के लिए सबसे महत्वपूर्ण चीजों में से एक यह है कि उन्हें क्रियाशील करने की आवश्यकता है। यद्यपि नैनोफिलर की क्रियाशीलता फैलाव को बढ़ाने में मदद करती है, फिर भी इसे (i) थर्मो-रेस्पॉन्सिव जेल निर्माण विधि द्वारा सेलुलर संरचना के गठन और (ii) ट्विन स्कू एक्सट्रूजन (TSE) तकनीक के माध्यम से पिघल मिश्रण द्वारा कंपाउंडिंग के संयोजन के साथ थर्मो-रासायनिक तकनीक को अपनाकर एक नवीन अवधारणा को अपनाकर और बेहतर बनाया

जा सकता है। फैलाव में वृद्धि से हीलियम गैस के टेढ़े-मेढ़े पथ की लंबाई में वृद्धि होती है जो गैस अवरोधक संपत्ति में सुधार करने में मुख्य भूमिका निभाती है।

कार्बोनेसियस नैनो-फिलर्स का उपयोग करके सेलुलर संरचना के साथ पॉलीयूरेथेन नैनोकम्पोजिट की इंटरफेशियल इंटरैक्शन और विशेषताओं की जांच की गई है। कार्बोनेसियस नैनोफिलर्स का प्रभाव निर्मित सेलुलर संरचनाओं के तन्व गुणों पर थर्मोप्लास्टिक पॉलीयूरेथेन (TPU) में 3डी नैनोफिलर्स के रूप में मल्टीवॉल कार्बन नैनोट्यूब (MWCNT), कुछ परत ग्राफीन (FLG) के टुकड़े और हाइड्रॉक्सिलेटेड एफएलजी (FLG-OH) में स्थिर किए गए कार्बोक्सिलेटेड एमडब्ल्यूसीएनटी का अध्ययन किया गया है। नैनोफिलर्स की सांद्रता 0.1, 1 और 5 wt% के रूप में भिन्न थी। परिणामों में टीपीयू सेलुलर संरचनाओं में शामिल 2डी और 3डी नैनोफिलर्स के लिए तन्व शक्ति और मापांक में उल्लेखनीय वृद्धि देखी गई है। प्रयोगात्मक तन्वता डेटा और पूर्वानुमानित मॉडल का उपयोग करके इंटरफेशियल आसंजन की गणना की गई थी। पुकन्ज़की समीकरण का उपयोग करके गणना की गई इंटरफेशियल आसंजन पैरामीटर (बी $\sigma$ ) को 2डी (बी $\sigma$ <sub>20</sub> = 195.8) और 3डी (बी $\sigma$ <sub>20</sub> = 192.0) फिलर्स के लिए काफी अधिक मूल्य पाया गया।

थर्मोप्लास्टिक पॉलीयूरेथेन में पदानुक्रमित (1डी, 2डी और 3डी) कार्बोनेसियस नैनोफिलर्स का बड़े पैमाने पर फैलाव दो मार्गों के माध्यम से किया गया है- (i) सुपरमॉलेक्यूलर सेल्फ-असेंबली रूट (SSAR) का उपयोग करके सेलुलर संरचना का निर्माण, इसके बाद ट्विन स्कू एक्सट्रूज़न (TSE) और (ii) प्रत्यक्ष टीएसई तकनीक। श्रेणीबद्ध नैनोफिलर्स अर्थात कार्बोक्सिलेटेड मल्टीवॉल कार्बन नैनोट्यूब (MWCNT-COOH), हाइड्रॉक्सिलेटेड कुछ परत ग्राफीन (FLG-OH) प्लेक्स, और हाइब्रिड 3D को TSE द्वारा थर्मोप्लास्टिक पॉलीयूरेथेन में फैलाया गया था। नैनोफिलर्स की सांद्रता 0.25, 0.5, 1.0, 2.0 और 5 wt% के रूप में भिन्न थी। फैलाव के स्तर को बढ़ाने के लिए, SSAR और TSE के माध्यम से सेलुलर संरचनाएं बनाकर हाइब्रिड 3डी

नैनोफिलर्स को भी थर्मोप्लास्टिक पॉलीयूरेथेन में शामिल किया गया था। प्रत्यक्ष TSE की तुलना में SSAR द्वारा टीएसई के बाद उच्च लोडिंग (2 wt%) पर बड़े पैमाने पर समान फैलाव देखा गया। हालाँकि, प्रत्यक्ष TSE द्वारा 1 wt% लोडिंग पर एकसमान फैलाव देखा गया।

प्रयोगात्मक डेटा को मान्य करने के लिए तंत्र, माप और गणितीय मॉडल को उन्नत गैस अवरोधक गुणों के साथ हाइब्रिड 3डी नैनोफिलर शामिल पॉलीयूरेथेन नैनोकम्पोजिट फिल्मों का उपयोग करके किया गया है। इस अध्ययन ने खंडित थर्मोप्लास्टिक पॉलीयूरेथेन फिल्म के हीलियम गैस अवरोधक गुणों में सुधार के लिए हाइब्रिड 3डी नैनोफिलर्स की क्षमता की सूचना दी। हाइब्रिड 3डी नैनोफिलर सम्मिलित पॉलीयूरेथेन नैनोकम्पोजिट (PUNC) फिल्में एसएसएआर के माध्यम से सेलुलर संरचना बनाकर और उसके बाद TSE और उसके बाद संपीड़न मोल्डिंग द्वारा तैयार की गईं। पॉलीयूरेथेन मैट्रिक्स में ग्राफीन शीट के एक समान फैलाव और उच्च एक्सफोलिएशन को प्राप्त करने के लिए हाइब्रिड 3डी नैनोफिलर्स की सांद्रता 0 से 5 wt% की सीमा के भीतर भिन्न थी। हाइब्रिड 3डी नैनोफिलर्स की सांद्रता बढ़ाने से नैनोकम्पोजिट फिल्मों के गैस अवरोधक गुणों में धीरे-धीरे सुधार हुआ। विशेष रूप से, हाइब्रिड 3डी नैनोफिलर्स की 2 wt% लोडिंग पर, हीलियम गैस पारगम्यता लगभग 63% कम हो गई। इन निष्कर्षों को मान्य करने के लिए, नील्सन, भारद्वाज और कुसलर-रैंडम ऐरे मॉडल जैसे अच्छी तरह से स्थापित मॉडल नियोजित किए गए थे। विशेष रूप से, 90 और 180 के पहलू अनुपात के साथ कुसलर-रैंडम ऐरे मॉडल, पीयू नैनोकम्पोजिट फिल्मों के गैस अवरोधक गुणों का आकलन करने के लिए सबसे प्रभावी (2 wt% लोडिंग तक) साबित हुआ। पॉलीयूरेथेन और हाइब्रिड 3डी नैनोफिलर के बीच मजबूत हाइड्रोजन बॉन्डिंग इंटरैक्शन ने पॉलीयूरेथेन मैट्रिक्स के भीतर उच्च स्तर के नैनोफिलर फैलाव को प्राप्त करने में महत्वपूर्ण भूमिका निभाई, जिसके परिणामस्वरूप पॉलीयूरेथेन नैनोकम्पोजिट फिल्मों के गैस अवरोधक गुणों में वृद्धि हुई।

हाइब्रिड 3डी कार्बोनेसियस नैनोफिलर्स की सतह पर धातु के नैनोकणों, विशेष रूप से लौह (Fe) और निकल (Ni) को सजाकर चुंबकीय विशेषताओं के समावेशन की भी जांच की गई है। हाइब्रिड 3डी नैनोफिलर्स के माइक्रोस्ट्रक्चरल और माइक्रोवेव अवशोषण गुणों के साथ-साथ उनके थर्मोप्लास्टिक पॉलीयूरेथेन नैनोकम्पोजिट्स पर इन धातु नैनोकणों के प्रभाव का 5, 10, 15 और 20 wt% लोडिंग से भिन्न सांद्रता पर पता लगाया गया है। Fe-3D और Ni-3D नैनोमटेरियल्स ने इलेक्ट्रोमैग्नेटिक इंटरफेरेंस (EMI) परिरक्षण अनुप्रयोगों के लिए काफी क्षमता प्रदर्शित की है, विशेष रूप से माइक्रोवेव अवशोषण के लिए जहां 10 dB मान की आवश्यकता होती है। उच्चतम EMI परिरक्षण प्रभावशीलता (EMI SE) क्षीणन Fe-3D नैनोमटेरियल्स के लिए देखा गया है, जो 28 dB तक पहुंच गया है, जो उनकी उच्च चालकता ( $16 \text{ Sm}^{-1}$ ) के कारण है। इसकी तुलना में, Ni-3D नैनोमटेरियल अपनी अपेक्षाकृत कम चालकता ( $8 \text{ Sm}^{-1}$ ) के कारण 22 dB की कम EMI SE प्रदर्शित करते हैं। नैनोफिलर्स के रूपात्मक कारक, जैसे पहलू अनुपात, पॉलिमरिक मैट्रिक्स के भीतर फैलाव, और नैनोफिलर सांद्रता, परिणामी TPU/Fe-3D और TPU/Ni-3D नैनोकम्पोजिट की परिरक्षण प्रभावशीलता को महत्वपूर्ण रूप से प्रभावित करते हैं। अध्ययन इस बात पर प्रकाश डालता है कि लगभग समान फैलाव वाले TPU/Fe-3D और TPU/Ni-3D नैनोकम्पोजिट को 5 wt% लोडिंग तक समाधान कास्टिंग मार्ग का उपयोग करके प्रभावी ढंग से तैयार किया जा सकता है। हालाँकि, उच्च लोडिंग (10, 15, और 20 wt%) पर, थर्मोप्लास्टिक पॉलीयूरेथेन नैनोकम्पोजिट्स में धातु-सजाए गए हाइब्रिड 3डी नैनोफिलर्स के कुछ-परत ग्राफीन (FLG) के ढेर का ढेर, गैर-समान फैलाव और रीस्टैकिंग देखी गई है। TPU/Fe-3D नैनोकम्पोजिट TPU/Ni-3D नैनोकम्पोजिट की तुलना में बेहतर EMI SE प्रदर्शित करते हैं। TPU/Fe-3D और TPU/Ni-3D नैनोकम्पोजिट दोनों 20 wt% की लोडिंग पर प्रभावी EMI परिरक्षण सामग्री के रूप में क्षमता प्रदर्शित करते हैं, जिससे Fe-3D और Ni-

के लिए 28 dB और 22 dB जैसे 10 dB से अधिक की कुल परिरक्षण प्रभावशीलता प्राप्त होती है। निष्कर्ष बताते हैं कि ये नैनोकम्पोजिट EMI परिरक्षण अनुप्रयोगों के लिए प्रभावी समाधान के रूप में काम कर सकते हैं।



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## List of Acronyms

|            |  |
|------------|--|
| CNTs       | Carbon nanotubes   |
| PNCs       | Polymer nanocomposites                                     |
| PU         | Polyurethane   |
| TPU/NPU    | Thermoplastic polyurethane/Neat thermoplastic polyurethane |
| HS         | Hard segments  |
| SS         | Soft segments  |
| GO         | Graphene oxide   |
| MWCNTs     | Multiwall carbon nanotubes                                 |
| f-MWCNTs   | Functionalized multiwall carbon nanotubes                  |
| MWCNT-COOH | Acid-functionalized multiwall carbon nanotubes             |
| FLG        | Few-layer graphene   |
| FLG-OH     | Hydroxylated few-layer graphene                            |
| LDCNs      | Low-dimensional carbonaceous nanofillers                   |
| VGCNFs     | Vapor grown carbon nanofibers                              |
| SWNTs      | Single wall nanotubes                                      |
| SSAR       | Supramolecular self-assembly route                         |
| TSE        | Twin crew extrusion  |
| MDI        | Methylene diphenyl diisocyanate                            |
| H12 MDI    | Hydrogenated MDI or 4,4'-diisocyanato dicyclohexylmethane  |
| HDI        | Hexamethylene diisocyanate                                 |
| IPDI       | Isophorone diisocyanate                                    |
| PVA        | Polyvinyl alcohol  |
| BIIR       | Brominated butyl rubber                                    |
| MMT        | Montmorillonite  |
| APTES      | Aminopropyl triethoxysilane                                |
| GNP        | Graphene nanoplatelet                                      |
| EVOH       | Ethylene vinyl alcohol copolymer                           |
| PVDC       | Polyvinylidene chloride                                    |
| PVDF       | Polyvinylidene fluoride                                    |
| PVF        | Polyvinyl fluoride   |
| BoPET      | Biaxially oriented polyester                               |

|          |   |
|----------|---|
| LDPE     | Low-density polyethylene  |
| PTFE     | Polytetrafluoroethylene   |
| FEP      | Fluorinated ethylene-propylene copolymer                            |
| POSS     | Polyhedral oligomeric silsesquioxane                                |
| DMF      | Dimethylformamide   |
| THF      | Tetrahydrofuran   |
| GNSs     | Graphene nanosheets   |
| RPUF     | Rigid PU foam   |
| EMI      | Electromagnetic interference  |
| MBRL     | Metal-backed reflection loss  |
| SE       | Shielding efficiency/effectiveness                                  |
| LTA      | Lighter than air  |
| FTIR     | Fourier transform infrared spectroscopy                             |
| TS       | Tensile strength  |
| TM       | Tensile modulus   |
| ATR-FTIR | Attenuated total reflection Fourier transform infrared spectroscopy |
| SEM      | Scanning electron microscopy  |
| WAXD     | Wide angle X-ray diffraction  |
| XRD      | X-ray diffraction   |
| TGA      | Thermogravimetric analysis  |
| XPS      | X-ray photoelectron spectroscopy                                    |
| TEM      | Transmission electron microscopy                                    |
| AFM      | Atomic force microscopy   |
| DMA      | Dynamic mechanical analysis   |

