

**TUNING THE BARRIER PROPERTIES OF COMPOSITE
FILM USING DISC SHAPED PARTICLES**

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JULY 2025

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Tuning the Barrier properties of Composite Film
using Disc Shaped Particles

by

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Submitted

In fulfilment of the requirement of doctor of philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

JULY 2025

Certificate

This is to certify that the thesis entitled “**Tuning the Barrier Properties of Composite Film Using Disc-Shaped Particles**” submitted by **Asad Abbas** in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy (PhD) in Chemical Engineering**, is a record of the original and bonafide research work carried out by him under my supervision and guidance.

The results embodied in this thesis have not been submitted to any other university or institution for the award of any degree or diploma.

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Acknowledgement

I would like to express my sincere gratitude to my **supervisor, Prof. Vikram Singh**, for his unwavering support, invaluable guidance, constant encouragement, and for placing his trust in me throughout the course of this research. His expertise and insightful suggestions have been instrumental in shaping this thesis.

I am also deeply thankful to my **SRC committee members — Prof. Anupam Shukla** (SRC Chair), **Prof. Sudip K. Pattanayek** (Department Expert), and **Prof. Leena Nebhani** (External Expert) — for their valuable feedback, regular evaluation, and constructive suggestions during the progress of my research.

I would like to extend my special thanks to the **Director of IIT Delhi** for providing institutional support and resources throughout this journey. My appreciation also goes to the **staff of the Central Research Facility (CRF)** and the **Nano Research Facility (NRF)** for their generous help with sample testing and analysis.

I extend my heartfelt thanks to my **dearest friend, Mohd. Faisal and Sayed Haider Abbas**, for being a constant source of motivation, positivity, and honest feedback. His friendship and support helped me navigate the highs and lows of this academic journey. I am also grateful to **all my labmates and juniors** for fostering a collaborative and intellectually stimulating research environment.

A **heartfelt and deepest thank you to my loving and caring family**, whose unconditional love, patience, and unwavering belief in me have been my foundation. Their emotional strength and sacrifices made this accomplishment possible.

This work is not merely the result of individual effort but a collective journey, made meaningful by the support and presence of all those around me.

Abstract

The barrier to transport of solutes (ions, molecules and gases) through a polymeric film could be varied by adding impermeable fillers or particles (clay, metal oxides, hexagonal boron nitre (hBN) and graphene etc). These impermeable particles in composites creates long tortuous paths for diffusion of solute and hence have shown to decrease their permeability by several degrees as compared to the pure polymer matrix. Such enhanced barrier properties of composites mainly depend on loading, aspect ratio (ratio of thickness to diameter), dispersion and interaction of such particles within the polymer matrix. Clay particles (laponite, kaolinite and montmorillonite) used in composites are present in different morphological states or phases (exfoliated, intercalated, stacked and aggregated states), hence the permeability of composite films are expected to vary with the distribution of such phases in the polymer matrix. One of the objectives of this work is to study the change in barrier properties of polyvinyl alcohol (PVA) film with added laponite clay for liquid (dilute hydrochloric acid) transport. A significant change from exfoliated state of embedded particles to that of highly aggregated state may vary the barrier properties of such composites. The complex behaviour of such particles in composites may not only vary the barrier to transport of gases and liquids, but it may also affect the optical transmission of such composites. Moreover, the use of high aspect ratio particles (like graphene or graphene oxide) could further enhance the barrier properties even at low loading. Graphene oxide (GO) being hydrophilic shows better dispersion in PVA as compared to graphene (being hydrophobic).

While factors like filler loading and their aspect ratio are well controlled in the experimental studies, factor like alignment of the particles are not well controlled. There has been limited experimental study so far where the tuning of the properties

of composites membranes with well controlled alignment of thin platelet shaped particles (or sheets) has been done.

The current work focuses on tuning the alignment of modified graphene oxide (mGO) using external magnetic field. The mGO is prepared via adsorbing the iron oxide nanoparticles (IONPs) on graphene oxide (GO) at low pH. The mGO sheets showing magnetic response are aligned in parallel and perpendicular configurations in the polymer matrix using external magnetic field, along with random aligned in absence in absence of magnetic field to form composite samples. The IONPs and magnetic GO exhibits superparamagnetic behavior, which could result in an ultrahigh magnetic response (UHMR), allowing alignments to be achieved at low magnetic fields. The well-aligned composites exhibit varying optical properties, reflecting the influence of particle orientation. Finally, the pure and composite samples are characterized using various techniques to assess their morphology, optical behavior, topology, and barrier properties.

सारांश

घुलनशील पदार्थों (आयन, अणु और गैसों) के एक पॉलिमरिक फिल्म के माध्यम से परिवहन में अवरोध को अपारगम्य फिल्स या कणों (जैसे कि क्ले, धात्विक ऑक्साइड्स, हेक्सागोनल बोरॉन नाइट्राइड (hBN) और ग्रेफीन आदि) को जोड़कर बदला जा सकता है। ये अपारगम्य कण कॉम्पोज़िट्स में घुलनशील पदार्थ के प्रसरण के लिए लंबा और पेचदार मार्ग बनाते हैं, जिससे इनकी पारगम्यता शुद्ध पॉलिमर मैट्रिक्स की तुलना में कई गुना घट जाती है। ऐसे कॉम्पोज़िट्स की उन्नत अवरोधक विशेषताएँ मुख्य रूप से इन कणों की मात्रा (लोडिंग), उनके आयाम अनुपात (मोटाई से व्यास का अनुपात), फैलाव (डिस्पर्सन), और पॉलिमर मैट्रिक्स के भीतर इन कणों की पारस्परिक क्रिया पर निर्भर करती हैं।

कॉम्पोज़िट्स में उपयोग किए जाने वाले क्ले कण (लापोनाइट, काओलिनाइट और मॉन्टमोरिलोनाइट) विभिन्न आकृतिक अवस्थाओं या चरणों (एक्सफोलिएटेड, इंटरक्लेटेड, स्टैक्ड और एग्रीगेटेड) में उपस्थित रहते हैं। अतः, इन अवस्थाओं के वितरण के आधार पर कॉम्पोज़िट फिल्मों की पारगम्यता में भिन्नता आना स्वाभाविक है। इस कार्य का एक उद्देश्य यह अध्ययन करना है कि लिक्विड (द्रव) जैसे कि पतला हाइड्रोक्लोरिक एसिड के परिवहन के लिए पॉलीविनाइल अल्कोहॉल (PVA) फिल्म में लापोनाइट क्ले जोड़ने से अवरोधक गुणों में क्या परिवर्तन आता है। यदि समाहित कणों की अवस्था एक्सफोलिएटेड से अत्यधिक एग्रीगेटेड अवस्था की ओर जाती है, तो ऐसे कॉम्पोज़िट्स की अवरोधक विशेषताएँ उल्लेखनीय रूप से परिवर्तित हो सकती हैं। इन कणों का जटिल व्यवहार न केवल गैसों और द्रवों के परिवहन में अवरोध को बदल सकता है, बल्कि यह कॉम्पोज़िट्स की ऑप्टिकल (प्रकाशीय) पारगम्यता को भी प्रभावित कर सकता है।

इसके अलावा, उच्च आयाम अनुपात वाले कणों (जैसे कि ग्रेफीन या ग्रेफीन ऑक्साइड) का उपयोग करने से, कम लोडिंग पर भी कॉम्पोज़िट्स की अवरोधक विशेषताओं में और अधिक वृद्धि की जा सकती है। ग्रेफीन ऑक्साइड (GO) हाइड्रोफिलिक होने के कारण PVA में ग्रेफीन (जो हाइड्रोफोबिक है) की तुलना में बेहतर रूप से फैलता है।

जहाँ फिलर की मात्रा और आयाम अनुपात जैसे कारकों को प्रयोगों में अच्छी तरह नियंत्रित किया गया है, वहीं कणों के संरेखण (alignment) जैसे कारकों पर अभी तक बहुत सीमित नियंत्रण देखा गया है। अब तक बहुत ही सीमित प्रयोगात्मक अध्ययन हुए हैं जहाँ प्लेटलेट-आकार के कणों (या शीट्स) के संरेखण को अच्छी तरह से नियंत्रित करके कॉम्पोज़िट मेम्ब्रेन की विशेषताओं को बदला गया हो।

वर्तमान कार्य का उद्देश्य बाहरी चुम्बकीय क्षेत्र का उपयोग करके संशोधित ग्रेफीन ऑक्साइड (mGO) के सरिखण को ट्यून करना है। mGO को ग्रेफीन ऑक्साइड (GO) पर कम pH पर लौह ऑक्साइड नैनोकणों (IONPs) को सोखाकर तैयार किया गया है। mGO शीट्स, जो चुम्बकीय प्रतिक्रिया दर्शाती हैं, उन्हें बाहरी चुम्बकीय क्षेत्र की मदद से पॉलिमर मैट्रिक्स में समांतर और लंबवत सरिखण में व्यवस्थित किया जाता है, जबकि चुम्बकीय क्षेत्र की अनुपस्थिति में वे यादृच्छिक रूप से सरिखित होती हैं और इन तीनों अवस्थाओं में कॉम्पोजिट सैंपल तैयार किए जाते हैं। IONPs और चुम्बकीय GO सुपरपैरामैग्नेटिक व्यवहार दिखाते हैं, जिससे अत्यंत उच्च चुम्बकीय प्रतिक्रिया (UHMR) प्राप्त होती है और कम चुम्बकीय क्षेत्र पर भी प्रभावी सरिखण संभव हो पाता है।

सुसरिखित कॉम्पोजिट्स विभिन्न प्रकाशीय गुण प्रदर्शित करते हैं, जो कणों की दिशा-स्थिति के प्रभाव को दर्शाते हैं। अंततः, शुद्ध और कॉम्पोजिट सैंपल्स की संरचना, प्रकाशीय व्यवहार, सतह टोपोलॉजी, और अवरोधक गुणों को विभिन्न तकनीकों के माध्यम से विश्लेषित किया गया है।

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Nomenclature

λ X-ray wavelength (nm)

θ Bragg angle (degrees)

d Interlayer spacing (nm)

Fe₃O₄ Standard IONPs (Sigma-Aldrich)

FESEM Field Emission Scanning Electron Microscopy

FTIR Fourier Transform Infrared Spectroscopy

GO Graphene oxide

GO–Fe₃O₄ GO modified using standard IONPs

GO–IONPs Graphene oxide with adsorbed iron oxide nanoparticles (IONPs)

Graphene–IONPs Standard graphene modified using IONPs

Graphite and Graphene Standard samples

Graphite exfoliated (sonicated) Graphite ultrasonicated in absence of IONPs

Graphite–IONPs Graphite ultrasonicated in presence of IONPs

IONPs Iron oxide nanoparticles

Lap Laponite

PVA-Lap PVA-Laponite composite

PVA Polyvinyl alcohol

TEM Transmission Electron Microscopy

XRD X-ray Diffraction