

**PERFORMANCE OPTIMIZATION AND EVALUATION OF
MULTIFUNCTIONAL NANOCOMPOSITES AS MONO AND
BILAYERED SMART PACKAGING FILMS**

VIKRAMSINGH THAKUR



DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2024

©Indian Institute of Technology Delhi (IITD), New Delhi, 2024

**PERFORMANCE OPTIMIZATION AND EVALUATION OF
MULTIFUNCTIONAL NANOCOMPOSITES AS MONO AND
BILAYERED SMART PACKAGING FILMS**

by

VIKRAMSINGH THAKUR

Department of Materials Science and Engineering

Submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2024



Dedicated to my family



Father : Late Rajendrasingh Thakur

Mother : Mrs. Asha Thakur

Wife : Mrs. Nidhi Gupta

This work is a reflection of our shared journey

CERTIFICATE

This is to certify that the thesis entitled “Performance optimization and evaluation of multifunctional nanocomposites as mono and bilayered smart packaging films” submitted to the Indian Institute of Technology Delhi by Mr. Vikramsingh Thakur, for the award of the degree of Doctor of Philosophy in the Department of Materials Science and Engineering, is a bonafide record of original research work carried out by the candidate. 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. I further certify that Mr. Vikramsingh Thakur has fulfilled all the requirements for the submission of the thesis.

Bhabani. K. Satapathy

Professor

Department of Materials Science and Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi- 110016

ACKNOWLEDGEMENTS

An undertaking of this kind would not have been realized without the collective efforts of many individuals. Firstly, I would like to express my sincere gratitude to my thesis supervisor, Prof. Bhabani Satapathy. I am indebted to him for the guidance and opportunities which will help me throughout my career. He has always encouraged me to develop a deep understanding and carry out meaningful scientific research. I am grateful for his generosity in countless discussions, insightful suggestions and for giving me academic freedom to develop various skills. It is also necessary to mention his continuous availability and support throughout my Ph.D. and even during the trying times of COVID-19 lockdown, which were instrumental in an uninterrupted workflow.

I would also like to thank the SRC members, Prof. Josemon Jacob, Prof. Bijay Tripathi, and Prof. Bhanu Nandan for their valuable suggestions, encouragement, and feedback from time to time. Additionally, I would like to thank DRC (DMSE) for organizing half-yearly seminars, allowing me to disseminate my research findings and progress to a broader audience.

It is my pleasure to thank Mr. Surendra Sharma, Mr. Gajraj Singh, Mr. E. Islam, Mr. Jitendra Kumar, Mr. Ashish Sharma, Mr. Brijesh Kumar, Mr. Ashok Kapoor, Mr. Gyanendra Kr. Yadav, Dr. Molla Mehedi Hassan, Mrs. Astha Sharma, Mr. Kshitij Sharma and Dr. Pooja Semalti, for tremendous support in performing various experimental characterizations. I especially thank Mr. E. Islam for supporting infrastructural developments for the film unit setup. Additionally, Mr. Subhash Chand, Mr. Amit Kumar, Mr. Sudhir Pandey, Mrs. Jyoti, Mr. Ramesh, Mr. Narendra, Mrs. Shalini, and Mrs. Sunita Rani Arora have immensely helped and supported in various documentations, organizing seminars, and purchasing activities.

I extend my sincere thanks to all the colleagues in Processing Laboratory – Dr. S. Samantaray, Dr. D. Saha, Dr. D. Sharma, Dr. P. Chauhan, Dr. U. Chakraborty, K. Das, K Dubey,

H Peshne, S. Pathak, V. Rai, D. Sharma, S. Rautela, S. Gupta, A. Kasera and A. Kumar. I especially thank Mr. Akhlesh Rajak, Mr. Raghav Bansal, Mr. Sonu Singh, Dr. Saroj, and Dr. Saha for stimulating academic and non-academic discussions. I acknowledge all the collaborators for countless hours working together and doing impactful research. Working with all of them was a great pleasure and learning opportunity. I would also like to acknowledge the enlightening and insightful discussions with all the group members during the Saturday meetings.

I greatly acknowledge the generous financial support from the Prime Minister Research Fellowship for the Ph.D. assistantship that enabled me to pursue my research and attend conferences nationally and internationally

Expressing my sincerest gratitude to my family for their unwavering support and love – my parents, Late Rajendrsingh Thakur and Asha Thakur, my wife Nidhi Gupta. Their love and constant belief in me give me the strength to face challenges with utmost courage. I am always indebted to them for their continuous encouragement and tireless efforts, which have been indispensable to my success.

Vikramsingh

•

ABSTRACT

This thesis investigates the development and evaluation of nanocomposite materials for improved food packaging purposes, focusing on significant challenges in achieving multifunctionality regarding the issues of mechanical strength, barrier qualities, shelf-life enhancement and intelligent functionality. The research encompasses four interlinked studies, with each study expanding upon the discoveries of the preceding effort. Linear low-density polyethylene (LLDPE) nanocomposites film with organically modified clay (Cloisite 30B) as a filler and LLDPE-grafted-maleic anhydride (LLDPE-g-MA) as a modifier was prepared by extrusion film blowing. The thermal properties, as investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), indicated increased crystallinity with enhanced thermal stability. Morphological attributes of nanocomposite films were demonstrated by transmission electron microscopy, and the thickness distribution of clay platelets was analyzed by kite plot. The radius of gyration (R_g) of LLDPE chains is studied by small-angle X-ray scattering (SAXS) from the Guinier region. The analysis of tear fracture and its associated surface morphology was done by scanning electron microscopy (SEM). The oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) were measured for nanocomposite films. The 5 wt. % clay-loaded nanocomposite film showed a $\sim 23.5\%$ and $\sim 33.4\%$ decrease in WVTR and OTR, respectively, compared to that of neat LLDPE films. The effect of crystallinity on tear energy and the influence of clay thickness in film transmittance on the barrier properties of various nanocomposite films with varied clay content were discussed. The paper demonstrated the correspondence between lower R_g values to low platelet thickness, which in turn remained directly correlated to OTR and WVTR. Our study comprehensively demonstrates that there exists a correspondence between lower R_g values and $t_{\text{platelets}}$ thickness, which in turn remained directly correlated to OTR and WVTR, leading to a

significantly enhanced extent of barrier performance. This study can further be extrapolated for the fillers used for improving the barrier performance in the LLDPE matrix.

Expanding upon these discoveries, the studies examined hybrid nanocomposites that combine organically modified montmorillonite (O-MMT) with halloysite nanotubes (HNT). The combination of nanosheets and nanotubes led to enhanced mechanical and barrier properties due to their synergistic effects. A smaller ratio of inter-particle distance to length ($\tau/d < 0.13$) was determined to be essential in order to achieve a high critical tear energy and outstanding barrier performance. The hybrid fillers exhibited improved ethylene absorption capability, indicating potential for prolonging the shelf life of fruits, namely bananas. Subsequently, the research advanced by integrating natural antioxidants, particularly resveratrol, into the nanocomposite system the strategy of using sustainable biomass resources instead of traditional antioxidants in synergy with nano-reinforced filler has been established as a food safety way to achieve ethylene scavenging efficiency with improved mecano-barrier performance. Herein, the effects of different content of resveratrol (0.5, 1.5, and 2 phr) and the inclusion of HNTs (5 wt. %) on the physiological weight loss, ripening index, and migratory properties of the resulting composite films for the enhanced shelf-life banana. The analysis of tear strength and its associated thermomechanical response was done using dynamic mechanical analysis. The oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) were measured for nanocomposite films. The 5 wt. % HNT-loaded nanocomposite film with 1.5 phr resveratrol showed a ~ 25.7 and $\sim 34.4\%$ decrease in WVTR and OTR, respectively, compared to that of neat LLDPE films. The ternary composite of LLDPE, HNT and resveratrol (LLHRe15) exhibited a maximum tear force of ~ 13.46 N, indicating a significant ~ 186.4 percent improvement compared to the neat LLDPE. Through the analysis of these factors in relation to banana preservation and the use of different substances that

simulate food, our goal is to clarify the mechanisms that contribute to the observed increase in shelf life and evaluate any potential restrictions in terms of migration behaviour.

The research resulted in the design of a novel packaging structure that consists of two layers and has advanced functional capabilities. Bilayered intelligent films based on electrospun polyvinyl alcohol/red cabbage extract-anthocyanins (PVA/RCA) nanofibrous mats, bolstered by oxygen-plasma treated clay-filled polyethylene/clay nanocomposites for monitoring the food freshness have been fabricated and evaluated. The nanofibrous mats (PVRC) of PVA/RCA were optimally fabricated by electrospinning, followed by their morphological and physio-mechanical characterization. The pH-responsive sensing of the PVRC mats to hydrochloric acid (HCl) and ammonia (NH₃) vapors as stimuli were analyzed using the absorption spectra corresponding to HCl and NH₃ at ~530 nm and ~650 nm, respectively. The oxygen transmission rate (OTR) of 1083.7 cc/m²/day and water-vapor transmission rate (WVTR) of 8 g/m²/day for the novel bi-layered electrospun mat-on-film packaging construct showed enhanced barrier performance with respect to stand-alone LLDPE blown-film (LL) with OTR and WVTR of 1502.8 cc/m²/day and 16.25 g/m²/day, respectively. The bi-layered constructs were further evaluated as freshness indicators by real-time monitoring of chickens and prawns for intelligent food packaging. This work makes a substantial contribution to the world of packaging science and technology through the development of a multifunctionality approach via utilizing natural/food-safe additives as active and intelligent agents for improved mechano-barrier, shelf-life enhancement, and integral intelligent functionalities.

सार

इस शोध प्रबंध में खाद्य पैकेजिंग के उद्देश्यों के लिए नैनोकॉम्पोजिट सामग्रियों के विकास और मूल्यांकन का अध्ययन किया गया है, जिसमें यांत्रिक शक्ति, अवरोध गुण, शेल्फ-लाइफ वृद्धि, और बुद्धिमान कार्यक्षमता के मुद्दों को लेकर बहुक्रियाशीलता प्राप्त करने की महत्वपूर्ण चुनौतियों पर ध्यान केंद्रित किया गया है। शोध में चार आपस में जुड़े अध्ययन शामिल हैं, जिनमें से प्रत्येक अध्ययन पिछले प्रयास की खोजों पर विस्तार करता है। क्लोइसाइट 30बी (Cloisite 30B) को फिलर और एलएलडीपीई-ग्लाइसेड-मेलिक एनहाइड्राइड (LLDPE-g-MA) को संशोधक के रूप में उपयोग करते हुए लीनियर लो-डेंसिटी पॉलीएथिलीन (LLDPE) नैनोकॉम्पोजिट फिल्म को एक्सट्रूजन फिल्म ब्लोइंग द्वारा तैयार किया गया। थर्मोग्रैविमेट्रिक विश्लेषण (TGA) और डिफरेंशियल स्कैनिंग कैलोरीमेट्री (DSC) द्वारा जांचे गए थर्मल गुणों ने थर्मल स्थिरता के साथ बढ़ी हुई क्रिस्टलीयता को संकेतित किया। नैनोकॉम्पोजिट फिल्मों के संरचनात्मक गुणों को ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी द्वारा प्रदर्शित किया गया, और मिट्टी के प्लेटलेट्स की मोटाई वितरण का विश्लेषण पतंग ग्राफ द्वारा किया गया। लीनियर लो-डेंसिटी पॉलीएथिलीन (LLDPE) श्रृंखला के जाईरेशन के त्रिज्या (R_g) का अध्ययन गिनियर क्षेत्र से स्मॉल-एंगल एक्स-रे स्कैटरिंग (SAXS) द्वारा किया गया। आंसू टूटने के विश्लेषण और इसके संबंधित सतह आकृति का अध्ययन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (SEM) द्वारा किया गया। नैनोकॉम्पोजिट फिल्मों के लिए ऑक्सीजन ट्रांसमिशन दर (OTR) और जल वाष्प ट्रांसमिशन दर (WVTR) को मापा गया। 5 wt. % क्ले-लोडेड नैनोकॉम्पोजिट फिल्म ने क्रमशः neat LLDPE फिल्मों की तुलना में WVTR और OTR में ~23.5 % और ~33.4 % की कमी दिखाई। विभिन्न नैनोकॉम्पोजिट फिल्मों के बैरियर गुणों पर फिल्म ट्रांसमिटेंस में आंसू ऊर्जा और क्ले मोटाई के प्रभाव की चर्चा की गई। इस अध्ययन से यह स्पष्ट हुआ कि निचले R_g मानों और प्लेटलेट्स की मोटाई के बीच संबंध है, जो बदले में OTR और WVTR से सीधे

संबंधित हैं, जिससे बैरियर प्रदर्शन में महत्वपूर्ण वृद्धि हुई है। इस अध्ययन को LLDPE मैट्रिक्स में बैरियर प्रदर्शन को बेहतर बनाने के लिए फिलर्स के उपयोग के लिए आगे बढ़ाया जा सकता है। इन खोजों का विस्तार करते हुए, शोधकर्ताओं ने ऑर्गेनिकली मॉडिफाइड मॉन्टमोरिलोनाइट (O-MMT) को हॉलोयसाइट नैनोट्यूब्स (HNT) के साथ मिलाकर हाइब्रिड नैनोकॉम्पोजिट्स का अध्ययन किया। नैनोशीट्स और नैनोट्यूब्स के संयोजन से उनके तालमेल प्रभावों के कारण यांत्रिक और अवरोध गुणों में वृद्धि हुई। उच्च क्रिटिकल आंसू ऊर्जा और उत्कृष्ट बैरियर प्रदर्शन प्राप्त करने के लिए कणों के बीच की दूरी से लंबाई का छोटा अनुपात ($\tau/d < 0.13$) आवश्यक पाया गया। हाइब्रिड फिलर्स ने बेहतर एथिलीन अवशोषण क्षमता दिखाई, जो फल, विशेष रूप से केले के शेल्फ जीवन को बढ़ाने की क्षमता को इंगित करता है। इसके बाद, शोध ने नैनोकॉम्पोजिट प्रणाली में प्राकृतिक एंटीऑक्सिडेंट्स, विशेष रूप से रेस्वेराट्रॉल को एकीकृत करके इसे आगे बढ़ाया। पारंपरिक एंटीऑक्सिडेंट्स के बजाय स्थायी बायोमास संसाधनों का उपयोग करने की रणनीति को नैनो-प्रबलित फिलर के साथ मिलाकर एथिलीन स्कैवेंजिंग दक्षता प्राप्त करने का एक खाद्य सुरक्षा तरीका स्थापित किया गया है, जिसमें मेहानो-बैरियर प्रदर्शन में सुधार हुआ है। यहां, रेस्वेराट्रॉल (0.5, 1.5, और 2 phr) की विभिन्न सामग्री और HNTs (5 wt. %) की सामग्री के प्रभाव को केले के शेल्फ जीवन को बढ़ाने के लिए प्राप्त होने वाली कॉम्पोजिट फिल्मों के शरीर के वजन घटाव, पकने का सूचकांक, और प्रवासन गुणों पर अध्ययन किया गया। डायनामिक मेकेनिकल विश्लेषण का उपयोग करके आंसू शक्ति और इसके संबंधित थर्मोमेकेनिकल प्रतिक्रिया का विश्लेषण किया गया। नैनोकॉम्पोजिट फिल्मों के लिए ऑक्सीजन ट्रांसमिशन दर (OTR) और जल वाष्प ट्रांसमिशन दर (WVTR) को मापा गया। 5 wt. % HNT-लोडेड नैनोकॉम्पोजिट फिल्म के साथ 1.5 phr रेस्वेराट्रॉल ने क्रमशः neat LLDPE फिल्मों की तुलना में WVTR और OTR में ~25.7 % और ~34.4 % की कमी दिखाई। तृतीयक कॉम्पोजिट (LLHRe15) ने ~13.46 N की अधिकतम आंसू बल प्रदर्शित की, जो neat LLDPE की तुलना में ~186.4 प्रतिशत सुधार दर्शाता है। केले के संरक्षण और विभिन्न पदार्थों के उपयोग के संबंध में इन कारकों का

विश्लेषण करके जो खाद्य पदार्थों का अनुकरण करते हैं, हमारा लक्ष्य शेल्फ लाइफ में देखी गई वृद्धि में योगदान देने वाले तंत्र को स्पष्ट करना और प्रवासन व्यवहार के संदर्भ में किसी भी संभावित प्रतिबंध का मूल्यांकन करना है। शोध का परिणाम एक नया पैकेजिंग संरचना डिजाइन में हुआ, जिसमें उन्नत कार्यात्मक क्षमताओं के साथ दो परतें शामिल हैं। भोजन की ताजगी की निगरानी के लिए इलेक्ट्रोस्पन पॉलीविनाइल अल्कोहल/रेड कैबेज एक्सट्रैक्ट-एंथोसाइनिन्स (PVA/RCA) नैनोफाइब्रस मैट्स पर आधारित बाइलेयर्ड बुद्धिमान फिल्मों का निर्माण और मूल्यांकन किया गया। PVA/RCA के नैनोफाइब्रस मैट्स (PVRC) का इलेक्ट्रोस्पनिंग द्वारा इष्टतम निर्माण किया गया, उसके बाद उनके संरचनात्मक और भौतिक-यांत्रिक गुणों का विश्लेषण किया गया। PVRC मैट्स की pH-संवेदनशील प्रतिक्रिया को हाइड्रोक्लोरिक एसिड (HCl) और अमोनिया (NH₃) वाष्प के रूप में उत्तेजनाओं के प्रति अवशोषण स्पेक्ट्रा का उपयोग करके विश्लेषित किया गया, जो क्रमशः ~530 nm और ~650 nm पर HCl और NH₃ से संबंधित था। नई बाइलेयर्ड इलेक्ट्रोस्पन मैट-ऑन-फिल्म पैकेजिंग संरचना के लिए ऑक्सीजन ट्रांसमिशन दर (OTR) 1083.7 cc/m²/day और जल वाष्प ट्रांसमिशन दर (WVTR) 8 g/m²/day थी, जो स्टैंडअलोन LLDPE ब्लोन-फिल्म (LL) के संबंध में बेहतर बैरियर प्रदर्शन दिखाती है, जिसमें क्रमशः OTR और WVTR 1502.8 cc/m²/day और 16.25 g/m²/day थी। बाइलेयर्ड संरचनाओं का आगे मूल्यांकन ताजगी सूचकों के रूप में किया गया, जिसमें बुद्धिमान खाद्य पैकेजिंग के लिए वास्तविक समय में मुर्गियों और झींगा का परीक्षण किया गया। यह कार्य खाद्य पैकेजिंग विज्ञान और प्रौद्योगिकी की दुनिया में महत्वपूर्ण योगदान करता है, जिसमें प्राकृतिक/खाद्य-सुरक्षित योजकों को सक्रिय और बुद्धिमान एजेंटों के रूप में उपयोग करके बहुक्रियाशीलता दृष्टिकोण का विकास किया गया है, जो बेहतर मेहानो-बैरियर, शेल्फ-लाइफ वृद्धि, और एकीकृत बुद्धिमान कार्यक्षमता प्राप्त करते हैं।

Table of Contents

CERTIFICATE.....	i
ACKNOWLEDGEMENTS.....	ii
ABSTRACT.....	iv
Table of Contents	x
List of Figures	xvi
List of Tables.....	xxi
List of Equations	xxiii
List of Symbols	xxiv
List of Abbreviations.....	xxvi
Chapter 1: Introduction and Literature Review	1-1
1.1 Introduction.....	1-1
1.2 Strategies for tear-resistant	1-4
1.3 Strategies for permeation resistance	1-8
1.3.1 Blending with High barrier polymers	1-8
1.3.2 Barrier Coating.....	1-9
1.3.3 Multilayer approaches.....	1-11
1.3.4 Filler Addition.....	1-13
1.4 Hybrid Strategies for tear-proof and permeation resistant.....	1-15
1.4.1 Thinner nanoplatelets via compatibilizer.....	1-15
1.4.2 Thinner platelets via filler modification.....	1-19

1.4.3 Improved interfacial adhesion via blending.....	1-20
1.5 Need of Hybrid Strategies is need in Multifunctional Active Packaging	1-21
compatibilizer	1-22
1.5.1 Super filler	1-23
1.5.2 Multilayer advanced approaches for Multifunctional properties.....	1-24
1.5.3 Antioxidant on shelf life as active packaging	1-25
1.5.4 Miscellaneous approaches for Multifunctionality	1-27
1.6 Intelligent agents for freshness detection.....	1-29
1.7 Migration concern of active and intelligent agents.....	1-31
Chapter 2: Materials and methodology	2-35
2.1 Materials	2-35
2.2 Fabrication of nanocomposites via melt mixing.....	2-36
2.3 Preparation of multifunctional mono-layered blown films.....	2-37
2.4 Preparation of bilayer halochromic films	2-38
2.4.1 Extraction of anthocyanins from red cabbage	2-38
2.4.2 Fabrication of PVA/RCA (PVRC) electrospun nanofibrous mat (Inner layer).....	2-39
2.4.3 Preparation and plasma treatment of LL/clay-based nanocomposite films (Outer layer)	2-40
2.4.4 Fabrication of consolidated Bilayered structure of PVRC mats deposited on LLC5 films	2-40
2.5 Characterization and evaluation of LLDPE/clay nanocomposites	2-41
2.5.1 Thermal characterization.....	2-41

2.5.2 Structural properties.....	2-42
2.5.3 Rheological measurements and transmittance	2-42
2.5.4 Mechanical Properties.....	2-43
2.5.5 Morphological analysis.....	2-44
2.5.6 Barrier properties	2-44
2.5.7 Antioxidant capacity	2-45
2.5.8 Water contact angle.....	2-45
2.6 Shelf life analysis.....	2-46
2.6.1 Ethylene absorption capacity	2-46
2.6.2 Shelf life analysis via physiological changes of banana.....	2-47
2.7 Migration analysis.....	2-47
2.8 Interaction assessment of electrospun mats with HCL and NH ₃ vapors.....	2-48
2.9 Responses of the indicator against fresh prawns and chicken-flesh	2-48
Chapter 3: Role of clay platelet thickness on tear mechanics and barrier performances of	
blown nanocomposite films	3-50
3.1 INTRODUCTION	3-51
3.2 Thermal analysis of LLDPE/clay nanocomposites.....	3-54
3.3 Rheological analysis of LLDPE/clay nanocomposites	3-56
3.4 X-ray diffraction (XRD) analysis of LLDPE/clay nanocomposites	3-58
3.5 Small-angle X-ray Scattering (SAXS).....	3-60
3.6 Transmission electron microscopy.....	3-64
3.6.1 Mechanical analysis	3-65

3.6.2 Uniaxial tensile response	3-65
3.6.3 Tear mechanics assessment	3-66
3.7 Dynamic mechanical analysis of nanocomposites.....	3-72
3.8 Assessment of barrier performance of nanocomposites.....	3-73
3.8.1 Water and gas barrier performance analysis	3-73
3.8.2 Theoretical modeling of oxygen transmission performance data	3-75
3.8.3 Theoretical modeling of oxygen transmission performance data	3-76
3.9 Summary	3-78
Chapter 4: Synergistic effect of halloysite and montmorillonite on permeation-resistance and shelf-life enhancement of packaging films	4-79
4.1 Introduction.....	4-80
4.2 Thermal and structural analysis of hybrid nanocomposites.....	4-84
4.3 Rheological analysis of hybrid nanocomposites.....	4-87
4.4 Dynamic mechanical analysis of nanocomposites.....	4-88
4.5 Mechanical properties.....	4-89
4.5.1 Uniaxial tensile response	4-89
4.5.2 Trouser tear testing.....	4-91
4.6 Transmission electron microscopy.....	4-95
4.7 Barrier properties of nanocomposites films	4-96
4.8 Shelf-life assessment of banana	4-99
4.9 Summary	4-101

Chapter 5: Combinatorial effects of halloysite nanotubes and resveratrol as antioxidant, on barrier performance and tear resistance blown nanocomposite films.....	5-102
5.1 Introduction.....	5-103
5.2 Thermal and Structural analysis of hybrid nanocomposites	5-105
5.3 Optical and barrier performance of blown films.....	5-110
5.4 Antioxidant capacity	5-113
5.4.1 DPPH Radical Scavenging Activity.....	5-113
5.4.2 ABTS Radical Scavenging Activity.....	5-114
5.5 Mechanical and thermomechanical analysis.....	5-116
5.5.1 Dynamic mechanical analysis.....	5-116
5.5.2 Trouser Tear Properties of LLDPE/Resveratrol and LLDPE/HNT/Resveratrol Nanocomposites.....	5-119
5.6 Shelf-life assessment.....	5-122
5.7 Migration concerns	5-127
5.8 Summary	5-129

Chapter 6: Electrospun nanofibrous mat-on-film bilayered constructs as halochromic freshness marker-enabled intelligent food packaging films with red cabbage anthocyanins ..	6-131
---	-------

6.1 Introduction.....	6-132
6.2 Spectral and color characterization of Red-cabbage anthocyanins.....	6-137
6.3 Structural analysis of the fabricated PVRC electrospun mats	6-140
6.4 Thermal and functional group analysis of PVRC mats	6-142

6.5 Interaction of PVRC mats with NH ₃ and HCl vapors	6-147
6.6 Mechanical properties and water contact angle of PVRC mats.....	6-150
6.7 Characterization of Oxygen-plasma of LL and LL/LL-g-MA/clay (outer layer)....	6-152
6.8 Barrier properties of bi-layered films of PVA mats on LL/clay type intelligent packaging film	6-158
6.9 Response of indicators with prawns and chicken flesh upon short-term storage/packaging	6-162
6.10 Summary	6-165
Chapter 7: Conclusion and future scope	7-167
7.1 Conclusion	7-167
7.2 Future scope	7-169
Bibliography	172
Appendix: I	208
Appendix: II.....	209
Publications and conferences.....	210
Biography.....	212

List of Figures

Figure 1.1 Schematic representation of multifunctional tear-proof and tear permeation resistant strategies	1-4
Figure 1.2 (a) Mechanism of tear propagation (b) and (c) tear fracture morphology of PP/POE/sCF, (d) Elmendorf tear sample, (e) surface morphology of PLA/PBS blends with nucleating agent, (g) Tear strength at different sCF concentration at MD and TD direction (Reproduced with permission from ref. [25] CC BY 4.0)	1-6
Figure 1.3 Platelets structure in (a) Uniaxial orientation (b) Biaxial orientation, (c) improvement in barrier via Al and PIB barrier coating on PET surface, and (d) Structure of Multilayer films	1-11
Figure 1.4 Strategies for improvement in tear and barrier properties (a) Melt mixing, (b) Thinner platelets via triad strategy, (c) and (d) dispersion morphology of aggregated and exfoliated nanofillers respectively, (e), (f) and (g) mechanism of melt mixing for improvement in gas barrier.	1-19
Figure 1.5 Active antioxidant packaging systems (adopted with permission from [100] Copyright © 2021 Elsevier Ltd.)	1-27
Figure 1.6 Different multifunctional films for improve barrier and tear performance (a) three-layered films of PET/CNC/ChCW, (b) Multifunctional Supper fillers, (c) crosslinked chitosan/tannic acid film, and (d) pH sensitive three-layer coating for shelf life improvement (Adapted with permission from [89] Copyright © 2024, American chemical society	1-30
Figure 2.1 Preparation of blown films	2-38
Figure 2.2 Extraction of anthocyanin from red cabbage.....	2-39
Figure 2.3 Trouser tear specimen.....	2-44
Figure 2.4 Set-up for ethylene absorption capacity	2-46

Figure 3.1 Schematic representation of the work hypothesis for developing barrier-resistant and tear-proof LLDPE/clay nanocomposites	3-54
Figure 3.2 DSC analysis (a) melting endotherm, (b) crystallization exotherm, (c) TGA, graphs, and (d) Complex viscosity vs. angular frequency curves.....	3-56
Figure 3.3 Apparent viscosity vs. shear rate graph for pure LLDPE and LLDPE/clay nanocomposites.....	3-58
Figure 3.4 (a) DTGA analysis and (b) XRD patterns for nanocomposites	3-59
Figure 3.5 SAXS Pattern for (a) LL, (b) LLC1, (c) LLC3, (d) LLC5, (e) LLC7 @25 °C and (f) LLC5 @100 °C	3-61
Figure 3.6 (a) SAXS In ((I(q)) vs. Q ² for the radius of gyration (R _g) by Guinier fit and (b) Kratky plot (c) Guinier approximation for the shape of nanoparticles (d) Pair distribution function for nanocomposites.....	3-63
Figure 3.7 Transmission electron microscopy images for (a) cloisite 30B, (b) LLC1, (c) LLC3, (d) LLC5, and (e) LLC7	3-65
Figure 3.8 (a) Stress versus elongation (%) for Tensile testing, (b) Tensile strength and % elongation of LLDPE and LLDPE/clay nanocomposites, (c) force vs. strain graph in the cross direction, (d) force vs. strain graph in the transverse direction, and (e) Tearing force in TD and CD, and (f) Kite plot	3-71
Figure 3.9 SEM images of tear-tested fractured surface for a) LLDPE, b) LLC1, c) LLC3, d) LLC5, and e) LLC7.....	3-72
Figure 3.10 DMA analysis graphs (a) Storage modulus vs. temperature (b) tan δ vs. temperature for LLDE and LLDPE/clay nanocomposites.....	3-73
Figure 3.11 (a) Crystallinity, clay size, transmittance, and WVTR (b) Critical tear energy and OTR LLDPE/clay nanocomposites film and (c) Prediction of relative oxygen gas permeability in terms of volume fraction of cloisite 30B	3-76

Figure 4.1 Melting endotherm of DSC, (b) TGA plots, (c) XRD plots, and (d) storage modulus (G') versus angular frequency (ω) curves	4-86
Figure 4.2 DMA analysis (a) Storage modulus vs. temperature and (b) $\tan \delta$ vs. temperature	4-89
Figure 4.3 (a) Stress versus elongation (%) for Tensile testing, (b) Tensile strength, yield strength, and % elongation at break, (c) trouser tear specimen, and (d) Tearing force in TD and CD for neat LLDPE and nanocomposites.	4-91
Figure 4.4 Post-tear fracture morphology for hybrid nanocomposites	4-94
Figure 4.5 TEM image (a) LLC5, (b) LLC4H1, (c) LLC3H2, (d) LLC2H1, (e) LLC1H4 and (f) LLH5 (Red circle: o-MMT and Yellow circle: HNT).....	4-95
Figure 4.6 (a) τ/d versus WVTR/TC and (b) WVTR, OTR, and transmittance % for hybrid nanocomposites.....	4-98
Figure 4.7 STEM image of LLC2H4.....	4-99
Figure 4.8 Real-time assessment of banana and EAC of LL/clay nanocomposites blown films.	4-100
Figure 5.1 (a) Cooling exothermic peaks (b) Melting endothermic peaks from DSC, (c) DTGA, and (d) XRD-pattern for LLDPE/HNT/Resveratrol nanocomposites.	5-108
Figure 5.2 (a) Transmittance %, (b) WVTR and OTR of blown films, TEM images of (c) LLH5, (d) LLHRe15	5-111
Figure 5.3 (a) Antioxidant capacity for DPPH and ABTS, DMA analysis (b) storage modulus, (c) Tan delta, and (c) Trouser tear force vs strain graphs for LLDPE/HNT/Resveratrol nanocomposites blown films.....	5-116
Figure 5.4 Average temperature of Delhi, India, during the storage time (Source: AccuWeather, 110016).....	5-123

Figure 5.5 (a) Images of banana over 12 days of storage, (b) firmness at day 0 for LLHRe15, (c) firmness at day 12 for LLHRe15, (c) Shore A hardness values at day 0 and day 12, (d) Physiological weight loss of banana during storage, (f) firmness values of banana	5-125
Figure 5.6 overall migration (a) simulant A & C and (b) simulant D	5-129
Figure 6.1 (a) Schematic diagram of the preparation of oxygen-plasma treated LLDPE/clay nanocomposites films and (b) Preparation of bilayered halochromic freshness marker enabled packaging construct for food packaging application.	6-137
Figure 6.2 (a) RCA solution at various pH, (b) electrospun mat dipped in RCA solution, and (c) absorption spectra of RCA	6-139
Figure 6.3 SEM images of an electrospun mat of PVA at the various composition of RCA at 15,000 x magnification	6-140
Figure 6.4 Fluorescence images of PVRC mats (a) PVRC10, (b) PVRC20, (c) PVRC30 and (d) PVRC40	6-142
Figure 6.5 (a) Average fiber diameter (b) DSC, (c) TGA, and (d) FTIR-ATR analysis of RCA-based PVA electrospun mats	6-144
Figure 6.6 FTIR-ATR of a) LL, LLP, LLC, and LLCP where characteristics peak of clays at 1080 cm ⁻¹ present in LLC and LLCP blown film and b) RCA at different pH (4,7,10)...	6-146
Figure 6.7 XRD spectra of electrospun PVA-Red cabbage extract mats.....	6-146
Figure 6.8 Absorption spectra of electrospun mats on HCl (a) PVRC30 (b) PVRC40 and NH ₃ vapors (c) PVRC30 (d) PVRC40 from 5 sec, 10 sec, 20 sec, 40 sec, 60 sec, and 120 sec	6-148
Figure 6.9 Pseudo second-order fitting at 530 nm for PVRC electrospun mats on HCl vapor sensing at the different exposure time.....	6-149
Figure 6.10 Water-contact angle for PVRCs-based electrospun mat with time	6-152
Figure 6.11 (a) Tensile strength vs. strain (%), (b) elongation at break and ductility ratio for PVRCs-based electrospun mats (n = 10) (*p ≤ 0.05, **p ≤ 0.01), (c) Contact angles for	

plasma treated and untreated LL and LLC (d) Oxygen/carbon atomic percentage for plasma-treated barrier films, (e) XPS C1s spectra of LLC and (f) LLCP.	6-153
Figure 6.12 EDX elemental mapping of oxygen and carbon for films.....	6-155
Figure 6.13 AFM images and average roughness of (a) LL, (b) LLC, (c) LLP, and (d) LLCP6-157	
Figure 6.14 (a) Cross-sectional TEM image of clay incorporated LL (LLC), (b) FESEM image of bilayer films (b) LLCP/PVRC40, (c) LLCP/PVRC30, and (d) zoomed image of LLCP/PVRC40	6-161
Figure 6.15 peel strength vs displacement for bilayer films.....	6-161
Figure 6.16 Response of freshness indicator in presence of chicken (skinless) (a) LLCP/PVRC30 and (b) LLCP/PVRC40 and in prawns (c) LLCP/PVRC30, (d) LLCP/PVRC40, (e) time-dependent TVB-N and ΔE for prawns and (f) schematic of bi-layered intelligent freshness indicator in the presence of acidic and basic vapors.....	6-164

List of Tables

Table 1.1 Increment in tear strength, fabrication, and compositions.	1-7
Table 1.2 Different strategies for the improvement in water and gas barrier in food packaging films	1-16
Table 1.3 Different strategies for tear-proof and permeation resistant	1-22
Table 1.4 Studies on active packaging with representative antioxidants.	1-26
Table 1.5 Latest technological advancement in the freshness indicators.....	1-32
Table 2.1 Details of materials	2-36
Table 2.2 Composition of LLDPE nanocomposites	2-37
Table 2.3 Details of PVA-Red cabbage electrospun mats.....	2-40
Table 3.1 Thermal analysis for LLDPE and LLDPE/clay nanocomposites	3-57
Table 3.2 MFI of the LLDPE/clay nanocomposites	3-58
Table 3.3 XRD analysis of polyethylene/clay composites.....	3-60
Table 3.4 Clay platelets thickness in LLDPE/clay nanocomposites by SAXS and TEM ...	3-65
Table 3.5 Mechanical analysis of LLDPE and LLDPE/Clay nanocomposites.....	3-68
Table 4.1 DSC and XRD data obtained for LL/clay nanocomposite films.	4-86
Table 4.2 TGA analysis and MFI for hybrid nanocomposites	4-87
Table 4.3 Analysis of tear mechanics response of LLDPE and LLDPE/Clay nanocomposites	4-93
Table 4.4 TEM analysis of LLC5, LLH5 and hybrid nanocomposites.....	4-96
Table 5.1 DSC analysis of nanocomposites based on resveratrol.....	5-106
Table 5.2 Barrier properties for resveratrol based blown films	5-112
Table 5.3 Mechanical and thermomechanical analysis.....	5-120
Table 5.4 Trouser tear analysis.....	5-121
Table 5.5 °Brix values post 12 days for blown films.....	5-126

Table 6.1 L x a x b and ΔE of PVRC mats at various pH	6-139
Table 6.2 Thermal behaviour investigation of PVRC electrospun mat	6-143
Table 6.3 Characteristics peaks for PVRC electrospun mats, LLDPE films, and RCA	6-145
Table 6.4 Parameter obtained by pseudo-second-order kinetic model	6-150
Table 6.5 Mechanical properties of PVRC electrospun mats	6-150
Table 6.6 Contact angle for untreated and plasma-treated LL and LLC films	6-154
Table 6.7 Oxygen/carbon atomic percentage for plasma-treated LLDPE blown film	6-156
Table 6.8 Composition of carbon-related bonds for a) LLC and b) LLCP via C1s spectra of XPS	6-157
Table 6.9 Barrier properties and transmittance of LL, LLC, LLP, LLCP, LLCP/PVRC30, and LLCP/PVRC40	6-159
Table 6.10 Color difference for the multi-layered halochromic films using L^*a^*b and dE	6-

List of Equations

Eq. 1	Bubble diameter = $(2/\pi) \times \text{Lay flat width}$	2-38
Eq. 2	BUR = bubble diameter / die diameter	2-38
Eq. 3	$\chi_c \text{ (DSC)} = (\Delta H_m / (\Delta H_m^\circ \times (1-\text{wt}))) \times 100$	2-41
Eq. 4	$t_{1/2} = (T_{\text{on}} - T_c) / \text{Rate of cooling}$	2-41
Eq. 5	$n \lambda = 2d \sin \theta$	2-42
Eq. 6	$D_p = 0.94 \lambda / (\beta \cos \theta)$	2-41
Eq. 7	% of antioxidant activity = $[(A_c - A_s) \div A_s] \times 100$	2-45
	8.	
Eq. 8	$\Delta A = A_c - A_s$	2-46
Eq. 9	$AC = \Delta A_2 - W \Delta A_1 / \Delta A_1$	2-46
Eq. 10	PLW = (Initial wt. - final wt.) / Initial wt. x 100	2-47
Eq. 11	RI = a / b	2-47
Eq. 12	$I_t = (k_{\text{let}}) / (1 + k_{\text{let}})$	2-48
Eq. 13	$I = I_0 e^{-(qRg)^{2/3}}$	3-60
Eq. 14	$I(q) = 4\pi \int_0^{D_{\text{max}}} p(r) \frac{\sin(qr)}{qr} dr \longleftrightarrow p(r) = \frac{r^2}{2\pi^2} \int_0^\infty q^2 I \frac{\sin(qr)}{qr} dq$	3-63
Eq. 15	$T_c = (2\lambda \text{LTF}/t) - \text{wEED}$	3-67
Eq. 16	$R_p = P / P_0 = (1 - \Phi) / \tau$	3-75
Eq. 17	$R_p = \frac{1-\Phi}{\left(1+\frac{\alpha\Phi}{3}\right)^2}$	3-77
Eq. 18	$R_p = \frac{1-\Phi}{1+\frac{\alpha}{3}(S+\frac{1}{2})\Phi}$	3-77
Eq. 20	$dE = \sqrt{[(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]}$	6-162

List of Symbols

α : Aspect ratio	a: Red-green color component
β : Line broadening at half the maximum intensity (FWHM)	A: Absorbance
χ_c : Degree of crystallinity	Ac: Absorbance of control solution
$\chi_c(\text{DSC})$: Degree of crystallinity from DSC	As: Absorbance of sample solution
$\chi_c(\text{XRD})$: Degree of crystallinity from XRD	b: Yellow-blue color component
Δ : Change in a quantity	d: Average length of HNT / d-spacing
ΔA : Difference in absorption	D: Diffusion coefficient
ΔE : Euclidean distance (color difference)	D_p : Average crystallite size
ΔH_m : Heat of enthalpy of melting peak	E' : Storage modulus
ΔH_m° : Heat of enthalpy for 100% crystalline polymer	$E\epsilon D$: Strain energy density
ϵ : Strain	F_{max} : Maximum load
ϵ_B : Elongation at break	G' : Storage modulus
$\epsilon\%$: Percent elongation	I: Scattering intensity
η^* : Complex viscosity	$I(q)$: Scattering intensity as a function of q
θ : Diffraction angle	I_0 : Initial intensity
λ : Wavelength	I_e : Equilibrium absorption intensity
λL : Extension ratio of legs	I_t : Absorption intensity in time
ν : Poisson's ratio	k: Rate constant
π : Pi (mathematical constant)	L: Lightness color component
ρ : Density	n: Order of reflection
σ : Stress	P: Gas permeability coefficient
	$P(r)$: Pair distance distribution function
	P_0 : Permeability of neat polymer

σ_s : Tensile strength	q : Scattering vector
σ_{TS} : Tensile strength	R : Universal gas constant
σ_{YS} : Yield strength	R_g : Radius of gyration
τ : Tortuosity factor / Inter-particle distance	R_p : Relative gas permeability
τ/d : Ratio of inter-particle distance to length	S : Solubility coefficient / Order parameter
Φ : Volume fraction of nanofiller	S_{max} : Maximum displacement
ω : Angular frequency	t : Thickness
	$t_{1/2}$: Half-time of crystallization
	t_c : Crystallization time
	T_c : Crystallization temperature / Critical
	tear energy
	TF : Tear force / Tearing force
	T_g : Glass transition temperature
	T_m : Melting temperature
	T_{max} : Maximum degradation temperature
	T_{on} : Crystallization onset temperature
	T_{onset} : Onset degradation temperature
	T_{offset} : Offset degradation temperature
	$t_{platelets}$: Thickness of clay platelets
	w : Weight fraction of clay in composites in
	TGA or width of specimen for mechanical
	testing

List of Abbreviations

A

ABTS: 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)
AFM: Atomic Force Microscopy
ALD: Atomic Layer Deposition
AR: Aspect Ratio
ATR: Attenuated Total Reflectance

C

C: Carbon
CA: Contact Angle
CAGR: Compound Annual Growth Rate
CD: Cross Direction
CMC-Na: Sodium Carboxyl Cellulose
CNC: Cellulose Nanocrystals
CO₂: Carbon Dioxide
CR: Polychloroprene Rubber
CS: Chitosan

E

EAC: Ethylene Absorption Capacity
EDX: Energy Dispersive X-ray
EDTA: Ethylenediaminetetraacetic Acid
EFSA: European Food Safety Authority
EPDM: Ethylene Propylene Diene Monomer
EU: European Union
EVA: Ethylene Vinyl Acetate
EVOH: Ethylene Vinyl Alcohol

G

G': Storage Modulus

B

BHA: Butylated Hydroxyanisole
BHT: Butylated Hydroxytoluene
BN: Boron Nitride
BUR: Blow-Up Ratio

D

DLC: Diamond-Like Carbon
DMA: Dynamic Mechanical Analysis
DPPH: 2,2-Diphenyl-1-picrylhydrazyl
DSC: Differential Scanning Calorimetry
DTGA: Differential Thermogravimetric Analysis

F

FCM: Food Contact Materials
FDA: Food and Drug Administration
FDM: Fused Deposition Modelling
FESEM: Field Emission Scanning Electron Microscopy
FTIR: Fourier Transform Infrared Spectroscopy
FWHM: Full Width at Half Maximum

H

H₂O: Water

GEO: Zingiber Officinale Rosc
GRAS: Generally Recognized as Safe

I

IFT: Indirect Fourier Transform

L

LAK: Dimethyl 5-sulfoisophthalate,
potassium salt

LDH: Layered Double Hydroxide

LDPE: Low-Density Polyethylene

LL: Linear Low-Density Polyethylene

LLC: LLDPE/Clay

LLCP: LLDPE/Clay Plasma-treated

LLDPE: Linear Low-Density Polyethylene

LLDPE-g-MA: Linear Low-Density

Polyethylene grafted with Maleic Anhydride

LLP: LLDPE Plasma-treated

LVR: Linear Viscoelastic Response

N

Na-MMT: Sodium Montmorillonite

NaOH: Sodium Hydroxide

NH₃: Ammonia

NH₄OH: Ammonium Hydroxide

NIAS: Non-Intentionally Added Substances

P

PA: Polyamide

PA6: Polyamide 6

PBAT: Poly (butylene adipate-co-
terephthalate)

PBS: Poly (butylene succinate)

PCL: Polycaprolactone

H₂S: Hydrogen Sulfide

HCl: Hydrochloric Acid

HDPE: High-Density Polyethylene

HDT: Heat Deflection Temperature

HNT: Halloysite Nanotubes

K

KGM: Konjac Glucomannan

M

MA: Maleic Anhydride

MD: Machine Direction

MFI: Melt Flow Index

MMT: Montmorillonite

MOF: Metal-Organic Framework

MoS₂: Molybdenum Disulfide

O

O: Oxygen

o-MMT: Organically Modified
Montmorillonite

OTR: Oxygen Transmission Rate

OWRK: Owens, Wendt, Rable, and Kaelble

R

RCA: Red Cabbage Anthocyanin

Re: Resveratrol

REO: Rosmarinus officinalis L

R_g: Radius of Gyration

RI: Ripening Index

rpm: Revolutions Per Minute

PCN: Polymer-Clay Nanocomposites
 PE: Polyethylene
 PE-CVD: Plasma-Enhanced Chemical Vapor Deposition
 PEO: Polyethylene Oxide
 PET: Polyethylene Terephthalate
 PIB: Poly(isobutylene)
 PLA: Polylactic Acid
 PLW: Physiological Weight Loss
 PMMA: Poly (methyl methacrylate)
 POE: Polyolefin Elastomer
 PP: Polypropylene
 PPC: Poly (propylene carbonate)
 PS: Polystyrene
 PVA: Polyvinyl Alcohol
 PVD: Physical Vapor Deposition
 PVDF-TFE: Poly (vinylidene fluoride-co-tetrafluoroethylene)
 PVP: Polyvinylpyrrolidone
 PVRC: PVA/Red Cabbage Anthocyanin

S

SAXS: Small-Angle X-ray Scattering
 SCCM: Standard Cubic Centimetres per Minute
 sCF: Short Carbon Fiber
 SEM: Scanning Electron Microscopy
 Si: Silicon
 SiO₂: Silicon Dioxide
 SiO_x: Silicon Oxide
 SPS: Starch/Polyvinyl Alcohol/Sodium Alginate
 SSPS: Soybean Polysaccharide

RSA: Radical Scavenging Activity

T

T-AC: Tetrahedral Amorphous Carbon
 TA: Tannic Acid
 TBHQ: Tert-Butylhydroquinone
 TD: Transverse Direction
 TEM: Transmission Electron Microscopy
 TGA: Thermogravimetric Analysis
 TPS: Thermoplastic Starch
 TVB-N: Total Volatile Basic Nitrogen

STEM: Scanning Transmission Electron
Microscopy

U

UV: Ultraviolet

UV-VIS: Ultraviolet-Visible

W

WCA: Water Contact Angle

WVTR: Water Vapor Transmission Rate

Z

ZnO: Zinc Oxide

ZrP: Zirconium Phosphate

V

VTMS: Vinyltrimethoxysilane

X

XPS: X-ray Photoelectron Spectroscopy

XRD: X-ray Diffraction