

**STUDIES ON HALLOYSITE AND SEPIOLITE REINFORCED
HIGH DENSITY POLYETHYLENE NANOCOMPOSITES**

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**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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HIGH DENSITY POLYETHYLENE NANOCOMPOSITES**

by

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DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

Submitted

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to the



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Dedicated to My Family

CERTIFICATE

*This is to certify that the thesis entitled “**Studies on Halloysite and Sepiolite Reinforced High Density Polyethylene Nanocomposites**” being submitted by **Mr. Vishwa Pratap Singh**, 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 him. Mr. Vishwa Pratap Singh has worked under our guidance and supervision and fulfilled all the requirements for the submission of 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 degree or diploma.

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ABSTRACT

The aim of the present study is to investigate systematically the effect of two naturally occurring nanoclays like Halloysite nanotubes and Sepiolite on various properties of HDPE and to develop HDPE based nanocomposite material for blow molding applications like fuel tank and solvent containers with reduced permeation of hydrocarbon solvents and liquid fuels.

HDPE is the most suitable material for the fabrication of containers for hydrocarbon solvent and fuel storage because it is recognized as a light weight, low cost and anticorrosion material having good stiffness to toughness ratio. However, HDPE has poor permeation resistance to hydrocarbon solvents (e.g. xylene and acetone) and fuels (e.g. gasoline, diesel and kerosene). Such permeation will result in environment pollution, safety and health problems. In order to improve this poor permeation resistance of HDPE, the nano-clay technology is currently generating a great deal of interest, due to its potential cost effective advantages in reinforcement, fire retardancy and dimensional stability along with barrier properties.

The thesis comprises of six chapters. Chapter 1 describes the literature background of polymer nanocomposites with particular attention to polyethylene (PE) based systems, challenges involved in dispersion of nanoclays and the effect of compatibilization. It also includes literature about the synergistic effect of nanoclays on the permeation properties, permeation rates and permeation mechanism of different hydrocarbon solvents and fuels on HDPE based systems. The motivation and objectives of the present study is also included at the end of this chapter.

Chapter 2 gives experimental details for melt blending HDPE with HNTs or Sepiolite, in absence and presence of compatibilizer [PE-g-MA] and characterization of nanocomposites using SEM, TEM and XRD (Morphological characterization), DSC and TGA (Thermal characterization), parallel plate, capillary rheometer and Rheotens (Rheological studies), DMA (Thermo-mechanical characterization), UTM (Mechanical properties i.e. tensile, flexural, impact), barrier properties and flammability by LOI test.

The effect of HNT loading and HNT to compatibiliser [PE-g-MA] ratio (1:0.5, 1:1, 1:1.5 keeping HNT content fixed at 10 wt%) on the morphological, mechanical, thermal and rheological properties (parallel plate, capillary rheometer and rheotens) of HDPE was investigated [chapter 3A and 3B]. SEM and TEM were conducted to analyze dispersion of HNTs in HDPE matrix. Tensile properties are described and correlated with different

theoretical models. Incorporation of HNTs up to 10 wt% did not affect the tensile properties. A marginal increase in tensile modulus was observed (~10 %) and it reduces upon the addition of compatibiliser but is always higher as compared to neat HDPE. It appears that the addition of halloysite nanotubes leads to an improvement in flexural modulus and strength. The percent increase is about 17 % for flexural modulus and 12 % for flexural strength at 5 wt% HNT loading. While increasing the filler fraction from 5 to 10 wt% did not show any significant effect on flexural properties but modulus decreased slightly in compatibilised composites which show the plasticization effect of compatibiliser or likely due to the lower crystallinity of PE-g-MA compared to HDPE. Thermal stability increases remarkably (48°C) with increasing amounts of HNT content upto 10 wt% HNT which further increases in the presence of compatibiliser.

Melt strength and drawability were determined using Rheotens whereas extensional viscosity was calculated from (i) Wagner's master curve (using Rheotens data) and (ii) modified Cogswell method (using convergent flow analysis from capillary rheometer data). In HDPE/HNT composites, melt extensional properties (melt strength, drawability and extensional viscosity) increased slightly with increase in HNT concentration up to 5% w/w followed by a decrease as HNT concentration was increased to 10% w/w. On the other hand, all these properties enhanced significantly in the presence of compatibiliser i.e. in HDPE/ PE-g-MA/HNTs nanocomposites. Optimum amount of compatibiliser was found to be 1:1 i.e. filler : compatibiliser ratio. The rheological properties of HD/HNT composites are also evaluated by capillary rheometer at different temperatures 190, 200 and 210 °C. Both Complex viscosity and storage modulus in oscillatory rheometry were highest for nanocomposites prepared using 10% w/w HNT and reduced slightly after incorporation of compatibiliser.

The influence of Sepiolite loading (1-10 wt %) and type of compatibiliser on morphology, mechanical, thermal, dynamic mechanical and rheological properties of HDPE was investigated and the results are compiled in Chapter 4A and 4B. Maleic anhydride grafted polyethylene (PE-g-MA) (having different MFI and maleic anhydride content) were used as compatibiliser to investigate systematically the effect of polarity and molecular weight on the properties of HDPE/Sepiolite nanocomposites. SEM and TEM revealed the better dispersion of Sepiolite in presence of compatibiliser; however, it was much better when PE-g-MA having higher MFI was used as compared to compatibiliser having lower MFI. Sepiolite-clay significantly enhanced the mechanical properties, melt strength and extensional viscosity with slight reduction in drawability at 10% w/w loading. For example, ~40% increase in

tensile modulus and ~50% improvement in flexural modulus was obtained at 10% w/w Sepiolite loading. The compatibiliser having lower MFI showed significant improvement in melt extensional properties as compared to compatibiliser having higher MFI. Storage modulus and loss modulus both in oscillatory rheometry and in DMA were highest for nanocomposite prepared using 10 wt % Sepiolite owing to the improved mechanical restraint by the dispersed phase. In the presence of compatibilizer, the values of storage modulus and loss modulus were lower as compared to uncompatibilized nanocomposites at same loading of Sepiolite. The reduction in modulus is more pronounced in composites prepared using compatibilizer of lower molar mass as compared to those prepared using higher molar mass compatibilizer.

Investigations on the barrier properties of HDPE, HDPE/Halloysites (HNT) and HDPE/Sepiolite composites against hydrocarbon solvents (xylene & acetone) and fuels (gasoline, diesel and kerosene) are reported in Chapter 5. It was found that the solvent and fuel permeation resistance was superior in nanocomposites as compared to neat HDPE. In addition, the barrier properties of HDPE were significantly influenced by the clay content and the maximum improvement in the permeation was observed at 10 wt% of clay loading. The best barrier properties were obtained with Sepiolite which has higher aspect ratio as compared to HNTs. The compatibilised composites with oriented Sepiolite fibres showed better improvement in barrier properties as compared to uncompatibilised nanocomposites. It was also observed that the rate of non polar solvent (xylene, gasoline) permeating through the bottles is much faster than that of polar solvent (acetone).

The summary, conclusions and the scope for future work is given in chapter 6.

सारांश

वर्तमान अध्ययन का उद्देश्य व्यवस्थित रूप से एचडीपीई के विभिन्न गुणों पर हेलोसाइट नैनोट्यूब और सेपियोलाइट जैसे दो प्राकृतिक रूप से पाए जाने वाले नैनोकलेज के प्रभाव की जांच करना और ब्लो मोल्डिंग अनुप्रयोगों जैसे हाइड्रोकार्बन सॉल्वेंट्स और तरल ईंधन के कम पारगम्यता के साथ ईंधन टैंक और विलायक कंटेनर के लिए एचडीपीई आधारित नैनोकॉम्पोजिट्स सामग्री विकसित करना है।

एचडीपीई हाइड्रोकार्बन विलायक और ईंधन भंडारण के लिए कंटेनर के निर्माण के लिए सबसे उपयुक्त सामग्री है क्योंकि इसे हल्के वजन, कम लागत और एंटीकोरोजन सामग्री के रूप में पहचाना जाता है जिसमें क्रूरता अनुपात में अच्छी कठोरता होती है। हालांकि, एचडीपीई में हाइड्रोकार्बन सॉल्वेंट्स (जैसे xylene और एसीटोन) और ईंधन (जैसे गैसोलीन, डीजल और केरोसिन) के लिए खराब पारगम्य प्रतिरोध है। इस तरह के पारगम्यता पर्यावरण प्रदूषण, सुरक्षा और स्वास्थ्य समस्याओं का परिणाम होगा। एचडीपीई के इस खराब पारगम्य प्रतिरोध में सुधार के लिए, नैनो-मिट्री प्रौद्योगिकी वर्तमान में मजबूती, अग्निरोधी और बाधा गुणों के साथ आयामी स्थिरता में संभावित लागत प्रभावी लाभों के कारण ब्याज का एक बड़ा सौदा पैदा कर रही है।

थीसिस में छह अध्याय शामिल हैं। अध्याय 1 पॉलिमर नैनोकॉम्पोजिट्स की साहित्य पृष्ठभूमि का वर्णन करता है जिसमें पॉलीथीन (पीई) आधारित सिस्टम, नैनोकले के फैलाव में शामिल चुनौतियों और संगतता के प्रभाव में विशेष ध्यान दिया जाता है। इसमें एचडीपीई आधारित प्रणालियों पर विभिन्न हाइड्रोकार्बन सॉल्वेंट्स और ईंधन के पारगम्य गुणों, पारगम्य दर और पारगम्य तंत्र पर नैनोकले के सहक्रियात्मक प्रभाव के बारे में साहित्य भी शामिल है। इस अध्याय के अंत में वर्तमान अध्ययन की प्रेरणा और उद्देश्यों को भी शामिल किया गया है।

अध्याय 2 एचएनटी या सीपीओलाइट के साथ पिघलते हुए एचडीपीई के लिए कंपैटिबलाइजर [पीई-जी-एमए] की उपस्थिति और अनुपस्थिति में, एसईएम, टीईएम और एक्सआरडी (मॉर्फोलॉजिकल कैरेक्शन), डीएससी और टीजीए (थर्मल कैरेक्शन), समानांतर प्लेट, केशिका रियोमीटर और रिहोटेंस (रिहोलॉजिकल स्टडीज), डीएमए (थर्मो-मैकेनिकल कैरेक्शन), यूटीएम (मैकेनिकल प्रॉपर्टी यानी तन्यता, लचीला, प्रभाव), अवरोध गुण और एलओआई परीक्षण द्वारा ज्वलनशीलता का उपयोग करते हुए नैनोकॉम्पोजिट्स की विशेषता प्रयोगात्मक विवरण देता है।

एचएफटी लोडिंग और एचएनटी [पीई-जी-एमए] अनुपात (1: 0.5, 1: 1, 1: 1.5 का प्रभाव compatibiliser एचएनटी सामग्री को 10 वाट% पर तय किया जाता है) morphological, यांत्रिक, थर्मल और rheological गुणों

(समानांतर पर) प्लेट, कैशिलरी रिहोमीटर और रिहोटेंस) एचडीपीई की जांच की गई [अध्याय 3 ए और 3 बी]। एचडीपीई मैट्रिक्स में एचएनटी के फैलाव का विश्लेषण करने के लिए एसईएम और टीईएम आयोजित किए गए थे। तन्यता गुणों को विभिन्न सैद्धांतिक मॉडल के साथ वर्णित और सहसंबंधित किया जाता है। 10 वाट% तक एचएनटी का निवेश तन्यता गुणों को प्रभावित नहीं करता है। तन्यता मॉड्यूलस में मामूली वृद्धि देखी गई (~ 10%) और यह compatibiliser के अलावा कम हो जाती है लेकिन साफ एचडीपीई की तुलना में हमेशा उच्च है। ऐसा प्रतीत होता है कि हेलोसाइट नैनोट्यूब के अतिरिक्त लचीला मॉड्यूलस और ताकत में सुधार होता है। लचीला मॉड्यूलस के लिए प्रतिशत वृद्धि और 5% एचएनटी लोडिंग पर लचीला ताकत के लिए 12% है। 5 से 10 वाट% तक फिलर अंश को बढ़ाने के दौरान फ्लेक्चरल गुणों पर कोई महत्वपूर्ण प्रभाव नहीं दिखाया गया था, लेकिन मॉड्यूलस कंपैटिबिलिज्ड कंपोजिट्स में थोड़ा कम हो गया है जो एचडीपीई की तुलना में पीई-जी-एमए की निचली क्रिस्टलीटी के कारण कंपैटिबिलिज़र के प्लास्टाइजेशन प्रभाव को दिखाता है या संभवतः। थर्मल स्थिरता 10 वाट% एचएनटी तक एचएनटी सामग्री की बढ़ती मात्रा के साथ उल्लेखनीय रूप से (480C) बढ़ जाती है जो compatibiliser की उपस्थिति में और बढ़ जाती है।

पिघलते हुए ताकत और खींच क्षमता को रेटोटेंस का उपयोग करके निर्धारित किया गया था, जबकि विस्तारित चिपचिपापन की गणना (i) वाग्नेर के मास्टर वक्र (रिहोटेंस डेटा का उपयोग करके) और (ii) संशोधित कॉग्सवेल विधि (केशिका रेहोमीटर डेटा से अभिसरण प्रवाह विश्लेषण का उपयोग करके) की गई थी। एचडीपीई / एचएनटी कंपोजिट्स में, विस्तारित गुणों को पिघलाएं (ताकत, खींचने योग्यता और विस्तारित चिपचिपाहट पिघलाएं) एचएनटी एकाग्रता में 5% डब्ल्यू / डब्ल्यू तक बढ़ने के साथ थोड़ी वृद्धि हुई है, इसके बाद एचएनटी एकाग्रता 10% w / w तक बढ़ी है। दूसरी तरफ, इन सभी गुणों ने एचडीपीई / पीईजी-एमए / एचएनटी नैनोकोमोसाइट्स में compatibiliser i.e. की उपस्थिति में उल्लेखनीय रूप से वृद्धि की। Compatibiliser की अधिकतम मात्रा 1: 1 यानी filler: compatibiliser अनुपात पाया गया था। एचडी / एचएनटी कंपोजिट्स के भौतिक गुणों का मूल्यांकन विभिन्न तापमान 190, 200 और 210 डिग्री सेल्सियस पर केशिका रियोमीटर द्वारा भी किया जाता है। ओसीलेटर रेमेट्री में कॉम्प्लेक्स चिपचिपाहट और भंडारण मॉड्यूलस दोनों नैनोकोमोसाइट्स के लिए उच्चतम थे जो 10% डब्ल्यू / डब्ल्यू एचएनटी का उपयोग करके तैयार किए गए थे और कंपैटिबिलिज़र के निगमन के बाद थोड़ा कम हो गए थे।

एचपीपीई के मॉर्फोलॉजी, मैकेनिकल, थर्मल, डायनामिक मैकेनिकल और रिहोलॉजिकल प्रॉपर्टीज पर सेपियोलाइट लोडिंग (1-10 वाट%) और कंपैटिबिलाइज़र का प्रभाव जांच की गई और परिणाम अध्याय 4 ए और 4 बी में संकलित किए गए। मालेनिक एनहाइड्राइड ग्राइटेड पॉलीथीन (पीई-जी-एमए) (विभिन्न एमएफआई और नरिक एनहाइड्राइड सामग्री होने) को एचडीपीई / सेपियोलाइट नैनोकोमोसाइट्स के गुणों पर ध्रुवीयता और आणविक भार के व्यवस्थित रूप से प्रभाव की जांच करने के लिए compatibiliser के रूप में उपयोग किया जाता था। एसईएम और टीईएम ने compatibiliser की उपस्थिति में Sepiolite के बेहतर फैलाव का खुलासा किया; हालांकि, यह बहुत बेहतर था जब पीई-जी-एमए उच्च एमएफआई का इस्तेमाल कम एमएफआई वाले कंपैटिबिलिसर की तुलना में किया गया था। सेपियोलाइट-मिटी ने मैकेनिकल गुणों में काफी वृद्धि की, 10% डब्ल्यू / डब्ल्यू लोडिंग पर खींचने में मामूली कमी के साथ ताकत और विस्तारित चिपचिपाहट पिघल गई। उदाहरण के लिए, तन्यता मॉड्यूलस में ~ 40% की वृद्धि और flexural modulus में ~ 50% सुधार 10% w / w Sepiolite लोडिंग पर प्राप्त किया गया था। कम एमएफआई वाले कंपैटिबिलिज़र में उच्च एमएफआई वाले कंपैटिबिलिसर की तुलना में विस्तारित गुणों को पिघलने में महत्वपूर्ण सुधार हुआ है। ऑक्सीलेटर रेमेट्री और डीएमए में भंडारण मॉड्यूलस और हानि मॉड्यूलस फैले चरण द्वारा बेहतर यांत्रिक रोकथाम के कारण 10 वाट% सेपोलियोइट का उपयोग करके तैयार नैनोकोमोसाइट के लिए उच्चतम थे। कंपैटिबिलाइज़र की उपस्थिति में, स्टोरेज मॉड्यूलस और हानि मॉड्यूलस के मूल्य कम से कम लोडिंग पर असंगत नैनोकोमोसाइट्स की तुलना में कम थे। उच्च दाढ़ी द्रव्यमान का उपयोग करके तैयार किए गए लोगों की तुलना में कम दाढ़ी द्रव्यमान के compatibilizer का उपयोग कर तैयार composites में मॉड्यूलस में कमी अधिक स्पष्ट है

एचडीपीई, एचडीपीई / हेलोसाइट्स (एचएनटी) और एचडीपीई / एचडीपीई / हाइड्रोकार्बन सॉल्वेंट्स (xylene और एसीटोन) और ईंधन (गैसोलीन, डीजल और केरोसिन) के खिलाफ ईंधनपीई कंपोजिट्स के बाधा गुणों पर जांच अध्याय 5 में दर्ज की गई है। यह पाया गया कि विलायक और ईंधन साफ एचडीपीई की तुलना में पारगम्य प्रतिरोध नैनोकोमोसाइट्स में बेहतर था। इसके अलावा, एचडीपीई के बाधा गुण मिटी की सामग्री से काफी प्रभावित थे और पारगम्यता में अधिकतम सुधार मिटी लोडिंग के 10 वाट% पर मनाया गया था। सर्वोत्तम बाधा गुणों को सेपियोलाइट के साथ प्राप्त किया गया था जिसमें एचएनटी की तुलना में उच्च पहलू अनुपात होता है। उन्मुख संप्रदाय फाइबर के साथ संगत कंपोजिट्स ने असंगत नैनोकोमोसाइट्स की तुलना में बाधा गुणों में

बेहतर सुधार दिखाया। यह भी देखा गया था कि बोतलों के माध्यम से फैलाने वाले गैर ध्रुवीय विलायक (xylene, गैसोलीन) की दर ध्रुवीय विलायक (एसीटोन) की तुलना में बहुत तेज है।

भविष्य के काम के लिए सारांश, निष्कर्ष और दायरा अध्याय 6 में दिया गया है।

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LIST OF ABBREVIATIONS & SYMBOLS

ASTM	American society for testing and materials
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EDX	Energy-dispersive X-ray spectroscopy
E'	Storage (Elastic) modulus in DMA
E''	Loss (Viscous) modulus in DMA
FT-IR	Fourier transform infra red spectroscopy
G'	Storage modulus in parallel plate rheology
G''	Loss modulus in parallel plate rheology
HNT	Halloysite nanotubes
LOI	Limiting oxygen index (LOI)
MFI	Melt flow index
HDPE	High density polyethylene
PE-g-MA	Maleic anhydride grafted polyethylene
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
T _c	Crystallization temperature
T _g	Glass transition temperature
T _m	Melting temperature
T _{max}	Temperature corresponding to maximum degradation
T _{0.1}	Temperature corresponding to 10% degradation
T _{0.5}	Temperature corresponding to 50% degradation
WAXD	Wide Angle X-ray Diffraction

X_c	Degree of crystallinity
ΔE	Activation energy
ΔH_m	Enthalpy of melting (fusion)
ΔH_c	Enthalpy of crystallization
Φ_f	Filler volume fraction
η^*	Complex viscosity
δ	Phase angle