

**STUDIES ON POLYPROPYLENE/CLAY NANOCOMPOSITES IN
PRESENCE OF NON-HALOGEN FLAME RETARDANT ADDITIVES**

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PRESENCE OF NON-HALOGEN FLAME RETARDANT ADDITIVES**

by

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Dedicated to my loving family
and
My little angel 'Shivika'

CERTIFICATE

*This is to certify that the thesis entitled “**Studies on Polypropylene/Clay Nanocomposites in Presence of Non-halogen Flame Retardant Additives**” being submitted by **Ms. Bindu Manchanda**, 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. Ms. Bindu Manchanda 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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Date:

Place: New Delhi

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ABSTRACT

Polypropylene (PP) is an important commercial plastic widely used to produce household goods and automotive parts due to its well-balanced physical and mechanical properties and easy processability at a relatively low cost. The applications of PP in various industrial sectors can be further expanded by the incorporation of various kinds of fillers. Therefore, PP has been a popular matrix used in association with all kinds of nanofillers such as carbon nanotubes (CNTs), layered silicates (clays such as montmorillonite (MMT) etc.) and nanoparticles such as silica, graphite and calcium carbonate, even though the nanofiller dispersion is challenging in that case and often remains an issue.

Recently, Scientists and Engineers have discovered and developed a large range of exciting new applications for Halloysite nanotubes and Sepiolite which are unique, cheap and abundantly available naturally occurring clays. However, it is very difficult to attain exfoliation/dispersion in case of higher loadings of these polar nanofillers in PP. To facilitate better dispersion of nanofillers and their interaction with PP, either maleic anhydride grafted polypropylene (PP-g-MA) has been used as a compatibilizer or modification of nanofiller has been done. This will make nanocomposites suitable for many commercial applications, e.g. used in parts of electrical equipment, building components and especially in automotive industries like cars, aeroplanes etc. However for these applications, polymer nanocomposites must be flame resistant and should have self-extinguishing characteristics. Very high loading of additives is needed to get flame resistant polyolefins which in turn negatively impact the mechanical, physical and rheological properties of the polymer. Development of high quality halogen free flame retardant (HFFR) PP nanocomposites requires a smart manipulation of additive and polymer technology.

The aim of the present study is to investigate systematically the effect of two naturally occurring nanofillers like Halloysite nanotubes and Sepiolite on various properties of PP and to develop halogen free flame retardant polypropylene nanocomposites with improved thermal and mechanical properties that may find applications in automotive industry.

The thesis comprises of seven chapters. Chapter 1 describes the literature background of polymer nanocomposites with particular attention to PP based systems, effect of compatibilization, intumescent flame retardant systems for PP and various methods of flammability testing, 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 PP with HNTs or Sepiolite, in absence and presence of compatibilizer [PP-g-MA], and combination of HNT or Sepiolite along with IFR and characterization of nanocomposites using FTIR (Structural characterization), SEM, TEM and XRD (Morphological characterization), DSC and TGA (Thermal characterization), parallel plate, capillary rheometer and Rheotens (Rheological studies), DMA (Thermo-mechanical characterization) , MTS (Mechanical properties i.e. tensile , flexural , impact) and flammability by LOI and UL-94 test .

The effect of HNT loading and compatibilizer to HNT ratio (1:1, 2:1,3:1 keeping HNT content fixed at 5 wt%) on the morphological, mechanical, thermal and rheological properties (parallel plate, capillary rheometer and rheotens) of PP was investigated [chapter 3A and 3B]. SEM and TEM were conducted to analyze dispersion of HNTs in PP matrix. About 20 % increase in tensile modulus and 25% increase in impact strength was observed upon incorporation of 5% HNT in PP. It was found that tensile modulus, flexural modulus and flexural strength increased by 35 %, 25 % and 30% respectively upon adding PP-g-MA: HNT in 2:1 ratio. The crystallization peak exothermic temperature, T_p showed an increase of 11°C for PP with 5% HNT and 13-14°C on adding higher amounts of HNTs while melting temperature remains unchanged. Thermal stability increases with increasing amounts of HNT content upto 5% HNT and then remained unchanged on further loading of HNT.

From capillary rheometry, high shear melt viscosity of PP /HNT composites follow the same trend as that of neat PP upto 5% of HNT loading. Extensional viscosity, determined using Cogswells convergent flow analyses and by performing rheotens experiment following Wagner's model, increased with increasing HNT content upto 5% and then decreased significantly at higher loadings. All the samples showed pseudoplastic (shear-thinning) behavior with power law index (n) in the range of 0.31-0.59. Storage modulus [G'] increased mainly in low frequency region upon adding HNT in PP confirming reinforcement of PP by HNT which was enhanced further in the presence of compatibilizer. Extensional viscosity also increased on adding PP-g-MA. From these studies it can be concluded that halloysite nanotubes upto ~5 wt % can be used as a filler to improve mechanical, thermal, melt strength and elongational properties of PP without affecting the processability which could be improved further by using PP-g-MA: HNT in the ratio of 2:1.

The effect of Sepiolite content (5 and 10 wt%) and compatibilizer to Sepiolite ratio (1:1, 2:1,3:1 keeping sepiolite content fixed at 5 wt%) on the morphological, mechanical, thermal and rheological properties of PP/Sepiolite nanocomposites was investigated and the results are compiled in Chapter 4. It was observed that Sepiolite could be better dispersed in PP matrix on adding PP-g-MA as compatibilizer. About 15 °C increase in T_p of PP on adding Sepiolite confirmed that Sepiolite is acting as a nucleating agent which is also supported by the increase in percent crystallinity and mechanical properties. On incorporating PP-g-MA in PP/Sepiolite nanocomposites, mechanical properties and thermal stability also improved. High shear viscosity increases on adding Sepiolite while for compatibilized PP/Sepiolite samples it is found to be comparable to neat PP.

Non-isothermal crystallization kinetic parameters of PP/HNT and PP/Sepiolite respectively in absence/presence of compatibilizer [maleic anhydride grafted-polypropylene (PP-g-MA)] was investigated using differential scanning calorimetry at four different cooling rates. Crystallization parameters were analyzed by Avrami, Jeziorny, Liu and Mo's models. Nucleation ability of HNT and Sepiolite was evaluated by employing Dobreva and Gutzowa models. The activation energy of non-isothermal crystallization kinetics process was estimated by using three isokinetic models (Augis–Bennet, Kissinger and Takhore). The value of ΔE increased on increasing HNT or Sepiolite content as they hinder the mobility of PP chains. However, ΔE decreased with increasing PP-g-MA content. This may be due to the enhanced adhesion between matrix and filler which facilitates the movement of PP chains.

The effect of IFR additive [Exolit AP-766] on flaming characteristics of PP, PP/HNT and PP/Sepiolite nanocomposites was investigated systematically and the results are summarized in Chapter 6. PP having 25% of IFR showed V-0 rating with slight deterioration of mechanical properties. The burning behaviour of composites prepared using combination of IFR and nanoclays i.e. PP: HNT: IFR / PP: Sepiolite: IFR in the ratio of 75:5:20 showed V-0 rating with a significant improvement in the mechanical properties. The modification of IFR was also carried out by treating IFR with pentaerythritol triacrylate (PETA) followed by UV curing and investigating its effect on the flaming behaviour and mechanical properties. There was a significant improvement in the performance [flammability and mechanical properties] of PP or PP nanocomposites when we used PETA modified IFR as additive.

The summary, conclusions and the scope for future work is given in chapter 7.

सार

पॉलीप्रोपलीलीन (पीपी) एक महत्वपूर्ण व्यावसायिक प्लास्टिक है जो घरेलू सामान और मोटर वाहन भागों का उत्पादन करने के लिए व्यापक रूप से उपयोग किया जाता है क्योंकि इसकी अच्छी-संतुलित भौतिक और यांत्रिक गुणों और अपेक्षाकृत कम लागत पर आसान प्रक्रियात्मकता होती है। विभिन्न औद्योगिक क्षेत्रों में पीपी के आवेदनों को विभिन्न प्रकार के फिलरों के समावेश द्वारा आगे बढ़ाया जा सकता है। इसलिए, पीपी एक लोकप्रिय मैट्रिक्स है, जैसे कि कार्बन नैनोट्यूब (सीएनटी), स्तरित सिलिकेट (मॉटमोरिलोनित (एमएमटी) आदि) और नैनोकणों जैसे सिलिका, ग्रेफाइट और कैल्शियम कार्बोनेट, के साथ-साथ सभी प्रकार के नैनोफिलर्स के साथ प्रयोग में हैं हालांकि उस मामले में नैनोफिलर फैलाव (डिस्पर्सन) चुनौतीपूर्ण है और अक्सर एक समस्या बनी हुई है।

हाल ही में, वैज्ञानिकों और इंजीनियरों ने हेलोसाइट नैनोट्यूब (एच. एन.टी) और सेपोलाइट के लिए रोमांचक नए अनुप्रयोगों की खोज की और विकसित की है जो अद्वितीय, सस्ता और प्रचुर मात्रा में प्राकृतिक रूप में उपलब्ध मिट्टी हैं। हालांकि, पीपी में इन ध्रुवीय नैनोफिलर्स के उच्च भार के मामले में फैलाव (डिस्पर्सन) प्राप्त करना बहुत कठिन है। नैनोफिलर्स के पीपी में बेहतर फैलाव को सुलझाने के लिए या तो मैलिक एनहाइड्राइड ग्राफिटड पॉलीप्रोपाइलीन (पीपी-जी-एमए) को कंपैटीबिलाइजर या नैनोफिलर के संशोधन के रूप इस्तेमाल किया गया है। इससे नैनोकोमोसाइट्स कई वाणिज्यिक अनुप्रयोगों के लिए उपयुक्त होंगे, उदाहरण के लिए-बिजली के उपकरणों के निर्माण, विशेष रूप से कारों, हवाई जहाज आदि जैसे ऑटोमोटिव उद्योगों में निर्माण के कुछ हिस्सों में इस्तेमाल किया जा सकता है। हालांकि इन अनुप्रयोगों के लिए, बहुलक (पॉलीमर) नैनोकोमोसाइट्स लौ प्रतिरोधी (फ्लेम रिटार्डेड) होनी चाहिए और स्व-शमन विशेषताओं का होना चाहिए। फ्लेम रिटार्डेड पॉलिऑलीफिंस प्राप्त करने के लिए बहुत अधिक मात्रा में ऐडटिव की आवश्यकता होती है जो बदले में पॉलिमर के यांत्रिक (मैकेनिकल), भौतिक (फिजिकल) और रियोलॉजिकल गुणों को नकारात्मक रूप से प्रभावित करते हैं। उच्च गुणवत्ता वाले हलोजन मुक्त फ्लेम रिटार्डेड (एचएफएफआर) पीपी नैनोकोमोसाइट के विकास के लिए योजक और बहुलक तकनीक का एक स्मार्ट हेर लगाना आवश्यक है।

वर्तमान अध्ययन का उद्देश्य व्यवस्थित रूप से पीपी के विभिन्न गुणों पर दो प्राकृतिक रूप से होने वाले नैनोफिलर्स जैसे हेलोसाइट नैनोट्यूब (एच. एन.टी) और सेपोलाइट के प्रभाव की जांच करना है और बेहतर थर्मल और मैकेनिकल गुणों के साथ हलोजन मुक्त फ्लेम रिटार्डेड पॉलीप्रोपाइलीन नैनोकोमोसाइट्स विकसित करना है जो कि मोटर वाहन उद्योग में आवेदन प्राप्त कर सकते हैं।

थीसिस में सात अध्याय शामिल हैं अध्याय 1 में पीपी आधारित सिस्टम, पीपी के लिए प्रेरणामय लौ लौटाने वाले प्रणालियों और ज्वलनशीलता परीक्षण के विभिन्न तरीकों के लिए विशेष रूप से ध्यान देने वाले बहुलक नैनोकोमोसाइट्स की साहित्य पृष्ठभूमि का वर्णन किया गया है, वर्तमान अध्ययन की प्रेरणा और उद्देश्यों को भी इसके अंत में शामिल किया गया है। अध्याय।

अध्याय 2 एफटीआईआर (स्ट्रक्चरल लक्षण वर्णन), एसईएम, का उपयोग करते हुए आईएफआर और नैनोकोमोसाइट्स के साथ एचएएनटी या सीपोलैइट के संयोजन, [पीपी-जी-एमए] की अनुपस्थिति में उपस्थिति और एचपीटी या सीपीओलाइट के साथ पिघल पीपी के लिए प्रायोगिक विवरण देता है। टीईएम और एक्सआरडी (आकृति विज्ञान लक्षण वर्णन), डीएससी और टीजीए (थर्मल कैरेक्चरेशन), समानांतर प्लेट, केशिका रेमोमीटर और रियोटेंस (रियोलॉजिकल स्टडीज), डीएमए (थर्मो-मैकेनिकल लक्षण वर्णन), एमटीएस (मैकेनिकल गुण यानी तन्यता, फोकल, प्रभाव) एलओआई और उल -94 टेस्ट।

एचएएनटी लोडिंग और कॉम्बिटीलाइज़र के एचएएनटी अनुपात (1: 1, 2: 1, 3: 1 को एचएनटी सामग्री को 5 वेट% पर तय किया गया है), प्रभावकारी, मैकेनिकल, थर्मल और रियोलॉजिकल गुणों (समानांतर प्लेट, केशिका रेमोमीटर और रियोटेंस) पर प्रभाव। पीपी की जांच [अध्याय 3 ए और 3 बी] की जांच की गई। पीपी मैट्रिक्स में एचएनटी के फैलाव का विश्लेषण करने के लिए एसईएम और मंदिर आयोजित किए गए थे। तन्यता मापांक में 20% की वृद्धि और प्रभाव शक्ति में 25% वृद्धि पीपी में 5% एचएनटी में शामिल होने पर मनाई गई थी। यह पाया गया कि तन्यता मापांक, flexural मापांक और flexural शक्ति क्रमशः 35%, 25% और 30% की वृद्धि हुई पीपी-जी-एमए: 2: 1 अनुपात में एचएनटी। क्रिस्टलीकरण पीक एक्सओथर्मिक तापमान, टीपी ने एचपीटी के उच्च मात्रा को जोड़ने पर 5% एचएनटी और 13-14 डिग्री सेल्सियस के साथ पीपी के लिए 11 डिग्री सेल्सियस की वृद्धि दिखायी, जबकि पिघलने का तापमान अपरिवर्तित रहता है। 5% एचएनटी तक एचएनटी सामग्री की बढ़ती मात्रा में थर्मल स्थिरता बढ़ जाती है और फिर एचएनटी के आगे लोड होने पर अपरिवर्तित रहे।

केशिका रेमेटी से, पीपी / एचएनटी कंपोजिट्स की चिपचिपापन में उच्च कतरनी पिघलती हैं, एचपीएन लोडिंग के 5% तक स्वच्छ पीपी के समान प्रवृत्ति का पालन करते हैं। कॉग्स्वेलों के अभिसरण प्रवाह का विश्लेषण करके और वैगनर के मॉडल के बाद रेयोटेंस प्रयोग करके, विस्तारित चिपचिपाहट, 5% तक बढ़ती एचएनटी सामग्री के साथ बढ़ी और फिर उच्च लोडिंग पर काफी कमी आई। सभी नमूने 0.31-0.5 9 की सीमा में पावर लॉ इंडेक्स (एन) के साथ छट्प्लास्टिक (कतरनी-पतलापन) व्यवहार दिखाते हैं। भंडारण मापांक [जी] एचपीटी द्वारा एचपी द्वारा पीपी की पुष्टि करने के लिए एचएनटी को जोड़ने के लिए कम आवृत्ति क्षेत्र में मुख्य रूप से वृद्धि हुई है, जो कम्पैटीबिलाइज़र की उपस्थिति में आगे बढ़ाया गया था। पीपी-जी-एमए जोड़ने पर विस्तारित चिपचिपापन भी बढ़ गया है इन अध्ययनों से यह निष्कर्ष निकाला जा सकता है कि ~ 5 वेट% तक के लिए हेलोसाइटी नैनोट्यूब का प्रयोग यांत्रिक, थर्मल, पिघल शक्ति और पीढ़ी के गुणीय गुणों को सुधारने के लिए पूरक के रूप में किया जा सकता है जो बिना पीपी-जी-एमए : 2: 1 के अनुपात में एचएनटी

पीपी के रूपात्मक, मैकेनिकल, थर्मल और रियोलॉजिकल गुणों पर सीपीओलाइट सामग्री (5 और 10 वेट%) का प्रभाव और सीपीओलाइट अनुपात (1: 1, 2: 1, 3: 1 रखते हुए सीपियोलिएट सामग्री को 5 वेट% पर तय किया गया है) से कम्पैटीबिलाइज़र। / सेपोलैटेस नैनोकोमोसाइट्स की जांच की गई और परिणाम अध्याय 4 में संकलित किए गए। यह देखा गया कि पीपी मैट्रिक्स में कंपोलिलाइज़र के रूप में पीपी

मैट्रिक्स में सीपोलिटिस को बेहतर ढंग से फैलाया जा सकता है। Sepiolite जोड़ने पर पीपी के टीपी में लगभग 15 डिग्री सेल्सियस वृद्धि पुष्टि की है कि Sepiolite एक nucleating एजेंट के रूप में अभिनय है जो भी प्रतिशत क्रिस्टलीयता और यांत्रिक गुणों में वृद्धि द्वारा समर्थित है पीपी / सीपीओलाइट नैनोकोमोसाइट्स में पीपी-जी-एमए को शामिल करने पर, यांत्रिक गुणों और थर्मल स्थिरता में भी सुधार हुआ। संयोजी पीपी / सीपीओलाइट नमूनों के लिए सीपीओलाइट जोड़ने पर उच्च कतरनी चिपचिपापन बढ़ता है, यह साफ पीपी के बराबर पाया जाता है।

अनुपस्थिति में पीपी / एचएनटी और पीपी / सीपीओलाइट के गैर इज़ोटोरामल क्रिस्टलाइजेशन काइनेटिक मापदंडों की अनुपस्थिति / संगतता की उपस्थिति में [मैरिक एनहाइड्राइड कलम-पॉलीप्रोपाइलीन (पीपी-जी-एमए)] चार अलग-अलग शीतलन दर पर अंतर स्कैनिंग कैलोरीमेट्री का उपयोग करके जांच की गई। क्रालाइजेशन मापदंडों को एविरामी, जेजोरनी, लियू और मो के मॉडल द्वारा विश्लेषण किया गया। एचओएनटी और सीपोलैइट की न्यूक्लेईज की क्षमता का मूल्यांकन डोबेरेवा और गटज़ोवा मॉडलों के द्वारा किया गया था। तीन isokinetic मॉडल (ऑगिस-बेनेट, किसिंजर और तखोर) का उपयोग करके गैर इज़ोटोरामल क्रिस्टलीकरण कैनेटीक्स प्रक्रिया की सक्रियण ऊर्जा अनुमानित थी। पीपी चेन की गतिशीलता में बाधा डालने के साथ-साथ एचएनटी या सीपोलैइट सामग्री बढ़ने पर ΔE का मूल्य बढ़ा है। हालांकि, बढ़ती पीपी-जी-एमए सामग्री के साथ ΔE कम हो गया यह मैट्रिक्स और भराव के बीच बढ़े हुए आसंजन के कारण हो सकता है जो पीपी चेन की आवाजाही को सुविधाजनक बनाता है।

पीपी, पीपी / एचएनटी और पीपी / सीपीओलाइट नैनोकोमोसाइट्स की ज्वलंत विशेषताओं पर आईएफआर योजक [एपीआर -766] का प्रभाव व्यवस्थित तरीके से जांच की गई और परिणाम अध्याय 6. में आईपीआर के 25% होने के साथ-साथ वी -0 रेटिंग को दिखाया गया है। यांत्रिक गुणों की गिरावट कंपोजिट के जलते व्यवहार आईएफआर और नैनोकल के संयोजन का उपयोग कर तैयार किया जाता है i.e. पीपी: एचएनटी: आईएफआर / पीपी: सीपीओलाइट: IFR 75: 5: 20 के अनुपात में यांत्रिक गुणों में महत्वपूर्ण सुधार के साथ वी 0 रेटिंग दिखाता है। आईएफआर के संशोधन को आईएफआर के साथ पेंटेरीथ्रिटोल ट्राइक्र्रीलाट (पीईटीए) के उपचार के बाद भी किया गया, जिसके बाद यूवी का इलाज किया गया और फ्लेमिंग व्यवहार और यांत्रिक गुणों पर इसके प्रभाव की जांच की गई। जब हम पीईटीए को संशोधित IFR को additive के रूप में इस्तेमाल करते थे, तो पीपी या पीपी नैनोकोमोसाइट्स के प्रदर्शन [फलंपबिलिटी और मैकेनिकल गुण] में एक महत्वपूर्ण सुधार हुआ था।

अध्याय 7 में सारांश, निष्कर्ष और भविष्य के काम के लिए अवसर दिया गया है।

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LIST OF ABBREVIATIONS & SYMBOLS

ASTM	American Society for Testing and Materials
APP	Ammonium polyphosphate
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
FR	Flame Retardant
FT-IR	Fourier transform infra red spectroscopy
G'	Storage modulus in parallel plate rheology
G''	Loss modulus in parallel plate rheology
HNT	Halloysite nanotubes
IFR	Intumescent flame retardant
LOI	Limiting Oxygen Index (LOI)
MFI	Melt flow index
MFR	Melt flow ratio
PETA	Pentaerythritol triacrylate
PP	Polypropylene
PP-g-MA	Maleic anhydride grafted PP
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_o	Temperature corresponding to 10% degradation
T_p	Crystallization peak temperature
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
Φ	Nucleation activity
β	Cooling rate