Fire retardancy behavior of polymer/clay nanocomposites

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NANYANG
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**FIRE RETARDANCY BEHAVIOR OF POLYMER/CLAY
NANOCOMPOSITES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

1st Aug 2016

Date

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Abstract

Polymer/clay nanocomposites show significant reduction in peak heat release rates (up to ~70 %) during combustion, which is instrumental in restricting the flame spread and subsequent fire growth. This makes clay a potential eco-benign flame retardant for polymers. However, majority of polymer/clay nanocomposites display lower ignition times, restricting their wide-spread usage. Though this is widely attributed to the catalytic reactivity of clay, this aspect is poorly studied so far. This essentially forms the basis of this work, which focuses on developing a detailed understanding of the influence of metal ions like Mg^{2+} , Al^{3+} , and Fe^{3+} that are inherent to clay structure on the decomposition behavior of organic matter (polymer and organic modifier).

To accomplish the above objective, in the first part of study, montmorillonite (MMT, from smectite clay family) was enriched with these metal-ions by cation exchange process to amplify their concentration at exchange position. Their effect on decomposition behavior of organic modifier, hexadecyltrimethylammonium bromide (HDTMA^+), and subsequently on combustion and thermo-oxidative decomposition behavior of polyamide 6 (PA6) matrix was evaluated. The second part of study focuses on the elucidating the catalytic activity of different smectite clays that are inherently and individually rich in one of these metal ions in their octahedral layer. Precisely, hectorite (rich in Mg^{2+}), montmorillonite (rich in Al^{3+}) and nontronite (rich in Fe^{3+}) are used.

It was observed that the catalytic activity of exchanged clays was a combined effect of Brønsted and Lewis acid characters associated with the metal ions. Brønsted acidity affected the initial stages of organic modifier decomposition, while Lewis acidity affected the oxidation stability of carbonaceous residue beyond clay dehydration temperatures. Mechanism of HDTMA^+ decomposition is provided adding fundamental knowledge to the field of organically modified clays. Even in PA6 matrix, each metal ion uniquely influenced different stages of decomposition depending on its concentration, location and degree of clay dispersion. By evaluating both condensed phase and gas phase chemical compositions, the effect of metal ions on thermo-oxidative decomposition mechanisms for PA6 are proposed. Briefly, the presence of Al^{3+} accelerated (time and temperature of)

decomposition during the initial stages, while Mg^{2+} rich composite displayed maximum thermo-oxidation stability and gave the highest char. Fe^{3+} has prominently altered the chemical composition of condensed phase during pre-ignition stages without having any noticeable effect on decomposition onset temperature. However, it also generated highest smoke.

Further, the catalytic effect of clays followed a similar pattern even when the metal ions are situated in the octahedral layer (lattice sites). Hectorite containing PA6 showed highest charring tendency synonymous to MgMMT; while nontronite (similar to FeMMT) reduced oxidation stability of carbonaceous matter and generated more smoke.

Last part of this work explores an avenue to restrict the interfacial interaction between clay surface and polymer matrix, virtually, making PCN combustion and decomposition independent of clay catalysis. To achieve this target, a simple route is proposed wherein organically modified clay was coated with high-temperature-resistant polymers like polyetherimide and polyimide using solution-suspension mixing. High glass transition temperatures/very high melting points of these coating polymers prevented direct contact between clay surfaces with neighboring decomposing PA6 matrix. This has led to prevention of (clay-catalysis assisted) early ignition while maintaining the unique advantage of polymer/clay nanocomposites i.e. reduction in peak heat release rate (~52 % as compared to the neat matrix).

In conclusion, this is the first-of-its-kind report providing a holistic insight into the effect of individual metal ions inherently present in clays on thermo-oxidation and combustion behaviors of polymer/clay nanocomposites. A performance matrix was also generated that associates each metal ion with different combustion and decomposition properties like decomposition time/temperature, total decomposition enthalpy, smoke generation and char formation. This matrix can be utilized in design and development of clays to impart superior flame and fire retardant properties to polymer/clay nanocomposites.

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“Break the problem into pieces and solve one piece at a time.”

“Take a risk- it is essential to grow and develop.”

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Abbreviations

ACN	Acetonitrile
ASTM	American Society for Testing Materials
APP	Ammonium polyphosphate
ATH	Aluminum trihydroxide
ATR	Attenuated total reflectance
BDEs	Bromodiphenylethers
CEC	Cation exchange capacity
DCP	Dicresyl phosphate
DMAc	Dimethyl acetamide
EVA	Ethylene vinylacetate
FR	Fire retardant
FT-IR	Fourier Transform Infrared Spectroscopy
T _g	Glass Transition Temperature
HDTMA-Br	Hexadecyltrimethyl ammonium bromide
Hec	Hectorite
HIPS	High impact polystyrene
HRR	Heat release rate
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
LOI	Limiting oxygen index
MDH	Magnesium dihydroxide
MLR	Mass loss rate
T _m	Melting point
MI-	Metal ion exchanged-
MMT	Montmorillonite
NIST	National Institute of Standards & Technology
Nnt	Nontronite
OMI-	Organically modified metal ion exchanged-
pHRR	Peak heat release rate
PAN	Polyacrylonitrile

ABS	Poly(acrylonitrile-co-butadiene-co-styrene)
PA6	Polyamide 6
PA66	Polyamide 6,6
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PE	Polyethylene
PET	Polyethylene terephthalate
POSS	Polyhedral oligomeric silsesquioxane
PI	Polyimide
PLA	Polylactic acid
PMMA	Poly(methyl methacrylate)
PCN	Polymer/clay nanocomposite
PP	Polypropylene
PAA	Poly(pyromellitic dianhydride-co-4,4'-oxydianiline)amic acid
PS	Polystyrene
SAN	Poly(styrene-co-acrylonitrile)
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
rpm	Revolutions per minute
Rip	Ripidolite
SEM	Scanning Electron Microscopy
TTI	Time to ignition
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
TG-IR	Thermogravimetric analyzer coupled with infrared spectrometer
THR	Total heat release
TSP	Total smoke produced
TSR	Total smoke release
TEM	Transmission Electron Microscopy

TCP	Tricresyl phosphate
TPhP	Triphenyl phosphate
UL	Underwriters' Laboratories
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter provides an overview of fire retardancy behavior of polymer/clay nanocomposites. Time-to-ignition, a major limiting factor of these materials is discussed in detail, followed by research motivation and objective. Briefly, the motivation of this work is to understand the role of clay during pre-ignition stages and its influence on ignition resistance of polymer/clay nanocomposites. Research objective is to elucidate the effect of catalytic activity of clay, more precisely, metal ions that are inherently present in its (structural) lattice on combustion properties of polymer/clay composites. Subsequently, research hypothesis is detailed. The last section of this chapter deals with an overview of thesis organization along with a short introduction of each chapter to follow.

1.1 Overview

Widespread use of polymers in our day-to-day life has aggravated concerns associated with their fire safety. Depending on final applications, different classes of fire retardants (FRs) are used, however, each class is associated with certain drawbacks¹⁻⁷. For example, halogenated FRs, although once perceived as best performing FRs, are linked to health and environmental concerns which have outweighed their usefulness. As a consequence, commonly used halogenated FRs like polychlorinated biphenyls (PCBs), penta-/octa-/deca-bromodiphenylethers (BDEs) are phased out from Americas and EU^{1-2, 7}. As an alternative, phosphorous based FRs (phosphates and phosphinates) are being used. However, recent toxicological studies are providing unfavorable evidence for certain well known FR phosphates. For example, triphenyl phosphate (TPhP), dicresyl phosphate (DCP) and tricresyl phosphate (TCP) are deemed as toxins especially for aquatic organisms while diethyl phosphinic acid is determined to be biologically persistent³. This has triggered dedicated research in the development of an efficient and eco-benign FRs. Metal hydroxides like aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH) come under this category. However, loading levels required for their effectiveness can be as high as 60 wt.% making them less viable for end applications those are critical to certain properties like toughness, product weight, among others (e.g. under-the-hood components in automobiles, etc.). They also pose challenges in processing and require high ratios of processing aids⁸⁻⁹.

On the other hand, polymer/clay nanocomposites (PCNs), in addition to their superior mechanical and barrier properties¹⁰, display improved fire retardancy with a significant reduction in heat release rates (HRR) (up to 70%) at loading levels as low as 3 - 5 wt.%¹¹⁻¹². Additionally, PCNs have already transitioned from academic research into commercial development. Some selected commercial applications of PCNs are reported in Table 1.1. It is estimated that total consumption for nanocomposites in 2019 will amount to ~585,000 MT valued at US\$ 4.2 billion out of which 60.2 % is estimated to be based on PCNs¹³. Because PCNs simultaneously bring many properties to the table, they are actively being perceived as potential FR alternative.

Despite the huge reductions in peak HRR (pHRR) of PCNs compared to their base polymers, PCNs most often ignite very early and the total heat released is similar to neat polymer⁸. This is the principle reason, restricting their use as stand-alone fire retardant system. As a result, commercial PCNs are used for other target properties but require incorporation of additional FRs to clear fire safety tests.

Table 1.1 Few selected commercialized PCN products¹⁴.

Matrix	Organo-clays	Processing	Application-properties	References
Polyamide (PA6/PA6,6/ PA6,12)	Nanomer [®] series T (Nanocor, Inc.)	Injection molding, blow and extrusion molding, film casting	Gas barrier films for food packaging & beverages, flame retardant, automotive parts (timing belts, barriers, fuel line and tank, body panel, bumpers)	Bayer AG (Durethan [®] KU 2-2601) RTPCompany (RTP 299 X series) Honeywell Polymers (Aegis [®] NC & OX) Nanocor Inc. (Imperm [®]) Ube (Ecobesta) NYCOA (nanoTUFF TM , nanoSEAL TM) Toyota Nanocor (Nanomer [®] series E) Nanocor (nanoMax [®])
Polyolefins (PE, PP, EVA)	Nanomer [®] (Nanocor, Inc.)	Injection molding, blow and extrusion molding, film casting	Flame retardant, automotive furniture appliance (step-assist for GMC Safari, Chevrolet Astro vans, and trims, center bridge, sail panel & box rail protector for Hummer)	Noble Polymer (Forte TM , Nubrid TM) General Motors Corp. (with Basell USA Inc. & Southern Clay Products, Inc.) PolyOne Corp. (Nanoblend TM)
Polyurethane	Cloisite [®] (Southern Clay Products, Inc. now BYK, Inc.)	Sheet molding	Hull, deck, and liner of Yamaha's WaveRunners [®] (personal water craft)	Yamaha Motor Corp. (NanoXcel [®])
Epoxy resin	Nanomer [®] series E (Nanocor, Inc.)	Injection molding, blow and extrusion molding, film casting	High voltage insulation	Nanocor (Nanomer [®] series E)
Polyvinyl alcohol	Vermiculite	Injection molding, blow and extrusion molding, film casting	Gas barrier films for food packaging	NanoPack Inc (nanoSEAL TM)
PP/PS blends	Nanofil [®] (Southern Clay Products Inc.)	Injection molding, blow and extrusion molding	Footwell heater vent for various Volkswagen & Audi models	Putsch Kunststoffe GmbH (Elan XP)

1.2 Motivation and Research Objectives

Many theories are proposed addressing this issue of early ignition such as decomposition of clay surfactant triggering matrix decomposition¹⁵⁻¹⁶, heat build-up on the surface due to

reduced thermal conduction¹⁷ as a result of clay platelets and most widely agreed upon theory of clay-initiated catalytic decomposition of polymer matrix¹⁸⁻²¹. With a lot of reports showing early ignition behavior with PCNs, recently, a few dedicated efforts are made to fundamentally understand the involved chemistry²¹⁻²².

In 2011, Fina et al.²¹ reported time-temperature correlation during PCN combustion. For different matrices studied (PP, PET, and PA6), it was observed that clay nanocomposites ignited as soon as the surface material reached its decomposition temperature while neat material showed significant delay before ignition. It was suggested that presence of clay platelets catalyze the oxidation of volatiles generated as a consequence of decomposition of the matrix (at surface) lowering the ignition times. While in the case of neat material, the ignition delay was associated with the time required for volatile build-up to reach critical level essential for self-sustained ignition. More recently, in 2013, Carvalho et al.²² provided experimental evidence for the radical trapping effect of Fe^{3+} . Reduction of structural Fe^{3+} to Fe^{2+} was observed when clay was incorporated in PMMA matrix and heated beyond decomposition temperature of the nanocomposite. This can be considered as a first significant step towards understanding clay catalysis and establishing the role of clay composition in thermal decomposition of polymer (organic matter).

Before discussing combustion of PCNs, it is important to understand a critical aspect associated with clays: cation migration. This is necessary to comprehend the influence of the structural composition of clay on the migration of interlayer cations because at high temperatures presented during combustion, it can change the chemical nature of clay surface, *in situ*. To support this idea, a few relevant clay mineralogical studies are highlighted as follows:

- Tettenhorst²³ reported that upon heating above 200 – 300 °C temperatures interlayer cations migrate into the vacant regions of tetrahedral and octahedral layers (refer to Figure 1.1) which subsequently affect the stretching vibration of $\text{Si-O}_{\text{basal}}\text{-Si}$ bond that can be detected using FT-IR. This migration was confirmed by observing shifts in FT-IR bands corresponding to $\text{Si-O}_{\text{basal}}$ to higher frequencies (from 1035 to 1055 cm^{-1}) and decreasing intensity of the band corresponding to Al-OH-Al (918 cm^{-1}).
- Chorom et al.²⁴ observed changes in surface characteristics for different homoionic clays as a result of thermal treatment up to 400 °C which were attributed to migration

of interlayer cations to vacant octahedral sites lowering the inherent negative charge of clay platelet. Figure 1.2 highlights the changes observed in pH values and zeta potentials for clays preheated to desired temperatures. Cation concentrations as determined by ICP-AES were reported which is plotted in Figure 1.2C.

Figure 1.1 Typical smectite clay structure.

Figure 1.2 Influence of heating on surface properties of different metal-ion exchanged clays as indicated by pH (A) and zeta potential (B) for their respective suspensions. Reduction of cation concentration due to migration of interlayer cations to octahedral vacant site as a result of heating is shown in (C)²⁴.

- Calvet et al.²⁵ observed a shift in the band from ~ 920 to ~ 932 cm^{-1} upon heating MgMMT at 400 °C and attributed this to the migration of Mg^{2+} into silica skeleton.

- Purnell et al.²⁶ observed that interlayer (exchanged) cations like Ni^{2+} , Co^{2+} and Zn^{2+} displayed inwards migration upon heating at 200 °C.
- Migration of Cu^{2+} into hexagonal holes upon heating Cu^{2+}MMT up to 350 °C has also been reported²⁷.
- Bakandritsos et al.²⁸ reported a reduction of intercalated Fe^{3+} to Fe^{2+} and its simultaneous migration to vacant octahedral locations.
- Kulbicki²⁹ reported phase developments in different homoionic MMTs. The changes in intensities of characteristic diffraction peak for different phases with increase in temperature are shown in Figure 1.3 which clearly highlight the effect of migration of exchange cations on overall phase transformations in MMT at high temperatures.

Figure 1.3 High-temperature phase transformation in MMT (cheto-type) exchanged with different cations. Neat cheto-type MMT predominantly have Ca^{2+} at exchange position along with some Mg^{2+} . Different phases are montmorillonite (M), quartz (Q), β -cristobalite (Cr), anorthite (An), cordierite (Co) and spinel (Sp)²⁹. Cheto MMT comes from Cheto, Arizona, USA.

- Acid activated MMT (H^+ -MMT) demonstrate autotransformation process where H^+ migrates from interlayer position to replace metal ions (Mg^{2+} , Al^{3+} , Fe^{3+}) from their lattice locations. These displaced ions then assume exchange positions, essentially converting H^+ -MMT into Mg-, Al- or FeMMT³⁰⁻³². Autotransformation leads to a reduction in mean layer charge by lowering number of strong acid sites while increasing weak acid sites. It is also suggested that protons preferentially attack $Mg(O, OH)_6$ octahedra during autotransformation³³.
- In addition to metal ion migration, Klopogge et al.³⁵ reported that even $-OH$ groups migrate from octahedral layer to siloxane layer during heating forming new silanol sites in smectites. Corresponding migration temperature is dependent on principle octahedral ions e.g. in Mg-smectites like hectorite, FT-IR signal corresponding to silanol group (3741 cm^{-1}) were observed above $250\text{ }^\circ\text{C}$ ³⁴ whereas they were observed at $\sim 3711\text{ cm}^{-1}$ above $400\text{ }^\circ\text{C}$ in case of Al-smectite like beidellite.

Quantification of such migrations within clay is a steep challenge. Alternatively, evaluation of the effect of all metal ions from clay on polymer decomposition can certainly help develop a holistic understanding of the associated *in situ* changes in clay reactivity (as a function of metal ions) during combustion. This can play an instrumental role in the (i) development of a mathematical model that can account for clay catalysis to predict the combustion properties of PCNs with greater accuracy; and (ii) design and synthesis of ‘tuned’ clay nano-platelets with proper proportions of metal ions from the viewpoint of fire safety applications.

Typical clays used in PCNs belong to smectite family and contain structural cations like Mg^{2+} , Al^{3+} , and Fe^{3+} in varied combinations³⁶. Although there are some reports on the role of Fe^{3+} on polymer decomposition, still the role of other metal ions inherently present in all naturally occurring clays remain elusive³⁷⁻³⁸. To the best of author’s knowledge, no systematic study has been reported that explores the role of these metal ions from clay on the decomposition of organic matter (polymer or surfactant). Addressing this vital link in associating clay chemistry with polymer combustion and in turn fire retardant properties of PCN forms the backbone of this work. It is expected that such focused approach will

generate new insights into reasons for early ignition along with other combustion properties. Filling this knowledge gap is precisely the motivation behind this work.

1.3 Research Hypothesis and Scope

There are two different categories of metal ions associated with the structure of clay, viz. exchangeable cations and structural cations. Exchangeable cations act as charge neutralizers to an excess negative charge created by isomorphous substitutions in smectite clays e.g. Mg^{2+} replacing Al^{3+} in MMT clay or Li^{+} replacing Mg^{2+} in Hec. These exchange cations, typically Na^{+} and Ca^{2+} , occupy interlayer positions. They can be easily replaced by ions with higher oxidation numbers by very well-documented phenomenon of cation-exchange. The extensive use of clays in trapping radioactive ions in ground to avoid contaminations is based on this phenomena³⁹. Structural metal ions, on the other hand, are present in tetrahedral and octahedral layers of clay lattice. They are ionically bonded with oxygen and/or hydroxyl groups. Different ratios and combinations of these structural metal ions are giving a unique identity to each naturally occurring clay regarding their reactivity, physio-thermal transformations, etc.³⁶.

While studying the chemical nature and catalytic reactivity of metal ions in clays (in this case, Mg^{2+} , Al^{3+} , and Fe^{3+}), it is equally important to evaluate their effect when they are present in exchange as well as structural position. As mentioned earlier, through “autotransformation”, hydrogen ion (in H^{+} -MMT) from interlayer position migrate into the clay lattice to knock-off other metal ions (Mg^{2+} , Al^{3+} or Fe^{3+}) from their structural locations³¹. This is of particular importance because decomposition of surfactant modified MMT also leads to the formation of H^{+} -MMT, *in situ*. Influence on the catalytic ability of clay as a result of possible metal ion migrations during decomposition of PCNs cannot be overlooked. Hence, it is necessary to evaluate the effect of each metal ion from clay on polymer decomposition for fundamental understanding. Accordingly, the following hypothesis is put forth for this work.

Principle Hypothesis: Different metal species inherently present in clay can catalytically affect various stages of organic decomposition (polymer and clay surfactant).

Further, clay dispersion is known to be critical component of PCN. It can significantly influence the combustion properties. This leads to a sub-hypothesis given as follows,

Sub-hypothesis 1: Clay dispersion and distribution are equally important as clay composition because they govern the quality and magnitude of organo-clay interaction throughout the bulk volume.

To validate the hypothesis put forth, it was important to study PCN incorporated with clays that have chemically neutral surfaces. For the main hypothesis to hold true, combustion properties of PCN with neutral clays should remain similar to that of neat matrix. Further, it should continue to maintain the advantage of reduced pHRR as it is perceived to be principally governed by the physical process of clay barrier development. Accordingly, following validation hypothesis is put forth,

Sub-hypothesis 2: Prevention of interface interaction between clay platelet and polymer matrix can prevent early ignition.

Scope:

To address principle hypothesis, NaMMT was separately modified with Mg^{2+} , Al^{3+} and Fe^{3+} ions using cation-exchange process. This led to increasing the concentration of each metal ion that would amplify their effect making it observable. These MI-clays were incorporated in PA6 matrix using melt blending. Decomposition and combustion properties of these PA6/MI-clay composites are evaluated to identify the effect of each metal ion. Maintaining same polymer matrix (PA6), same base clay (MMT) and same clay surfactant (HDTMA-Br) any changes observed are, therefore, attributed to the metal ions at exchange position.

In addition to MMT (which is rich in structural Al^{3+}), Hec and Nnt were studied as they are rich in structural Mg^{2+} and Fe^{3+} , respectively. As all these clays belong to (expandable) smectite family and all have platelet shapes, a controlled comparative analysis is carried out in Chapter 6.

Further, the cross-comparison between decomposition and combustion properties of PA6/MI-clay composites and PA6/clay composites helped to generate a performance matrix associating each metal ion with different properties.

To address sub-hypothesis 1, organically modified clays were used to make PA6 composites. MI-clays upon organic modification were expected to experience reduced metal ion concentration due to direct competition between metal ions and ammonium ion from surfactant to occupy exchange positions. Although OMI-clays contained lower metal ion concentrations their superior dispersion in PA6 matrix facilitated enhanced organo-clay interaction due to increased interfacial area between PA6 and OMI-clays. A comparison amongst PA6/OMI-clay nanocomposites provided an effect of metal ions on decomposition. In addition, cross-comparison with PA6/MI-clay provided insights into effect of clay dispersion on combustion properties as influenced by residual metal ions.

As metal ions in MMT, Hec and Nnt are structural; their end concentrations cannot change with organic modification. Only their dispersion and distribution got influenced. As these clays belong to the same family, use of same surfactant (HDTMA-Br) was possible. This removed, otherwise significant, variable while comparing properties with their PA6/OMI-clay counterparts.

To address sub-hypothesis 2, commercially available organically modified clay was used. It was physically coated with two different high-temperature-resistant polymers, polyetherimide (PEI) and polyimide (PI) via solution mixing. Each coating polymer displays very high glass transitions and melting points which will continue to prevent direct contact between clay surface and polymer matrix while PA6 matrix undergoes a transition from solid-to-melting-to-decomposition. Morphology and subsequent effect of coating procedure (solution-precipitation for PEI and solution-imidization-precipitation for PI coating) on interaction with PA6 matrix have been discussed.

Hence, with acquired knowledge effort is made to provide answers with experimental evidence for clay catalyzed early ignition in PCNs.

1.4 Novel Findings and Outcomes

This research addresses important issues related to combustion properties of PA6/clay nanocomposites yielding novel and fundamental insights. They include:

1. A systematic analysis has been carried out to elaborate on the effect of different metal ions inherently present in clay on the decomposition and combustion properties of PCN. A performance matrix is being generated for each metal ion (Mg^{2+} , Al^{3+} , and Fe^{3+}) associating with different stages and crucial aspects of decomposition viz. ignition, total heat release, smoke generation, and char formation. The performance matrix also incorporates the impact of location of metal ion in clay lattice. Depending on end properties required for PCN, this matrix can be used to identify appropriate clay composition. For example, optimum ratio and/or concentration of Mg^{2+} and Al^{3+} can make clay act as a char promoter. On the other hand, Al^{3+} , Fe^{3+} or their combinations can provide an accelerated decomposition of PCN from the viewpoint of the end-of-life properties.
2. It is established that both, clay composition and clay dispersion, are equally important as they govern the interfacial interaction between matrix and clay surface.
3. For the first time coated clays are used as an experimental confirmation directly linking early ignition with the catalytic activity of clay as influenced by interfacial interaction between polymer matrix and clay surface.
4. Coated clays can also be considered as a potential solution to prevent early ignition for PCNs without affecting their ability to reduce heat release rates.

1.5 Thesis Organization

So far in *Chapter 1* a brief introduction to the problem statement and motivation for this work was discussed. Hypothesis and scope have also been put forth. Novelty of research findings is listed. Hereafter, a brief structure of the rest of the thesis is given below:

Chapter 2 reviews the literature concerning fundamentals of combustion and fire retardancy. An overview of different commercial FR systems and their limitations is provided. The importance of eco-benign FRs has also been provided to justify this research

work. Structural details of clay have been discussed followed by a detailed review on various stages of combustion and corresponding theories associated with PCNs.

Chapter 3 discusses the rationale behind the material selection, principles underlying the synthesis of different clays and characterization techniques employed. The justification for test methodologies has been provided. Utilization of each technique for data analysis and possible shortcomings, limitations and errors are discussed.

Chapter 4 elaborates the effect of metal ions in clay on altering the decomposition of organic modifier. Structural aspects of clays and their thermo-oxidative decomposition have been reported. Combining multiple characterization techniques, a possible mechanism has been proposed that underline the effects of metal ions on the decomposition of OMI-clays.

Chapter 5 thoroughly evaluates the effect of exchanged clays on thermo-oxidative and combustion properties of PA6 nanocomposites. Unique effects of each metal ion have been established with regards to combustion parameters. Finally, decomposition mechanism has been proposed for PA6 which is prone to catalysis by metal ions.

Chapter 6 elaborates the study of PA6/clay nanocomposites wherein clays used vary in their structural compositions. TGA, cone calorimetry, condensed- and gas-phase analyses of the composites are carried out and correlated with clay structures. A possible decomposition mechanism is proposed for PA6 in the presence of these clays.

Chapter 7 elaborates on avenues to restrict or entirely prevent direct interface between PA6 and clay surface by incorporating physical polymer coat on the clay surface. The details regarding analysis and morphology of coated clays have been reported. Thermo-oxidative and combustion properties of PA6/coated clay nanocomposites have also been reported and analyzed.

Chapter 8 summarizes and draws conclusions that validate the hypothesis put forth. Certain continuing questions are briefly discussed with the inception of strategies for future work.

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Chapter 2

Literature Review

This chapter reviews the literature concerning fundamentals of combustion and fire retardancy of polymer/clay nanocomposites. Different commercial fire retardant systems and their limitations have been reviewed. The importance of eco-benign fire retardant has been provided to justify the need of this research work for polymer/clay nanocomposites. Structural details of clay have been discussed followed by a detailed review on the influence of clays on various stages of combustion and corresponding theories associated with polymer/clay nanocomposites is furnished.

2.1 Fire Hazards: Need of Fire Retardancy

Increasing usage of synthetic polymers in a variety of applications including films, fibers, textiles, insulation, molded interiors, foams and coatings in our day-to-day life has significantly improved the quality of comfort. However, on the flip side, their inherent combustible nature has posed severe concerns regarding fire hazards and risks. These risks can be a combination of different factors like ignitability, flammability of volatiles generated, the total amount of heat release, the rate of heat release, flame spread rate, smoke density, smoke toxicity and fire scenario¹⁻².

According to fire statistics, one person dies in a fire every 169 minutes or is injured every 30 minutes in USA alone³. Of all reported cases of fire in the USA in 2009, about 85% occurred in homes and households³ with polymer-based materials like mattress, appliance bodies, furniture, electrical insulation coatings, etc. being the first-to-ignite. To give a perspective, statistical distribution between deaths and subsequent property damages based on usual household items that ignite first is tabulated in Table 2.1⁴. Counter-intuitively most victims die from inhalation of carbon monoxide, smoke, and other toxic gases and not from burning⁵. The USA alone, in 2009, incurred US\$ 14 billion as direct losses towards fire, while Singapore lost SG\$ 115 million, which highlight the gravity of the situation⁶.

Table 2.1 Household fire statistics between 2003-2006 in the USA⁴.

First item ignited	Fires	Deaths	Injuries	Property damage (\$B)
Upholstered furniture	7400	590	900	0.4
Mattress/bedding	11,200	380	1390	0.4
Thermoplastics	29,400	280	1160	0.7
Structural member, component, insulation	32,500	240	620	1.3
Other furniture or utensils	6000	170	500	0.2
Confined cooking fire/materials	134,900	130	3670	0.3
Interior wall covering	8200	120	340	0.3
Subtotal of above categories	229,600	1910	8560	3.6
Totals	378,600	2850	13,090	6.1

A general downtrend has been observed for deaths due to fire since past few decades which is attributed to newer stringent regulations and legislations associated with fire safety. This

has led to marked increase in development and demand of FRs. In 2014, global demand for FRs reached nearly US\$ 6.08 billion and is expected to soar up to US\$ 8.2 billion by 2019⁷. Apart from household items, use of FRs has become crucial especially in public transportation systems (aircraft, buses and trains) where life safety is of prime importance followed by limiting property damages⁸.

2.2 Fire and Combustion

2.2.1 Fundamental Combustion Mechanism

Three vital components are essential to initiate and sustain combustion viz. *fuel-oxygen-heat* or more popularly known as “*fire triangle*”⁹⁻¹⁰. Polymer combustion is a complex heat-mass transfer process involving two distinct phases^{9, 11}, *gas-phase* and *condensed-phase*. Upon exposure to thermal radiation or flame, melting followed by decomposition of polymeric material takes place in condensed phase generating volatile products. Bubbles of volatiles migrate to the surface and enter gas-phase above the surface where they act as a fuel source. In the presence of air (oxygen), combustion of these volatiles takes place in gas-phase which results into flame.

Chemically, combustion of organic volatiles leads to the formation of highly reactive hydrogen radicals ($H^{\bullet}$). These hydrogen radicals combine with atmospheric oxygen to produce hydroxyl ($OH^{\bullet}$) and oxygen radical ($O^{\bullet}$) [reaction (i)]. Combination reaction between hydroxyl radical and carbon monoxide (CO) is highly exothermic which generates heat in flame [reaction (ii)]. The hydrogen radical generated in reaction (ii) is fed back to reaction (i) thereby leading to a self-sustained combustion process¹².

Parallel to gas-phase reactions, decomposition in condensed-phase continue to provide replacement fuel. There are two principle decomposition mechanisms followed by polymers; *thermal* and *thermo-oxidative*, depending on availability of oxygen. In the absence of oxygen i.e. under an inert atmosphere, polymers experience volatilization via

thermal decomposition whereas under atmospheric condition thermo-oxidative decomposition predominates. Thermo-oxidative decomposition is more influential during pre-ignition stage while under flaming combustion it is thermal decomposition (i.e. anaerobic decomposition) which feeds the flame. Further, importance and degree of thermo-oxidative decomposition is governed by susceptibility of polymer chain to oxygen attack. Overall combustion scheme for polymeric material is schematically depicted in Figure 2.1 where non-flammable condensed-phase decomposition products are termed as charred residues. Charred residues are intrinsically thermally stable, however, they can still undergo oxidation, although very slow, via solid-oxidation reactions as displayed by glowing and smoldering.

Figure 2.1 Thermo-oxidative decomposition scheme for polymeric materials¹³.

2.2.2 Stages of Fire

Fire can be described in five different stages from its inception (Figure 2.2). Typical growth sequence is¹²:

Figure 2.2 Stages of fire growth¹²

1. Ignition: Ignition signifies the point where volatiles developed by overheated material under the presence or absence of external ignition source leads to self-sustained combustion of material.
2. Growth: Flame growth depends on volatiles and their rate of generation. The higher rate of generation and availability of oxygen govern flame growth and subsequent rise in temperature.
3. Flashover: Flashover marks onset of full-blown fire from the initial flame. The temperature hits maximum for burning material (known as ceiling temperature). Delaying the flashover is critical during rescue operations. To put it in perspective, Figure 2.3 shows a typical time scale for activation of sprinkler system and average response time from fire department (in the USA) with respect to fire propagation in real life scenario¹⁴.
4. Fully developed fire: This post-flashover stages sees peak heat release rates and the highest rate of combustion. Fully developed fires are best left alone till all combustible material is consumed.
5. Decay: This is the final stage where all combustible material is consumed and temperature starts to fall. Any residues left behind contribute towards char.

Figure 2.3 An average time scale for activation of sprinklers and fire department response time in the USA against fire propagation and growth in real life fire scenario¹⁴.

2.3 Fire Retardant Systems

Although the history of FRs can be traced back to Egyptian times when timber was treated with solutions of alum (i.e. hydrated potassium aluminum sulfate), it was not until the 1960s when the growth of plastics led to the use of FRs as standard practice. With dedicated research and awareness, FR systems have been evolving based on demands. Table 2.2 showcases the evolution of FR development.

Table 2.2 Principle drivers in research and development of FRs¹⁵.

Decade	Event	Demand
1960s	Widespread availability of cheap polymer products—more serious fires	Reduced ignitability
1970s	Smoke much worse	Reduced smoke
1980–1990s	Development of Cone Calorimeter (and emphasis on peak heat release rate, rather than ignitability) Increase in deaths from smoke inhalation	Reduced Peak Heat Release Reduced Fire Toxicity
2000s	Halogen FRs found across the ecosystem	Halogen-free FRs
2010s	Climate change and other environmental concerns become mainstream	Sustainable FRs

2.3.1 Classification of Fire Retardants

FR additives are primarily classified based on their mode of action⁹⁻¹⁰. A typical classification flow chart for FR is shown in Figure 2.4.

Figure 2.4 Typical classification of FR systems¹⁵

Gas-phase additives:

These additives act through chemical mode in the gas phase to scavenge free radicals generated as a result of thermo-oxidative decomposition of polymer. This in turn restricts radical chain reactions in flame. Some of these additives can also demonstrate physical mode of action in the gas phase that either generates a significant amount of non-combustible gases that dilute the flammable gases or those which endothermically dissociate to slow down the combustion by reducing flame temperature.

Condensed-phase additives:

Barrier promoters are most widely used condensed-phase FR additives. Intumescent systems are more commonly used where a porous carbonaceous foam barrier is created which restricts thermal transport to base material as well as cutting off the oxygen supply,

hence, extinguishing the flame. Char promoters promote charring either by chemically interacting with a polymer or by physically constraining and reducing polymer volatilization. Mediated catalysis or oxidative dehydrogenation by additives can also improve charring. While inorganic additives go through endothermic dissociation in condensed phase generating non-combustible residues or simply act through the physical mode of action by creating tortuous path limiting volatilization.

2.3.2 Different Fire Retardant Systems

2.3.2.1 Halogen-based Systems

Their unmatched flame extinguishing properties led to their widespread usage since the early 1970s. Halogen-based FRs are synonymous to chlorine-based and bromine-based compounds that can form halogen radicals ($X^\bullet$) just below or at polymer decomposition temperatures. These radicals abstract hydrogen from polymer chains to form hydrogen halide that volatilizes leaving behind the radical site in polymer chain ($R_1^\bullet$, $R_2^\bullet$, etc.), a precursor for unsaturation and eventual char formation. Overall mechanism is depicted in reaction between (iv – vii)¹⁶⁻¹⁷. Reactions (v) along with (vi + vii) form a chain reaction in which hydrogen halide act as a catalyst to self propel the reactions. The gaseous hydrogen halide act as radical scavengers for (highly reactive) gas-phase hydrogen and hydroxyl radicals formed as a result of combustion. Due to reduction in hydrogen and hydroxyl radicals overall radical chain propagation rate is reduced lowering the evolved heat, thus, lowering the flame temperature. This limits the generation of combustible volatiles eventually extinguishing the flame.

However, use of certain halogenated FRs is restricted due to their inherent toxicity and detrimental environmental effects. Further, generation of a substantial quantity of highly

corrosive gases (halides) has risen concerns regarding their safety in confined spaces like aircraft fuselage or marine hull compartments¹⁸. Generation of hazardous dioxins and dibenzo-furans during end-of-life processes like recycling and incinerations have serious environmental repercussions. As a result, European Union, USA, and Canada have phased out some widely used brominated FRs like BDEs and hexabromocyclododecane¹⁹. However, a new breed of less severe halogenated fire retardants are being developed.

2.3.2.2 Phosphorous-based Systems

Phosphorous based-FRs are most widely used alternative to halogen-based FRs. Their condensed phase reactivity leads to the formation of phosphoric acid as a result of thermal decomposition of FR, which through elimination of water forms phosphates. The water release causes dilution of combustible gases. They can further catalyze char formation in condensed phase²⁰. Some phosphorous based-FRs volatilize to form active radicals in gas-phase like $\text{PO}_2^\bullet$, $\text{PO}^\bullet$, $\text{HPO}^\bullet$ that readily scavenge hydrogen or hydroxyl radicals from the gas phase to restrict combustion²¹.

Although broad spectrum toxicity studies are yet to be made for phosphorous-based FRs, initial studies have suggested that some of these compounds might be neurotoxicants, but their usage remains unhampered until further strong evidence is obtained²². Furthermore, the condensate of gas phase phosphorous-based volatiles promotes stress corrosion leading to cracking of various parts²².

2.3.2.3 Metal Hydroxides & Metal Carbonates

Most common metal hydroxides used as FRs for polymers are ATH and MDH. They decompose endothermically reducing the temperature in addition to the release of free water which further cool down the pyrolysis zone²³⁻²⁴. Table 2.3 provides decomposition temperatures and corresponding (endothermic) enthalpies for common mineral fillers. Also, it was proposed that anhydrous alumina can catalyze dehydration of some polymers to enhance charring¹⁶. The selection of one over the other depends on polymeric matrix. For instance, ATH starts to decompose around 180 °C, while MDH decomposes from 300 °C;

this clearly indicates that the processing temperature of polymer governs their selection as well.

Table 2.3 Decomposition temperatures and endothermic enthalpies for common mineral fillers¹⁵.

Filler	Formula	T _{decomp} /°C	ΔH _{decomp} /kJ g ⁻¹
Aluminium hydroxide	Al(OH) ₃	180–200	1300
Magnesium hydroxide	Mg(OH) ₂	300–320	1450
Calcium hydroxide	Ca(OH) ₂	430–450	1150
Nesquehonite	MgCO ₃ ·3H ₂ O	70–100	1750
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	220–240	1300
Huntite	Mg ₃ Ca(CO ₃) ₄	400	980
Ultracarb	Hydromagnesite/Huntite	220–400	1172
Boehmite	AlO(OH)	340–350	560

where, T_{decomp} is decomposition temperature range and ΔH_{decomp} is corresponding (endothermic) decomposition enthalpy.

Globally by weight, ATH is single largest commercially produced fire retardant²⁵. Their biggest drawback is the very high loading level requirements, 35 % - 65 %, to be an effective fire retardant. This severely hampers final impact strength (toughness) of a composite and final product weight²⁶.

2.3.2.4 Melamine-based Systems

Nitrogen-rich melamine and corresponding salts are considered as eco-friendly alternatives to their halogen counter-parts. They contain 67 wt.% nitrogen and tend to sublime at ~350 °C absorbing significant energy eventually reducing the condensed-phase temperature. Mechanism of melamine partially differs from that of melamine salts. Ammonia evolved as a result of melamine decomposition (volatilization) not only dilutes the combustible volatiles in the gas phase but also produce thermally stable condensation products like melam, melem, and melon that can enhance thermal stability of condensed phase and increase char yield²⁷.

Melamine salts, on the other hand, decompose and form melamine, which to a greater extent undergo condensation rather than volatilization²⁸. As a result, melamine salts

contribute more towards condensed phase chemistry. Melamine salts like melamine phosphates have added advantages owing to their phosphorous content. The phosphoric acid generated as a result of thermal decomposition reacts with melamine condensates at temperatures exceeding 600 °C where triazine rings are opened up causing crosslinking. The phosphorous oxynitride formed eventually have very high thermal stability and, thus, improves char content and integrity²⁹. This synergistic effect is also exploited by using ammonium polyphosphate (APP) in conjunction with melamine FRs.

Melamine cyanurate (MC), however, further differ in FR mechanism. Thermal decomposition of MC leads to the formation of cyanuric acid that catalyzes chain scission reaction, especially in polyamides causing a drastic reduction in melt viscosity eventually leading to melt dripping. Dripping removes the heat away causing the extinction of flame³⁰. However, MC cannot be used in filled (inorganic) systems due to contradictory process as fillers tend to reduce melt dripping.

2.3.2.5 Intumescent Systems

This class of FRs utilizes well-known phenomenon of intumescence where material swells substantially upon heating forming a carbonaceous foam structure, thus creating a barrier which cuts off oxygen supply and restricts further combustion³¹⁻³². Three agents are required in this approach: an acid (or a source yielding acidic species at temperatures in the range 100-250 °C), a carbonizing agent (or a char forming agent), and a foaming agent. The process begins with esterification of carbon source by an acid generated. The ester, then, decomposes via dehydration yielding a carbonaceous residue. The released gases from the above reactions and decomposition products cause the carbonizing material to foam. APP is a well know intumescent agent used in conjunction with pentaerythritol for PP and polyamides³³⁻³⁴.

Restriction for intumescent systems is a need of precise control of chemical reactions and order of reactions involving acid generation, availability of readily reactive carbon source followed by decomposition of foaming agent. A mismatch can make this system worthless. Being a reactive system proper optimization according to the base polymer matrix is crucial.

2.3.3 Eco-benign Fire Retardant Systems

In recent times, eco-benign materials like clays are explored for their fire retardant properties. PCNs demonstrate significant reductions (as much as 70 %) in pHRRs as compared to neat polymers, which is believed to help control fire spread³⁵. This can provide precious time facilitating quick evacuation that can prevent human loss.

As mentioned previously, most of the deaths under fire situations are due to inhalation of smoke (polyaromatic hydrocarbons, PAHs) and toxic combustion products like carbon monoxide. The barrier phenomena demonstrated by PCNs have the potential to delay the evolution of these gases during initial stages of burning, which can help reduce excess inhalation of toxic gases until evacuation is complete. Low loading level requirements (3-7 wt.%), easy processibility and easy recyclability without generation of additional toxic products make PCNs an attractive, viable, sustainable and potential FR systems.

However, PCNs exhibit certain limitations that restrict their recognition as an eco-benign FR system. Currently, PCNs inherently lack the ignition resistance. They also tend to burn completely with indifferent THR as compared to neat polymers. Although considerable work has been done with different PCN systems to evaluate their effectiveness in reducing pHRR, only recently focus is growing on their ignition characteristics. With few targeted studies on ignition issues there exist a gap in basic understanding associated with the correlation between pre-ignition chemistry and clay catalysis for PCNs. This forms the motivation for this work. To investigate this matter further, hereafter, the discussion will be concentrated on structural chemistry of clay, types of interfacial interactions between polymer-clay surface and chemical factors of clay that can potentially affect fire retardancy of PCN systems.

2.4 Structural Chemistry of Clays

Clays are layered silicate minerals distinguished by a number of sheets present in each clay layer. For example, a 1:1 structure as in the case of kaolinites indicates that a silica tetrahedral sheet is connected with aluminum octahedron through an oxygen atom. Clays traditionally used in polymer nanocomposites, like MMT, belong to the 2:1 phyllosilicate

family where each layer is a stack of two silica tetrahedral sheets, one on each side, connected to a central octahedral alumina sheet through edge sharing as shown in Figure 2.5.

Figure 2.5 Schematic representation of montmorillonite³⁶.

Each layer is approximately 1 nm thick with lateral dimensions ranging from 20 nm to several microns. Adjacent layers are held together by secondary van der Waals force. Isomorphous substitution of Si^{4+} by Al^{3+} in tetrahedral coordination and Al^{3+} by Mg^{2+} , Fe^{2+} , Fe^{3+} in octahedral coordination develop a net permanent negative charge on layer surface which are neutralized by counter-cations, mainly Na^{+} or Ca^{2+} , situated at interlayer gallery locations. The layer charge is commonly expressed in terms of cation exchange capacity (CEC) quantified as meq/100 g of clay. Because of non-uniform isomorphous substitutions, there exist charge variations between layers and as a result CEC value for clay is an average value over the whole crystal and is a principle reason why clays from different regions vary in CEC values although they belong to the same family.

Low miscibility of clays due to high surface energy and hydrophilic nature greatly restrict their direct use in polymer systems, thus, requiring organic modifications. There are two routes to modify clay, (i) through cation exchange by organic surfactant and (ii) through silane modification making use of surface and edge hydroxyl groups. Although quantities

of surface and edge hydroxyl groups are measured to be as high as 4.6 wt.% of total CEC³⁷, organic cation exchange technique remains popular as it yields larger interlayer distances for organoclays.

Structurally, MMT contains both Brønsted and Lewis acid sites³⁶. There are three sources for Brønsted acidity: interlamellar (free) water, strongly acidic bridging hydroxyl groups and weakly acidic silanol groups located at the edges. Lewis acidity is a result of partially coordinated Al^{3+} at edges and crystallographic defect sites. Dehydrated metal cations at exchange locations can also contribute towards Lewis acidity. For the easier correlation to attain better understanding, further details on clay structures are discussed in relevant chapters.

2.5 Polymer/Clay Nanocomposites

In-situ polymerization and blending are two principle methodologies used to prepare PCNs. In the case of in-situ polymerization, monomer units being small, penetrate & intercalate clay galleries. Initiating the polymerization at this stage leads to the formation of PCNs with better clay dispersion. The blending technique can either be a solution or melt blending. In solution blending organically modified clay is dispersed in a polymer solution followed by evaporation/extraction of solvent. Melt blending constitute of dispersing organically modified clay in polymer melt using shear force in a melt extruder.

Depending on polymer matrix, organic modification, and processing conditions, clay layers can present three dispersion configurations viz. (i) phase separated, (ii) intercalated and (iii) exfoliated morphologies. Such nano-morphologies are best studied using XRD characterization technique as depicted in Figure 2.6. An imaging technique like TEM also provides visual observation of clay dispersion and distribution. It is imperative to study nano-morphologies in PCNs as it can affect the performance of fire retardancy in different ways³⁸⁻³⁹.

Figure 2.6 Possible PCN morphologies⁴⁰.

2.6 Influence of Clay on Thermal Decomposition of Polymer – Overview

Thermal decomposition mechanism of the neat polymer depends on its chemical structure like the presence of side groups, aromatic rings or hetero atoms, secondary bonding, etc. Accordingly, polymer can follow any one or more chemical mechanisms^{15, 41} as stated below,

Random-chain scission

Random homolytic scission throughout the polymer backbone chain.

Examples include;

PE and PP generating alkanes, alkenes

PS generating monomer, dimer and trimer

End-chain scission (unzipping)

Successive removal of monomer units from chain end.

Examples include;

PMMA and PTFE generating very high ratios of monomers

Chain-stripping

Cleavage of side groups or side chains from backbone chain.

Examples include;

PVC generating HCl and char

PVOH generating water and char

Cross-linking

Formation of interchain or intrachain covalent bond leading to an interconnected network.

Examples include;

PAN generating HCN and char

PEEK generating aromatic volatiles and char.

However, in the presence of well-dispersed clay platelets, deviation in decomposition mechanisms is observed. In the case of EVA, it was reported that presence of clay ‘contained’ the degrading polymer for a longer time, which facilitated radical recombination reaction⁴². This not only led to change the quantities of decomposition products evolved but also new products were observed, which otherwise were absent in case neat EVA. This deviation is not restricted to EVA, but many more polymers as seen from Table 2.4. Exact decomposition mechanisms for many of the polymers are yet to be proven, however, mentioned mechanisms are generally accepted. It is evident that PCNs undergo a change in decomposition mechanism as compared to neat polymers. According to an alternate theory, iron inherently present in a clay structure act as a radical trap, subsequently altering the decomposition process⁴³⁻⁴⁴. This was recently validated by Carvalho et al.⁴⁴. Also, an increase in char content observed upon incorporation of clay in otherwise non-charring polymers implies the possible role of clay particles in the promotion of char through their catalytic activities. It can, thus, be inferred there might exist chemical interaction between clay and polymer matrix affecting different stages of decomposition mechanisms.

Table 2.4 Thermal decomposition mechanisms for different polymers and their clay nanocomposites.

Polymer Matrix	<u>Decomposition mechanisms for</u>	
	Neat polymer	Polymer/clay nanocomposite
PE ⁴⁵	Disproportionation	Hydrogen abstraction
PP ⁴⁶	β -scission, disproportionation	Random scission
EVA ⁴²	Chain stripping, disproportionation	Hydrogen abstraction, random scission followed by radical recombination
PMMA ⁴⁷⁻⁴⁸	β -scission, unzipping	No change
PA6 ⁴⁹	Intra-aminolysis/acidolysis, random scission	Inter-aminolysis/acidolysis, random scission
PS ⁵⁰ , HIPS ⁵¹ , SAN ⁵² , ABS ⁵¹	β -scission (chain end and middle)	Recombination, random scission
PAN ⁵¹	Cyclization, random scission	No change

2.7 Fire Retardancy Aspects for Polymer/Clay Nanocomposites

2.7.1 Time-to-Ignition

Time-to-Ignition (TTI) is of particular interest in the case of PCNs. Although there are few studies demonstrating improvement in TTI for PCNs^{48, 53-54}, the majority show no improvements or rather reductions in TTI. Factors considered affecting TTI include:

- Volatiles evolved as a result of decomposition of clay surfactants at lower temperatures⁵⁵⁻⁵⁹
- Catalytic effect of clay⁶⁰⁻⁶¹
- Hindered thermal transport through the matrix⁶²⁻⁶³.

Of these three factors, thermal decomposition of organic modifier and catalytic activity of clays require explanations and are detailed below.

2.7.1.1 Decomposition of Organic Surfactant

Organic modifications based on conventional alkyl ammonium surfactants, although provide better dispersion of clay platelets in a polymer matrix, have lower thermal stability. They start to decompose starting ~180 °C. The volatiles produced as a result of decomposition of organic surfactants are argued to be a cause for quicker ignition for PCNs⁵⁵⁻⁵⁹. Two mechanisms are possible for thermal decomposition of organically modified clays⁶⁴⁻⁶⁵, Hoffman elimination reaction, and S_N2 nucleophilic substitution reaction. Hoffman elimination reaction leaves behind proton at exchange position on clay surface which serves as Brønsted acid site⁶⁶ that can catalytically interact with polymer matrix resulting in hydrocarbon cracking^{55, 65-67} and might lead to early ignition of PCNs. Supporting evidence was provided by a kinetic study performed on thermal decomposition reaction for neat PP and PP/clay nanocomposites by Qin et al.⁴⁶. It was reported that PP nanocomposite displayed a “zero-order” reaction as compared to “first-order” thermal decomposition reaction by neat PP. This deviation was attributed to the protonic site generated on the clay surface as a result of decomposition of surfactant through Hoffman elimination reaction. However, this H⁺MMT can also demonstrate autotransformation⁶⁸⁻⁷¹. This can radically change the reactivity of clay surface.

Alternate routes explored to avoid use of conventional alkyl ammonium surfactants with lower thermal stability include,

- Reduction in quantity of surfactants through partial exchange⁷²,
- Hydrothermally generate organic silicates through sol-gel technique⁷³,
- Use of thermally stable surfactants like imidazolium⁷⁴, phosphonium⁷⁵, quinolinium⁷⁶ and pyridinium⁷⁶ to increase thermal stability of organoclays,
- Water-assisted clay dispersion⁷⁷⁻⁷⁸,
- Surfactant-free technique⁷⁹.

Although some of these approaches exhibit marked improvement in overall thermal stability for PCNs, no specific improvement in TTI was observed. This requires further attention to more fundamental issues like clay structure and its reactivity towards polymer decomposition.

2.7.1.2 Catalytic Activity of Clay

Clays are well-known for their catalytic activity in organic reactions including cracking of heavy petroleum products⁸⁰. Qin et al. observed that addition of MMT led to a reduction of ignition time from 52 s for neat PP to 43 s for nanocomposites of PP with dioctadecyl dimethyl ammonium modified MMT and 42 s for PP with acid treated, protonic MMT (H-MMT)⁶⁰. They attributed similar magnitude of reduction in TTI for both PP composites to the catalytic acidity of clays as a result of acidic site present in H-MMT and same eventually generated on OMMT following Hoffman elimination. The same study also reported PP/NaMMT composite with ignition time of 45 s. This indicates that NaMMT has other inherent acidic sites which also play an active role during pre-ignition stages. It was also concluded that initial decomposition of PP matrix was a result of oxidative decomposition of matrix catalyzed by clay in addition to volatilization of decomposed surfactant. Even in EVA/clay nanocomposite system, Costache et al. observed accelerated decomposition onset compared to neat EVA. It was suggested that hydroxyl groups present on edges of clay layers catalyzed the chain stripping reaction for EVA matrix⁴². Rapid loss of acetic acid as a result of chain stripping led to earlier decomposition onset for nanocomposite. In the case of PS/clay nanocomposites, Zhu et al. observed that clays with higher structural iron content demonstrated delayed ignition⁴³. Neat PS had TTI of 35 s, whereas 5 wt.% PS nanocomposites with iron-rich and iron-less clays displayed TTI of 45 s and 20 s, respectively. Elemental composition of Fe₂O₃ in iron-rich and iron-less clay were 4.2 % and 0.02 %, respectively. It was argued that clay with structural iron act as a radical trap retarding the decomposition of a matrix. No plausible reason was provided for experimental observation which pointed out that the radical trapping effect was less effective in exfoliated systems. To substantiate the effect of iron, PS/graphite system was also studied where graphite was doped with iron. However, no change was observed for composites of graphite with and without iron and was attributed to poor dispersion of iron in graphite. Cai et al. argued that reduction in decomposition onset temperature for PA6/FeMMT system was due to oxidation-reduction catalytic reaction prominent with transition metal ions including ferric ions⁸¹.

Further, to study the catalytic activity of clay, Fina et al. carried out an experiment on PET/clay nanocomposite in which they measured (upper) surface temperature of the sample during combustion test⁶¹. Figure 2.7 shows the surface temperature and HRR profiles for PET/clay system. It was observed that for both neat polymer and PCN, sample temperature rises quickly and stabilize around the melting point of PET (~255 °C) owing to the latent heat of melting. Although both samples showed sharp temperature rise upon completion of melting, PCN quickly ignited (~380 s, 407 °C) while neat polymer displayed a temperature plateau and delayed ignition (~730 s, 413 °C). This observation of similar ignition temperatures but with different ignition times was attributed to the catalytic activity of clay. It was argued that clays catalytically oxidize volatiles generated on the surface resulting in earlier ignition. Furthermore, cross-sectional study of test samples demonstrated the participation of only top surface in the ignition of PCN while whole thickness was involved in the case of the neat polymer during ignition.

Figure 2.7 HRR and surface temperature profile for PET/clay nanocomposite during combustion test^{61, 82}.

Corres et al. made an interesting observation in case of phenoxy/clay nanocomposites⁸³. They believed that the presence of residual metal cation as a result of incomplete surfactant cation exchange process intensified the catalysis decomposition of phenoxy matrix. Some studies have also attributed the catalytic activity of montmorillonite to bound water released at higher temperatures that can subsequently lead to hydrolysis of matrix^{64, 84-85}.

2.7.2 Migration of Filler

Migration of nanoparticle during combustion is major physical factors, which constitute towards barrier formation in nanocomposites which lead to reduction in pHRR. Different driving forces were presumed to be responsible for this migration⁸⁶⁻⁹⁰ and include:

- Convection currents through the sample thickness that facilitates migration due to a thermal gradient.
- Surface free energy difference between clay surface and the polymer matrix.
- Rising bubbles of volatile decomposition products that carry filler.

To understand the migration pattern, Lewin et al. carried out annealing experiments for PP/clay composites under controlled condition using attenuated total reflectance FT-IR spectroscopy⁹⁰. It was observed that clay concentration on the surface is increased with increase in oxygen content in test atmosphere employed for annealing, with maximum clay concentration observed under air atmosphere. This migration behavior was explained on the basis of thermal oxidation of PP matrix as evident by increased carbonyl groups. That is, higher oxygen concentration in the annealing atmosphere leads to higher thermal oxidation of PP, thus, more clay migration. Although annealing conditions are very different from fire conditions as observed in traditional cone calorimeter, it was demonstrated that clay migration is also a function of the interaction between the polymer matrix and surrounding atmosphere and not just restricted to condensed phase behavior.

Prior to ignition and during the early stage of combustion, a crust formed due to the migration of clay particles from material near top surface is observed to be non-uniform with agglomeration and island-like floccules. It is attributed to bursting of volatile bubbles that rise through bulk and disrupt the top crust exposing combustibles to flame. Kashiwagi et al. demonstrated that collapsing clay layered network structure lack the physical strength required to prevent the formation of micro-cracks especially during initial stages of gasification process due to lower stiffness and absence of entangled structure⁹¹.

During the later stages of combustion, it was observed that not all filler migrates through to the top surface. There are numerous clay layers present at intermittent depths as shown in Figure 2.8⁹². As a result, the torturous path is created throughout the thickness which

retard volatile migration rate by suppressing the vigorous bubbling due to volatile evolution⁹³⁻⁹⁴. This reduction in fuel-supply not only leads to lowering of flame intensity but also reduces the heat release rate. However, complete trapping of volatiles cannot be observed due to the presence of fine surface cracks as shown in Figure 2.9 that leak the volatiles. This eventually leads extension of burning time and cause complete burn-off without much reduction in THR.

Figure 2.8 X-ray tomogram of PLA/silicate nanocomposites showing the structural organization of silicates across the thickness of residue as highlighted by arrows⁹².

Figure 2.9 Generation of surface char and its eventual cracking that leads to volatile escape in case of PS/5 wt.% clay nanocomposite⁹⁵.

Efforts have been made to increase the integrity of surface barrier through the incorporation of carbon nanotubes (CNTs) in PCNs⁹⁶⁻⁹⁷. It was argued that presence of fibrous CNT in addition to clay platelets form a rigid entangled barrier, enhancing the trapping of volatiles.

In another approach, Huang et al. studied ethylene-based copolymer/PDMS/CaCO₃ system where CaCO₃ react with decomposition product upon migration to surface forming a ceramic-like barrier⁹⁸. Although improvement in char content was obtained, their ignition times remained unchanged. Other approaches including the use of nanoparticles modified with high-temperature silica precursor, use of additives like low melting glass and zinc borate and use of POSS as sealant were also implemented to enhance char integrity⁹⁹⁻¹⁰¹. All these materials form a ceramic-like material that can interconnect clay layers at high temperatures which can provide an enhanced coating or fill up the porosity in char. Further investigations are required to verify their effectiveness on overall thermo-oxidative decomposition process, especially on TTI.

2.7.3 Char Formation

Carbon forms a major component in most of the polymer system. An approach to convert this polymer carbon into carbonaceous residue instead of combustible volatiles to delay or avoid combustion forms the basis of char enhancement approach. This reduction in the fuel can be directly correlated to reduced heat release rate and total heat release¹⁰². A correlation between char residue and limiting oxygen index (LOI) of the polymer was put forth by van Krevelen, who empirically demonstrated that polymer with higher char has lower flammability¹⁰³. Main properties of char are density, continuity, coherence, resistance to oxidation, thermal insulation, and permeability⁴¹. Char formation takes places when the decomposing polymer has a tendency to crosslink and also possess aromatic fragments or consist of conjugation prone to aromatization during thermal decomposition¹⁰⁴.

In the presence of oxygen, Benson et al. argued that polymer decomposition at lower temperatures follow free radical mechanism where random chain scission leads to subsequent volatilization through the generation of oxygenated species like peroxides¹⁰⁵⁻¹⁰⁸. However, oxidative dehydrogenation mechanism prevails at a higher temperature in which oxygen molecules randomly abstracts hydrogen from polymer chain creating active alkyl radical. Subsequent recombination of these alkyl radicals can lead to the aromatic structure. Increased aromatization and reduced oxidation rates suggest that polymer may

follow latter mechanism in the presence of clay particles generating transient char having higher oxidation temperatures^{39, 109-110}.

Chemistry of char formation and effectiveness of char enhancers depends on polymer decomposition temperature and the chemical interaction of catalyst with both polymer and decomposition products. Traditionally, catalysts based on Lewis acids or Friedel-Crafts alkylation reagents are used to enhance char in polymer systems¹¹¹⁻¹¹². Zinc borate and PVC were also used as effective char enhancers^{99, 113}. Zinc facilitates the formation of aliphatic hydrocarbons which upon cross-linking leads to suppressed smoke evolution and increased char content whereas PVC acts through intermolecular crosslinking reaction.

2.7.3.1 Confinement Effect by Clay

Confined and superheated environments as presented by layered silicates are attributed as one of the reasons for deviation in thermal decomposition mechanism observed for PCNs as pointed out previously in Table 2.4. During decomposition of PCNs, neighboring clay layers collapse over each other forming a confined space of nanometric size where decomposing polymer chain and decomposition products experience physical restrictions in their mobility (cage effect)⁵¹. Along with superheated nature of this nano-confined space, trapped organic matter undergoes additional decomposition pathways otherwise absent in the case of neat polymer. Physically restrained newly formed radical can significantly increase the possibility of bimolecular reactions¹¹⁴. This favors intermolecular reactions forming intermediate complexes further reducing the volatilization. Polymer backbone having aromatic rings or oxygen linkages are more prone towards this effect and may further assist in char formation¹⁰³. For example, PA6 nanocomposites show more interchain aminolysis/acidolysis reactions that yield decomposition products other than caprolactam, obtained otherwise in neat PA6⁴⁹. For polymers like EVA, PS, which follows radical mechanism for decomposition, depending on radical stability, can lead to radical recombination forming complex decomposition product with reduced volatility. Hence, it can be argued that nanoconfinement effect can promote char formation by reducing the volatility of decomposition products, thus, reducing HRR^{50, 52}.

2.7.3.2 Catalytic Activity of Clay

Clay particles are also claimed to promote char formation through their catalytic activity. It is argued that acidic proton site on clay surface generated as a result of thermal decomposition of organically modified clays can interact with polymer matrix resulting in hydrocarbon cracking and/or aromatization^{55, 65-67}. Char formation can also be promoted by Brønsted and Lewis acid sites inherently present in clay structure itself. These Lewis acid sites can accept electrons from donor molecules³⁶; they can coordinate with organic radicals⁶⁴ and can abstract an electron from vinylic sites promoting crosslinking of matrix^{39, 60, 65}.

Increased char was observed by Qin et al. in case PP/clay nanocomposites⁶⁰. While PP showed no charring, increase in char by 7.6 % for PP/H-MMT and 6.9 % for PP/OMMT was attributed to an acidic site present in H-MMT and the same eventually generated OMMT upon Hoffman elimination. It was suggested that the acidic site on clay can catalyze dehydrogenation and crosslinking of polymer leading to higher char as schematically represented in Figure 2.10. Oxidative dehydrogenation crosslinking catalyzed by acidic sites on clay was also attributed to higher char content in ABS/clay nanocomposite¹¹⁵. Similar studies carried out on PE¹⁰⁹, EVA¹¹⁰, PS³⁸, and PA¹¹⁶, all inherently non-charring polymers, displayed increased char content upon incorporation of nano-dispersed clays particles. EVA inherently tend to form a surface protective layer of cross-linked polyene during initial stages of decomposition. Hull et al. reported that clay-catalysis accelerates deacetylation of EVA at slightly lower temperatures as compared to neat EVA¹¹⁷. This increased the time available for crosslinking, and as a consequence a stronger protective layer was developed. Kashiwagi et al. attributed the increased charring in the case of PA6/clay system to higher viscosity as a result of physical crosslinking-like effect enforced by network structure of decomposing matrix and collapsing clay particles⁶². Cai et al. studied the effect of hydrothermally synthesized FeMMT clay on thermal stability of PA6 fibers^{81, 118}. Higher char was attributed to the catalytic effect of Fe³⁺ ions from FeMMT that facilitates formation of radicals in the decomposing polymer, which in turn promoted molecular crosslinking leading to increased char. Efforts were also made to increase the charring in PCN by “doping” clay typically with transition metal atoms.

Prakalathan et al. reported 31 wt.% and 29 wt.% increase in char for zinc and copper modified MMT when incorporated in PLA matrix¹¹⁹. This effect was attributed to the catalytic activity of dopant along with barrier formation effect. However, no chemical mechanism was proposed. Nawani et al. studied EVA/clay nanocomposites where they doped organically modified clay through ion exchange using Cu^{2+} and Fe^{3+} ions¹²⁰. They hypothesized that transition metal ions catalyze the crosslinking of non-saturated products of thermal decomposition as well as promote oxidative dehydrogenation resulting in aromatization. Even though both being transition metals, the Cu^{2+} -exchanged system gave more char; while Fe^{3+} -exchanged system yielded char even lesser than un-exchanged organically modified clay system. Exact physiochemical mechanism regarding charring was not proposed.

Figure 2.10 Catalytic charring mechanism proposed for PP/clay nanocomposite⁶⁰.

As evident from different studies, complete consensus is yet to be reached regarding exact mechanism of catalytic charring influenced by clay. But it is generally believed that stages

of charring during polymer decomposition include formation of conjugation, cyclization, aromatization, aromatic ring fusion, generation of turbo-static char and graphitization¹²¹.

2.7.4 Smoke Characteristics

Smoke generation and smoke toxicity are fundamentally dependent on polymer back bone-chain, ventilation conditions, and testing methods¹²². Stec et al.¹²³ evaluated the smoke density, CO, CO₂ and hydrocarbon content generated during combustion of PA6 with organically modified clay (denoted as NC) and commercial FR. It was reported that smoke generation significantly depends on ventilation conditions during combustion as it affects the fuel-to-air ratio. It was reported that under all ventilation conditions, PA6 with commercial FR continued to show highest smoke yield and smoke density as seen from Figure 2.11A-B. In contrast, PA6/clay nanocomposite gave similar or better performance compared to neat PA6 except under large under-ventilated systems. It was reported that under well-ventilated conditions much higher yields of CO were seen for PA6/FR and PA6/NC as compared to neat PA6. As compared to a steady increase for PA6/FR, CO yield varied marginally under both under-ventilated conditions for PA6/NC while registering values lower than neat PA6 (refer Figure 2.11C). Lastly, for hydrocarbon yield (Figure 2.11D), under all ventilation conditions PA6/clay nanocomposites always fared better than neat PA6. PA6/FR, although registered lower hydrocarbon yields for well- and small under-ventilated systems, a linear increase was observed, which continued to large under-ventilated systems making it worse performing composite. This study carried out in accordance to BS 7900, ISO TS 19700 has provided sufficient evidence of the superior behavior of PA6/clay nanocomposites regarding smoke characteristics, in general.

During combustion of PCNs, quantitative change observed for smoke is believed to be the result of modification of condensed phase chemistry rather than gas phase¹²⁴⁻¹²⁵. Reduced smoke production has been reported for PCNs owing to barrier effect of clays^{53, 126}. However, higher smoke level has also been reported in certain cases, which may be attributed to increased evolution of aromatic and carbonaceous compounds as a result of secondary dehydrogenation reactions promoted by clay^{60, 127}. Table 2.5 provides averages

for CO yield for different PCN systems and their relative changes as compared to neat polymers.

Figure 2.11 Smoke yield (A), smoke density (B), CO yield (C) and hydrocarbon yield (D) for PA6 composites containing clays (NC) and commercial FR¹²³.

Table 2.5 CO yields for different PCN systems.

PCN Systems	Average CO yield (kg/kg)	% change w.r.t. neat base polymer	Average CO ₂ yield (kg/kg)	% change w.r.t. neat base polymer
LDPE ¹²⁸	0.0358	+ 60%	1.6301	+ 14 %
PP ¹²⁹	0.025	+ 14 %	-	-
EVA ¹²⁸	0.0376	+ 90 %	1.6056	+ 15.5 %
PA6 ³⁵	0.02	+ 50%	-	-
PU ¹³⁰	0.37	- 84 %	1.91	- 48 %

2.8 Summary

From literature review summarized above, it is evident that PCN systems show great potential as eco-benign FR systems on account of their significant reductions in pHRR. However, their tendency for early ignition is currently limiting their use as stand-alone FR system and is widely attributed to, yet poorly understood phenomena of, clay catalysis (during combustion). To address this missing link which associates clay catalysis with various stages of combustion (TTI, char formation and smoke characteristics), it is necessary to understand the nature of interactions between organic matter and clay. These interactions primarily dependent on inherent clay structure which is in turn governed by metal ions (Mg^{2+} , Al^{3+} and Fe^{3+}) that occupy octahedral locations in clay lattice. Accordingly, following work deals with MMT modified to amplify concentrations of these particular ions at exchange positions and clays (Hec, MMT and Nnt) which are inherently rich in one metal ion. Influence of exchangeable metal ions on MMT surfactant (HDTMA^+) is separately dealt in Chapter 4. Significant insights into the role of each metal ion on to polymer-clay interaction are established by evaluating the influence of these clays on decomposition and combustion properties of PA6 matrix (Chapter 5 and 6). The importance of interfacial interaction between polymer and clay on ignition characteristics is presented in Chapter 7. Lastly, the overall discussion on clay catalysis and conclusions are provided in Chapter 8.

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Chapter 3

Experimental Methodology

This chapter focuses on the rationale behind the use of polyamide 6 and montmorillonite, cationic exchange of montmorillonite, treatment of montmorillonite with a surfactant, and finally, compounding of polyamide 6/montmorillonite composites. Characterization techniques employed to understand different chemical and thermal (including combustion) properties are also described. Evaluation of evolved gases during thermo-oxidative decomposition of the prepared composites with thermogravimetric analyzer coupled with infrared spectrometer is emphasized in particular. Possible shortcomings are also highlighted.

3.1 Material Selection - *Rationale*

PA6 is an engineering polymer with a wide range of commercial applications. Commercial utility and well-documented combustion and decomposition studies for PA6 with different commercial FRs¹⁻⁶ and nano-additives including clays⁷⁻¹⁰ provided an opportunity for extensive data mining. This provided an opportunity to correlate the reported data (tests & characterization, decomposition mechanisms, etc.) with new insights developed in this work.

As discussed earlier, char formation is one of the strategies to improve fire retardancy. It is well-accepted that under stable flame condition (like in cone calorimeter, used in this study), the majority of decomposition takes place under anaerobic conditions instead of oxidizing conditions¹¹. Only top surface experiences oxidation before ignition. This precisely justified the use of PA6 because it is well-known fact that PA6 forms a skin of char prior to ignition. Although char from neat PA6 eventually oxidizes, it is worth exploiting this char-forming behavior to enhance surface char stability and/or change the decomposition mechanism of PA6/clay composite altogether to increase residual char content by one of the clay-catalysis strategies. Hence, throughout this study, testing was carried out only under oxidative conditions wherever such control was possible.

Material details:

A commercial grade of PA6, *Ultramid B3S* was obtained from BASF, Singapore. It has a melting point of 220 °C and a V-2 rating in UL94 (vertical burning test) for the thickness of 1.6 mm. Before melt compounding and testing, PA6 was dried at 80 °C for at least 24 h under vacuum of 20 mBar.

PEI and PI were used for coating organically modified clays. Their high T_g in addition to their chemical inertness and solution processability make them ideal for coating the clay layers.

Material details:

Commercial solvent-soluble *ULTEM 1000* PEI was obtained from SABIC Innovative Plastics. T_g of this PEI was reported to be ~217 °C and melting range between 320-355 °C. poly(pyromellitic dianhydride-co-4,4'-oxydianiline)amic acid (PAA) solution, a precursor

for PI, was obtained from Sigma-Aldrich, Singapore. The reported concentration of PAA solution was 15 wt.% $\pm$ 5 wt.% in NMP/aromatic hydrocarbons (80%/20% solvent ratio). PI formed upon imidization of PAA have $T_g > 300$ °C, it does not melt and decomposes at temperatures beyond 540 °C.

For clays, MMT, Hec and Nnt were used as they all belong to same smectite family, and same surfactant (HDTMA-Br) was used to modify all these clays organically. MMT was used for cation exchange experiments because of its high CEC value and its metal ion exchanged forms are being widely reported in clay mineralogical studies. Large knowledge pool of fundamental behavior and associated mechanism in cation exchanged MMT can directly be used to evaluate and understand results in the current study. Use of commercially available organically modified MMT (*CloisiteTM 30B* or *C30B*) for PA6/coated clay nanocomposites was a conscious decision. This facilitated direct comparison with combustion and decomposition data available for PA6/C30B, which is widely reported system throughout the literature. It made it simpler to observe and justify the significance of the last section of experiments in the current study.

Material details:

NaMMT, commercially known as *CloisiteTM Na⁺* and *C30B* were procured from BYK-Chemie GmbH. The mean unit formula for NaMMT is $\text{Na}_{0.65}[\text{Al,Fe}]_4\text{Si}_8\text{O}_{20}(\text{OH})_2$ with CEC of 92 meq/100 g¹². Organic modifier for C30B is methyl, dehydrogenated tallow ammonium chloride. Hec [SHCa-1, San Bernardino County, CA, USA] and Nnt [NAu-2, Uley graphite mine, South Australia] were obtained from The Clay Minerals Society, Source Clay Minerals Repository, USA. MMT and Hec were received in powder form and were used without further purification. Nnt was received in raw (clay-rock) form. It was powdered using ball mill under the mild condition to prevent their structural disintegration. Use of simple yet widely reported organic surfactant (HDTMA-Br) was essential as to reduce any complexity in the decomposition of the matrix as a result of surfactant-matrix interaction. Also, HDTMA⁺ modified MMT have been reported for superior dispersion in PA6 matrix.

List of remaining chemicals is given in following Table 3.1,

Table 3.1 List of remaining chemicals used throughout the study.

Chemical name	Abbreviation	Supplier	Product ID
Magnesium chloride, anhydrous	MgCl ₂	Sigma-Aldrich	M8266
Aluminum nitrate nonahydrate	Al(NO ₃) ₃	Sigma-Aldrich	229415
Iron (III) chloride	FeCl ₃	Sigma-Aldrich	157740
Hexadecyltrimethylammonium bromide	HDTMA-Br	Sigma-Aldrich	52370
Silver nitrate	AgNO ₃	Merck Millipore	109080
Tetrahydrofuran	THF	Merck Millipore	109731
N, N-Dimethylacetamide	DMAc	Merck Millipore	803235

3.2 Material Preparation

3.2.1 Preparation of Metal-ion Exchanged Clays

MI-clays were prepared by standard cation exchange technique. In a typical procedure, 20 g of Na⁺ MMT clay was suspended in 1 L deionized water under mechanical stirring at 600 rpm for 24 h. Metal salt solutions (Mg²⁺, Al³⁺, Fe³⁺), 20 % excess of CEC value were dissolved separately in 500 mL deionized water. MMT suspensions were heated to 80 °C to which metal salt solutions were added drop-wise over a period of 30 min while stirring mechanically at 600 rpm. The suspensions were left stirring for 24 h to get maximum cation exchange. Each suspension was then filtered and thoroughly washed with deionized water. Silver nitrate test for halides was conducted to confirm the thoroughness of washing. Finally, MI-clays were dried at 110 °C and ground into fine powder (200 μm).

3.2.2 Organic Modification of Clays

MI-clays and clays rich in structural metal ions were further modified using HDTMA-Br obtained from Sigma-Aldrich. Clays (20 g each) were separately suspended in 1 L deionized water heated at 80 °C for 24 h; while surfactant solutions were made by dissolving HDTMA-Br in 200 mL deionized water. HDTMA-Br solution was then added drop-wise to each clay suspension over a period of 10 min with mechanical stirring at 600 rpm. The suspensions were stirred and maintained at 80 °C for 12 h followed by cooling to room temperature with continued stirring. Each suspension was then filtered and washed

thoroughly with deionized water. Silver nitrate test for bromide was conducted to confirm the thoroughness of washing. Subsequently, obtained organically modified clays were dried at 110 °C and ground into fine powder (200 µm).

3.2.3 Preparation of Coated Clays

3.2.3.1 Polyetherimide Coated Clay

10 g C30B clay was dispersed in 300 mL 1:1 mixture of DMAc and THF for 3 h at 80 °C. C30B exfoliates in organic solvents readily as a result higher quantity of C30B lead to the formation of dough instead of fluid suspension limiting the ratio of C30B to the solvent to be minimum 1:30. Separately, 10 g of PEI pellets were dissolved in 300 mL 1:1 mixture of DMAc and THF for 3 h at 80 °C and 500 rpm. It was observed that dissolution of PEI was complete within 2 h under conditions employed.

At the end of 3 h, PEI solution was slowly added at the rate of 25-30 mL/min to mechanically stirred C30B suspension at 500 rpm with the temperature maintained at 80 °C. The mixture was stirred for 2 h. Using syringe pump, hot PEI-C30B solution mixture was pumped at 20 mL/min into 1600 mL water bath mechanically stirred at 1200 rpm. PEI immediately precipitates out. C30B provides the surface over which PEI precipitates forming a coating. The water bath was stirred for 6 h before preliminary filtration using crucible funnel with pore size of 16-40 µm. Cake formed was re-dispersed in 2000 mL water at room temperature and 1200 rpm followed by filtration. The process was repeated at least three times to make sure best possible washing of DMAc from filtered cake.

The cake formed dried in a convection oven at 110 °C for 24 h. The dried solids obtained were ball milled at 180 rpm for 10 min/cycle (+ 3 min pause time) with 5 repetitions. The powder obtained was sieved using 200 µm sieve. Collected powdered PEI coated C30B was kept under vacuum of 20 mbar at 140 °C for 24 h to remove any traces of DMAc. PEI-C30B, thus, obtained was used for further characterization and in making PA6/PEI-C30B nanocomposite.

3.2.3.2 Polyimide Coated Clay

15 g C30B clay was dispersed in 750 mL DMAc for 3 h with mechanical stirring at 500 rpm. Instead of using C30B:solvent ratio of 1:30 as used previously for the PEI-C30B system, more dilute ratio of 1:50 was employed because excess DMAc will be used to dilute PAA solution. After 3 h, the temperature of the suspension was reduced under 10 °C using an ice-water bath. Once the suspension temperature is stabilized, 110 g of PAA solution was introduced. It is critical to maintain the temperature of the mixture under 10 °C as the molecular weight of PAA continue to reduce at room temperature. The mixture was stirred at 1200 rpm for 15-20 min before it was transferred to a metal container.

Metal container with solution mixture was placed in preheated convection oven at 200 °C for 40 min. Condensation imidization of PAA starts around 180 °C. To attain maximum imidization, convection oven temperature was increased to 230 °C with continued heating for additional 60 min. Intermittent stirring using glass rod was done to break dried surface layer allowing the escape of solvent/water from underneath. At the end of heating, the cake was obtained with some residual solvent. Complete drying was avoided to facilitate removal of PI-C30B from the container.

Metal container was then removed from the oven and cooled to around 130-140 °C after which 500 mL cold water was added. Precaution was taken to avoid steam splash by performing this addition in a closed fume hood and using heat resistant gloves. Similar to PEI, PI immediately precipitates out in water. Globules of precipitated PI-C30B broken using glass rod were later transferred to 2000 mL water stirred at 1200 rpm. Washing/drying/milling protocol same as PEI-C30B system was employed to obtain PI-C30B powder later to be used for analysis and in PA6/PI-C30B nanocomposites.

3.2.4 Extrusion

Extrusion is most commonly used process where neat polymer granules are melt mixed with fillers and other additives. The intermeshing co-rotating twin screw is known to provide superior dispersion.

5 wt.% clays (10 wt.% of coated clays) were melt mixed with PA6 using Leistritz Micro 18 twin screw extruder at 80 rpm. 120 rpm was used for coated clays to assist in uniform distribution. PA6 was pre-dried under vacuum of 20 mbar at 80 °C for 24 h while all clays were pre-dried at 100 °C for 24 h prior to mixing. Extruded strands were granulated using pelletizer. Temperature profile set are shown in Figure 3.1. The granulated material was compression molded into test specimens (100 x 100 x 5 mm) for cone calorimetry test using the Carver Hot Press maintained at 250 °C with a molding pressure of 5 bar and a total molding time of 20 min.

Figure 3.1 Extruder schematic with temperature profile employed for PA6 nanocomposite extrusion.

3.3 Testing Methods

3.3.1 Cone Calorimeter

The cone calorimeter developed by NIST, USA is a bench-scale and widely used technique to analyze combustion properties of materials. A sample of area 100 x 100 mm² and thickness between 1 - 50 mm is irradiated by a preset conical flux meter at a specific heat flux of interest. In current study, all samples were 5 mm thick and were irradiated with 35 kW/m² flux (temperature of ~692 °C). Spark ignitor is used to ignite combustible volatiles produced as a result of gasification. Throughout the test, all gases (smoke, CO, and CO₂) travel through chimney where smoke density is registered using a laser. 35 kW/m² is

typically recommended for initial tests and is frequently used as it produces reproducible data¹². However, use of external heat flux depends on end applications for which material is being tested, e.g. aviation regulations require 35 kW/m², interior materials in metro/subway trains need 50 kW/m², while naval application require 100 kW/m²¹³.

The ability for simultaneous measurements of various fire parameters and close prediction of material behaviors under large-scale fire situations make this one of the most important technique in fire analysis. Fire-relevant properties such as TTI, HRR, pHRR, MLR, TSP, CO₂ and CO yield are measured in this test according to ISO 5660-1 and ASTM E1354. All these measurements are based on oxygen consumption principle¹⁴, that is, for complete combustion of a wide range of fuels, 13.1 (± 5 %) kJ of energy is produced for every 1 g of oxygen consumed by the fire. Schematic of a typical cone calorimeter is shown in Figure 3.2. The inset shows a typical HRR versus time curve.

It is important to note that all data acquired from cone calorimeter is under forced flaming condition (presence of spark ignitor and a draft of air forcing the combustion). This data applies to developing fire situations which can rank flame spread and contribution of burning material to heat release. Fundamental flammability properties are determined by other techniques like LOI or UL94 classification. However, from the point of view of a real-life scenario, data on flame spread, heat release, smoke generated, etc. provide more insight than just knowing fundamental flammability of material. Other important fire testing techniques are listed in Table 3.2.

It is of prime importance to determine the uncertainties associated with measurements made by cone calorimeter as any error or oversight will lead to erroneous interpretation of combustion properties. As a result, detailed analysis has been made and reported addressing the uncertainties, assumptions and errors involved with cone calorimeter¹⁶⁻¹⁷. For higher accuracy standardized evaluation of uncertainties can be made in accordance with ISO 29473:2010¹⁸. Uncertainties in cone calorimeter data are known to be reduced by simultaneous usage multiple analyzers i.e. for CO, CO₂, and H₂O in addition to O₂¹⁷. As additional measurements for CO and CO₂ were made in the current study, results are expected to have lower uncertainties. Under external flux of 35 kW/m², cone calorimeter measurements are reproducible within ± 10 % based on cumulative data collected for thousands of combusted samples¹⁹.

Figure 3.2 Schematic of a cone calorimeter¹⁴. In a typical test, accurately weighed sample (100 mm x 100 mm x 5 mm) is placed on load cell and is exposed to preset constant heat flux irradiated from truncated cone-shaped heating elements simulating fire scenario. External spark igniter is employed to ignite gases evolved from the sample surface as a result of thermal decomposition. Eventual smoke released is drawn away by exhaust located over the top of truncated cone. Exhaustion of volatile fuel marks the end of the test.

Table 3.2 List of common fire testing techniques and corresponding parameters assessed¹⁵.

	Radiant ignition test (ISO 5657)	Glow wire test (IEC 60695-2- 10-13)	Small- flame ignitability test (ISO 11925)	UL-94 (IEC 60695- 11-10)	Cone calorimeter (ISO 5660)	Laterally induced flame test (ISO 5658)	Limiting oxygen index (ISO 4589-2)	Smoke density chamber (ISO 5659)	Steady state tube furnace (ISO 19700)
Ignitability	x	x	x	x	x	x			
Rate of flame spread			x	x		x			
Rate of heat release					x				
Ease of extinction							x		
Smoke production					x			x	x
Effluent toxicity									x

Instrument details:

Cone calorimeter from Fire Testing Technology, UK was used to determine the combustion response of compression molded PA6 and its composites. The tests were carried out according to ISO 5660 at an irradiant heat flux of 35 kW/m². Samples were molded in the size of 100 x 100 x 5 mm.

3.3.2 Thermogravimetric Analyzer coupled with Infrared Spectrometer

Thermogravimetric analysis is one of the simplest and widely used techniques to evaluate decomposition behavior of materials. It is based on the simple principle of determining of mass loss as a result of gasification with an increase in temperature. Decomposition under pyrolytic or oxidative conditions can be studied by selecting appropriate purge gas i.e. nitrogen or air, respectively. As compared to cone calorimeter, TGA requires smaller sample sizes between 5 - 50 mg, so it is considered to provide fundamental decomposition behavior of materials 'without bulk effects'. Mass loss rate curves can be used to evaluate overall decomposition profiles, which can be related to decomposition mechanism, decomposition kinetics or both. As observed with multiple repetitions, TG data is reproducible within ± 1 °C.

Instrument details:

TG analysis for clays was carried out on TA Instruments 2950 and Q500, under air and nitrogen atmospheres. All samples were pre-dried at 110 °C for 24 hours in convection oven. Tests were carried out from room temperature to 750 °C employing heating rate of 20 °C/min.

Combining TGA with the infrared spectrometer (Figure 3.3) is most commonly used setup for Evolved Gas Analysis (EGA)²⁰⁻²⁴. Instead of venting purge gas from TGA, it is transferred to an IR cell. The volatiles and combustion products, thus, carried by purge gas can be analyzed for their functional groups. This is an in-line process, and IR scans are continuously registered from start to end of test with a preset time interval between two successive spectra. A 3D FT-IR signal profile provides simple visualization of the development of signal peaks within the range of 4000 - 400 cm⁻¹ with an increase in

temperature. Scan resolution and number of scans are critical parameters. A higher number of scans and resolution may lead to better sensitivity but being an in-line system will result in escape of gases at small temperature increments without detection. It also depends on heating rate employed in TGA unit. At higher heating rates ($20\text{ }^{\circ}\text{C}/\text{min}$ and above), the rate of generation of volatiles is very high so to maintain lower time interval between successive scans, rapid IR scanning is essential (recommended), and as a consequence, lower resolution (2 cm^{-1}) and only one scan can be employed. Another important factor is the temperature of metal transfer line and IR gas cell, which according to manufacturer's recommendation were maintained at $150\text{ }^{\circ}\text{C}$. This is of particular importance because evolved gases will be a mixture of a range of molecules with different boiling points. Unfortunately, molecules with a boiling point higher than $150\text{ }^{\circ}\text{C}$ will not reach IR gas cell as they condense on the inner wall of the transfer tube. This is an instrumentation limitation (for current study). However, new technologically advanced TG-IR set-ups are made available by a different manufacturer that can allow temperatures as high as $300\text{ }^{\circ}\text{C}$.

Figure 3.3 Typical set-up for thermogravimetric analyzer coupled with infrared spectrometer (image adapted from PerkinElmer product brochure).

One of the most important limitations of TG technique (for current study) is heating rates employed. Heating rates permitted by TG instrument ($1 - 20\text{ }^{\circ}\text{C}/\text{min}$) is less than heating rates experienced in real fire scenarios (including in cone calorimeter), which are typically of the magnitude greater than $100\text{ }^{\circ}\text{C}/\text{min}$. As a consequence, reaction rates and constants determined from TGA may not be able to capture decomposition kinetics/mechanisms

accurately as decomposition kinetics are dependent on the rate of heating. This may affect decomposition mechanism as well.

Instrument details:

TG-IR used was from Perkin-Elmer TGA-7 with TGA Pyris 7.0 software having an interface with Perkin-Elmer Spectrum GX system for FT-IR. Temperature range employed was from 30 °C to 750 °C at a heating rate of 20 °C/min. Dry air at a flow rate of 20 mL/min carried gaseous decomposition products through IR interface into IR detection chamber. Metal transfer line as well as FT-IR gas cell was maintained at 150 °C. All IR spectra were acquired in the range of 400-4000 cm^{-1} using one scan with a resolution of 2 cm^{-1} . Consecutive readings were taken with a time interval of ~11.3 sec (i.e., 3.7 °C resolution). All samples were pre-dried at 80 °C for 12 h before test.

3.3.3 Isothermal Studies using Furnace

High-temperature oxidative decomposition of samples under isothermal conditions was performed using a box furnace preheated to desired temperatures. In addition to cone calorimeter and TG analysis, sample heated at controlled conditions facilitate deeper analysis which provide answers regarding changes in condensed phase on a macro level, as well as analysis of evolved gases collected by condensation, can provide certain insights on the gas phase.

The source of error in this isothermal test set-up is the temperature fluctuation that happens while placing the sample in preheated furnace. Opening the furnace door starts to reduce the furnace temperature, as a result, it is very critical to place the sample in the furnace in the least possible time. Typically for the furnace used in the current study, it was observed that furnace temperature drops by 8-10 °C during sample loading that takes around 5-7 s. To re-stabilize to a preset temperature, it takes 40-50 s depending on preset temperature. Accordingly, the test time of 300 s was established to ensure temperature uniformity. It was observed that this re-stabilization time was almost 120-130 sec when the furnace was at a lower temperature like 275 °C and 70-80 sec for 300 °C. As a result, all isothermal studies were carried out at and above 325 °C. Besides, to avoid any unnecessary damage to ceramic heating elements and also keeping the personal safety in mind, maximum temperature used

for the isothermal study was kept at 500 °C (used for volatile condensation study).

For condensation of evolved gas, because the sample is placed in test-tube, uniform ventilation cannot be attained. This was also observed during the test. The dense white fumes generated towards the end of the 240 s are heavier than air. As a result, they remained in test-tube. Hence, there was no control on atmosphere just above sample while it decomposed. This mostly facilitates anaerobic decomposition instead of oxidative decomposition especially during later stages of the test. The condensate collected, nonetheless, were analyzed to evaluate the effect of clay under anaerobic conditions.

Instrument details:

Isothermal studies were carried out using Nabertherm muffle furnace Model LE4/11 preheated to the desired temperature with 30 min temperature stabilization time. 5 g material was placed in a furnace for 5 min preheated at 325, 350, 375, 400, 425, 450 and 475 °C while 20 g material was combusted at 750 °C for 15 min for high-temperature isothermal study (residue study).

To collect the condensable gases, 2 g material placed in borosilicate test-tube was kept inside the furnace preheated to 500 °C. The test-tube was kept erect using a metal stand. After 5 min, metal stand with test-tube was removed from the furnace and allowed to cool, in the case of flame at the opening, it was blown-off. Condensation of vapor was observed on the inner wall of the test tube. 2 mL LC-MS grade acetonitrile (ACN) was slowly added along the walls to dissolve yellowish condensate. Additional 3 mL ACN was added before sealing the tube with parafilm. Vigorous shaking followed by ultra-sonication for 5 min guaranteed dissolution of soluble condensate. The solution was filtered using 0.22 µm syringe filter to remove solids including clay particles. This solution was used for FT-IR analysis. ACN solution was repeatedly dropped at the same spot on filter paper while drying off ACN after every drop at 110 °C using a convection oven. After 14-15 drops, a thick dark yellow peripheral ring was observed due to condensates as shown in Figure 3.4. ATR FT-IR was performed at this yellow ring. Using blank filter paper as a background, the spectra obtained was attributed to condensate alone as no peak corresponding to residual ACN was observed.

Figure 3.4 Build-up of condensate on filter paper by continuous evaporation ACN solvent.

3.4 Characterization Techniques

3.4.1 Inductively coupled Plasma Atomic Emission Spectrometer

ICP-AES is one of the most widely used analytical technique to quantify minor (even trace) amounts of elements present in solution. Working principle involves atomization of solution into mist-cloud, which is carried by argon gas into argon plasma that has temperatures close to 7000 °C. This leads to excitation of the outer shell of the electron for elements present in starting solution. Return of these excited electrons to the ground state is accompanied by the emission of photons with characteristic energies associated with each element. These emissions are diffracted through grating, which leads to separation of light according to their wavelengths. Photodetectors measure the light intensity and send an electronic signal to the computer which then converts it into concentration.

ICP-AES was used to quantify metal concentration in MI-clays and OMI-clays. As this is a quantitative technique, it is crucial to have precise control on solution concentrations during digestion of clay and subsequent dilution for comparative studies.

Instrumental details:

Elemental concentrations in different MI-clays and OMI-clays were determined using PerkinElmer Optima2000 ICP-AES with detectors analyzing for Na, Mg, Al, and Fe. For sample preparation, accurately weighed 200 mg of MI-clay (or OMI-clay) was dissolved in 30 mL of 1.0 M HCl for 3 h using an ultrasonic bath. The suspension was subsequently centrifuged at 6000 rpm for 5 min. The supernatant was collected into a 100 mL volumetric flask while the settled clay was re-suspended in 30 mL of 1.0 M HCl and procedure was repeated. Upon centrifugation, the supernatant was added to the earlier solution, after that,

the solution was diluted to 100 mL mark using DI water. 15 mL of this solution was used for quantifying respective ion content. The same procedure was employed to prepare test samples for all clays. It is to be noted that concentrated acid pair (HCl-HF) is necessary to digest the clay in order to extract metal ions from lattice positions²⁵. However, following the reported sample preparation²⁶, dilute HCl was used to extract and quantify exchangeable metal ions.

3.4.2 CHNS Elemental Analyzer

CHNS elemental analyzers are routinely used to quantify percentages of carbon, hydrogen, nitrogen and sulfur. Working principle is very simple. Sample containing any or all elements (C, H, N and S) is combusted at 1000 °C in an oxygen-rich environment. As a result, C, H, N and S get converted into CO₂, H₂O, N₂/NO/NO₂ and SO₂ respectively. These gases are carried to detector chamber by inert gas (like helium) over highly pure copper. Copper removes unused excess oxygen from the gas stream and convert NO/NO₂ into N₂. Post-GC separation, detection of these gases is done by thermal conductivity detection. Similar to ICP-AES this is a quantitative technique requiring a precise measurement of sample weight and calibration before use. The presence of halides can affect the results. Thus, it is necessary to use halide traps/absorbents. Data to be collected at least in triplicates. High standard deviation indicates non-homogeneity of the sample and has to be prepared again.

Instrument details:

PerkinElmer Series II 2400 CHNS Elementary Analyzer was used to determine carbon content in OMI-clays and their residues. All samples tested were pre-dried at 110 °C for 30 min. Carbon content values reported are averaged based on triplicate results.

3.4.3 Fourier Transform Infrared Spectrometer

FT-IR is an important technique used to identify functional groups present in samples (solid, liquid or gaseous). Working principle is based on interference phenomena (constructive and destructive). The material absorbs a certain amount of incident energy based on

different functional groups present when radiated with infrared light while reradiating rest back. Recombining this reflected radiation with unperturbed one using instrumentation (beam splitter, movable and stationary mirrors), the interference is recorded to give interferogram (intensity vs. time spectra). Applying Fourier transform it is converted to transmittance (or absorption) spectra (intensity vs. frequency). Each functional group has unique frequencies like a chemical fingerprint which are used in identification.

One of the major limitations in FT-IR in the analysis of partially decomposed material is the lack of resolution. For example, polymers like PA6 generate a range of decomposition compounds most of them containing carbonyl groups (aldehydes, imides, carboxylic, peptides, etc.). As a result, instead of sharp peaks, broader peaks with strong shoulders are generated due to overlaps, making precise identification difficult. Their analysis requires additional mathematical tools like curve-fitting for deconvolution. Another limitation of FT-IR while analyzing char residues is the low signal strength. High absorptivity of infrared radiations by carbonaceous matter (black body effect) reduce the signal. Further, a significant proportion of C–C bonds in char is of non-polar nature which does not have any dipole moment. Consequently, no IR signals are registered. While analyzing clays, one of the potential errors occur during automatic H₂O/CO₂ cancellation. Clays have a certain amount of adsorbed free water. Auto-cancellation may lead to reduced intensities for water inherently present in clay.

Instrument details:

Fourier transform infrared (FT-IR) spectra of PA6 materials, clays and powdered residues (prepared using KBr pellets) were collected using Perkin-Elmer SpectrumGX spectrometer and Perkin-Elmer Frontier Spectrometer (ATR FT-IR). All spectra were acquired in the range of 400–4000 cm⁻¹ using 64 scans and resolution of 4 cm⁻¹.

3.4.4 X-ray Diffraction Spectrometer

XRD is an analytical technique which enables rapid phase identification in crystalline materials and also provides information on unit cells²⁷. For semi-crystalline polymers like PA6, XRD can help identify the presence of different phases (like α and γ) and their magnitude. In the case of clays, XRD can provide interlayer distances between platelets

along with their possible structural compositions²⁸. Working principle of XRD is based on diffraction and interference (constructive). A focused beam of monochromatic X-rays is incident on the sample. Interaction of the incident beam with the sample leads to constructive interference (and a diffracted ray) only when Bragg's Law conditions are satisfied. This law correlates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Diffracted X-rays are then detected. Schematic representation of XRD set-up and typical MMT diffraction pattern is shown in Figure 3.5. As a result of random orientation in powder, scanning the sample through 2θ angles help detect all possible diffraction directions of the lattice. Using Bragg's Law, all diffraction peaks are converted to d-spacing. One possible limitation of XRD in char analysis is the inability to identify amorphous carbonaceous matter.

Figure 3.5 Schematic of XRD set-up with diffraction pattern (for MMT) satisfying Bragg's Law where θ is incident angle w.r.t. normal, d_{hkl} is interlayer distance, λ is X-ray wavelength and n is order.

Instrument details:

XRD measurements were performed on Shimadzu XRD6000 (40kV, 30mA, Cu α , $\lambda = 1.542 \text{ \AA}$) with a scan speed of $1^\circ/\text{min}$, scan range of $3\text{--}45^\circ$ and step size of 0.02° . For sample preparation, all clay samples were ground using mortar pastel to obtain a fine powder, approximately $\sim 200 \text{ }\mu\text{m}$. Compression molded pieces were used for polymer nanocomposites. Polymer nanocomposite residues were prepared similarly to clay powder samples.

3.4.5 Differential Scanning Calorimeter

DSC is a widely used thermo-analytical technique to identify isotherms associated with different changes/transitions occurring in any given material upon heating and cooling. It records the amount of heat need to be supplied to reference pan in order to nullify temperature difference with respect to the sample containing pan. Schematic of DSC set-up is shown in Figure 3.6.

Incorporation of well dispersed clay in PA6 preferentially lead to development of γ -phase which has lower thermodynamic stability as compared to α -phase in PA6²⁹. Thus, γ -phase requires lower energy to melt consequently displaying lower T_m . Because of such polymorphism, DSC is widely used for morphological studies to analyze PA6/clay nanocomposites.

Figure 3.6 Schematic of typical DSC set-up.

Instrument details:

Melting and crystallization characteristics of neat PA6 and its composites were determined using a DSC from TA Instruments (model: Q10). Two complete heating/cooling cycles between 30 - 240 °C were performed at a rate of 10 °C/min.

3.4.6 Scanning Electron Microscope

SEM is an imaging technique which produces images by scanning the sample surface with

a focused high-energy electron beam. Interaction of electrons with atoms at sample surface generates a variety of signals revealing information about surface texture/morphology and chemical (elemental) compositions³⁰. There are two modes for imaging, secondary electron imaging (SEI) and backscattered electron imaging (BEI) based on depth of incident electron beam penetration into the surface it is illuminating. Secondary electrons are emitted by atoms near the surface of a sample when bombarded with electron beam. Secondary electron imaging, being more surface sensitive, has greater resolution and provide more details regarding surface topography. As a result, SEI mode was used to study polymer coated clay surfaces. On the other hand, backscattered electrons are emitted from atom at much greater depth as shown in Figure 3.7. As a result, they suffer in resolution. They are more sensitive to the atomic mass of the nuclei they scatter from, hence, BEI is less suited in current study.

Figure 3.7 Schematic representation of penetration depth for electron beam into sample.

Instrument details:

Clay surface morphology was observed using JEOL field emission scanning electron microscope, FESEM 6340F. Secondary electron imaging was used with accelerating voltage of 10-20 kV and at a working distance between 7-9 mm. All samples were sputter coated with platinum for 10 s, at a distance of 30 mm from platinum source and voltage of 20 kV.

3.4.7 Transmission Electron Microscope

TEM is another imaging technique in which a focused beam of high energy electrons is transmitted through an ultra-thin section of the sample. Depending on the interaction of electrons with the specimen, an image with differential contrast is generated which is magnified and detected by a sensor (CCD camera)³⁰⁻³¹. Contrast depends on inherent atomic mass differences amongst different segments present in specimen. For example, in thin section of PCN, clay platelets, due to high density (~ 2.5 g/cc), scatter the electron beam to larger extent making them appear darker as compared to polymer which is relatively transparent owing to low density (1.13 g/cc). Thus, creating required contrast for imaging. A general schematic is shown in Figure 3.8. It is difficult to attain sufficient contrast between two polymers like in case of PA6-PEI and PA6-PI because of lack of sufficient density differences (density of PEI and PI is 1.27 and 1.45 g/cc, respectively), however, selective staining can be used to achieve contrast.

Figure 3.8 Schematic of contrast generation in TEM imaging for PCN sample.

Instrument details:

To observe clay dispersion in polymer matrix, trimmed polymer composite samples were ultra-microtomed at 0.2 mm/s using a diamond knife on Leica Ultracut UCT in liquid N₂ environment at -100 °C to get 70-110 nm thick sections. The sections were picked up using

a droplet of 2.3 mol sucrose and placed on formvar/carbon coated 400-mesh copper grids. After thorough rinsing with distilled water to wash away the sucrose, sections were observed using a Carl Zeiss transmission electron microscope (TEM), LIBRA 120, in bright field mode and at an accelerating voltage of 120 kV.

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Chapter 4

Decomposition Behavior of Metal-ion Exchanged Clays

This chapter deals with exploring the effect of different metal ions like Mg^{2+} , Al^{3+} , and Fe^{3+} present in/on MI-clays in altering the kinetics and/or decomposition mechanism of organic modifier, HDTMA-Br. The catalytic activity is seen to be a combined effect of Brønsted and Lewis acid characters associated with the metal ions. The effect varies significantly with the predominant cation in organically modified MI-clays (OMI-clays). Knowing the effect of each metal ion separately, the correlation between clay structural chemistry and organic decomposition onset is established.

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4.1 Introduction

As mentioned earlier, there are various structural aspects of smectite clay (MMT) that are needed to be considered to understand source and nature of a catalytic site. For the sake of continuity, some of these aspects are highlighted again in more details here. The catalytic nature of MMT is influenced by the acidity of surface hydroxyl groups, the number of defect sites and edges exposing unbalanced structural metal ions, dehydration along with dehydroxylation temperatures and type of exchange cations. Reactivity of MMT is altered by replacing exchangeable cations like Na^+ and Ca^{2+} from their surfaces by higher valency metal ions like Mg^{2+} , Zn^{2+} , Cu^{2+} , Al^{3+} or Fe^{3+} ¹. This ability has been widely exploited for applications like catalysis²⁻³. Depending on their locations, metal ions render inherent acidic nature to MMT in the form of Brønsted acidity and Lewis acidity¹. Although there are some reports related to metal ion exchanged clays and their effects on decomposition of organic matter⁵⁻⁶ (one of them is shown in Figure 4.1), the exact role of different metal ions, particularly those that are present in the clay structure on the decomposition of organic matter is still unclear.

Figure 4.1 TG curves under oxidative condition for organically modified MMT (C20A) subsequently doped with different transition metal ions by cation exchange process were reported by Nawani et al.⁴. The variations in decomposition onset temperatures and char content were attributed to catalytic activities of metal ions.

Further, organic modifier in MMT upon decomposition leaves behind H^+ at exchange position following the well accepted Hoffmann elimination mechanism. Acid activated MMT could demonstrate a physical process of autotransformation where protons migrate and replace metal ions at structural positions in tetrahedral layers⁷⁻⁸. These "knocked-off" metal ions like Al^{3+} then assume positions at exchange sites increasing the reactivity of clay towards molten polymer matrix. Increased catalytic activity of acid treated tetra-alkyl-ammonium cation exchanged smectites have already been reported⁹. Thus, the possibility of increasing concentration of metal ions like Mg^{2+} , Al^{3+} or Fe^{3+} at exchange position beyond surfactant decomposition temperature via possible autotransformation cannot be overlooked. Although control on the exact kinetics of autotransformation process may not be currently feasible, knowing the effect of each metal ion on decomposition kinetics of organic matter can help answer some unanswered questions. Therefore, in this Chapter, the effect of metal ions inherently present in clay (Mg^{2+} , Al^{3+} , Fe^{3+}) on thermal decomposition of organic modifier is studied.

A detailed description of the synthesis of MI-clays and OMI-clays was given in Chapter 3. To briefly put, the overall process is schematically represented in Figure 4.2.

Figure 4.2 Schematic representation of modification of NaMMT clay to obtain MI-clays and subsequently OMI-clays. Aq. M^{z+} denotes aqueous solution of metal salts (Mg^{2+} , Al^{3+} or Fe^{3+}).

4.2 Results and Discussion

4.2.1 Structural Aspects of MI-clays and OMI-clays

Exchanged metal cations are known to have a profound effect on various structural aspects of MMT including changes in their basal spacing (d_{001}), interlayer water structures and their dehydration behaviors¹⁰⁻¹¹. Their ability to form thermodynamically stable hydration complexes in the presence of water has been widely reported¹⁰. Such hydration complexes are formed as a result of cations surrounded by coordinately bonded water molecules (schematically shown in Figure 4.3). They are represented as $[M^{z+}(H_2O)_6]^{z+}$ where z is the valency of cation M . Strength of these hydration complexes is governed by the charge density of the cations present at core position (i.e., in terms of their ionic character - strength and radius, as well as polarizing power). Greater ionic character leads to stronger association, thus, requiring higher activation energy to dissociate the complex. This in turn delays their exposure to organic matter.

Apart from strength, polarizing power of cations also affects the sizes of these hydration spheres¹⁰. Complex shrinks in size with increase in polarizing power of cation (i.e. increasing attractive force); this is apparent from reducing distances between the metal ion and oxygen from water molecule (M-O distance) as listed in Table 4.1. As trivalent cations, Al^{3+} and Fe^{3+} inherently have different sizes ($Fe > Al$), variation in attractive force exerted by these towards oxygen is different.

Figure 4.3 Schematic representation of metal-water complex¹² ($M^{z+} = Na^+, Mg^{2+}, Al^{3+}, Fe^{3+}$).

In Table 4.1, acid dissociation values (pKa) are also given, which correspond to hydrolysis reactions where proton is dissociated from metal-aqua complex in a multistage process¹³⁻¹⁴. Lower value signifies easier dissociation i.e. higher acid strength. In fact, the values of Fe^{3+} and Al^{3+} water complexes are comparable to that of weak acids like acetic acid (pKa 4.76). However, understanding the kinetics of dissociation reactions to completely apprehend the observations is beyond the scope of this work. Further, instead of one hydration sphere surrounding the cation, concentric hydration spheres¹⁵ are formed in case of polyvalent cations whose strengths are governed by their polarizing capacity. Subsequently, Na^+ forms one hydration sphere while Mg^{2+} , Al^{3+} , and Fe^{3+} can form up to two concentric hydration spheres, which explain observed increment in basal spacing for polyvalent MI-clays as compared to NaMMT. XRD curves for MI-clays shown in Figure 4.4A.

Furthermore, modification of these exchanged clays with HDTMA^+ resulted in similar interlayer distances in all cases irrespective of the strength and polarizing power of cations. Hence, it may be suggested that the final basal spacing is relatively independent of sizes of respective hydration spheres as a consequence of much larger size of HDTMA^+ compared to these hydration spheres. Basal spacings for OMI-clays are also shown in Figure 4.4B. d_{001} values reported here are comparable with those reported previously¹⁶⁻¹⁷.

Table 4.1 Metal ion radius (R_i), metal ion-oxygen distance (M-O) and typical acid dissociation constants (pKa values) reported for metal ion-water complexes^{14, 18}.

MI-Clay	Aqua Complex	$\text{M}^{z+} R_i$ (Å)	M-O distance (Å)	pKa
NaMMT	$[\text{Na}(\text{H}_2\text{O})_6]^+$	1.09	2.43	13.9
MgMMT	$[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$	0.76	2.10	11.2
AlMMT	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	0.55	1.89	5.0
FeMMT	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	0.66	2.00	2.2

Figure 4.4 XRD for MI-clays (A) and OMI-clays (B).

In summary, the total bound-water content for MI-clays dictates their Brønsted acid character and the magnitude is governed by polarizing capacity of the respective metal ion present at exchange positions.

4.2.2 Quantitative Analysis for Metal Concentrations in Exchanged Clays

To help correlate the magnitude of metal ions present in different exchanged clays with Brønsted and Lewis acidity and their subsequent effect on decomposition of organic surfactant, ICP-AES analysis was carried out. ICP-AES results (Table 4.2) indicate that NaMMT inherently has varying proportions of each metal ion under consideration in this study. This suggests that any effect shown by NaMMT (or ONaMMT) can be considered as cumulative effect of all the metal ions instead of only Na^+ . Upon exchange with various metal ions, a clear amplification of the respective metal ion is evident. Based on the valency of metal ions exchanged, their calculated CEC values varied. Cations with higher valencies replaced those with lower valency resulting in progressively higher concentration values, which are similar to those reported previously^{2, 11} (Table 4.3). The slight variations observed in concentrations of exchanged cations can be attributed to difference in origins of sodium MMT that has been used as well as synthesis procedures implemented.

In contrast, in OMI-clays, steric hindrance experienced by HDTMA^+ ions from neighboring exchange sites as a result of long organic chain can prevent complete exchange of interlayer cations by organic surfactant molecules. This results in residual irreplaceable

exchangeable cations even after organic modification as seen from Table 4.2, which might affect decomposition of surfactant or polymer matrix. Organic modification of polyvalent MI-clays using mono-valent ammonium ion can be explained further based on clay-cation preferences. As compared to larger ammonium ion in HDTMA-Br, metal ions are much smaller and possess higher aqueous-phase preference. Thermodynamically, it was also demonstrated that clay has a stronger preference to larger head-group cation, as in the case of HDTMA⁺, which has lower aqueous-phase affinity as compared to metal ions¹⁹. Increasing hydrophobicity of clay surfaces results in strong repulsive forces between hydrophobic HDTMA⁺ and water from hydration sphere surrounding the cation core. As a result, metal ions that do not have ionic bonding with clay surfaces are expelled, thus, lowering the metal ion concentrations in OMI-clays.

Table 4.2 ICP-AES results showing the concentration of selected metal (ions) in NaMMT, MI-clays and OMI-clays (values in meq/100 g of clay).

	Na	Mg	Al	Fe	Total CEC
NaMMT	83.0	11.3	31.9	9.4	135
ONaMMT	10.6	8.7	27.8	7.1	54
MgMMT	12.6	85.7	34.7	10.3	143
OMgMMT	9.1	15.2	28.9	7.0	60
AlMMT	12.6	6.8	131.7	9.0	160
OAlMMT	9.0	3.7	46.0	4.6	63
FeMMT	15.9	7.6	54.3	265.4	343
OFeMMT	8.9	3.5	22.1	185.0	219

As mentioned before, other factors that affect the final concentration of metal ions in OMI-clays are ionic radii (R_i) and distances between metal ion and oxygen atom (M-O) from hydration sphere (see Table 4.1). In particular, the differences between trivalent Al and Fe modifications could be explained based on their M-O distances. Smaller Al³⁺ aqua complexes readily exit the interlayer space as a result of repulsive force exerted by incoming organic cation. This is not the case with bigger Fe³⁺ aqua complexes. In fact, it was reported that they tend to precipitate in insoluble hydrous form on hydrophobic clay surfaces, in turn causing only marginal drop in final concentrations¹⁷. Accordingly, it was

suggested that in the case of OFeMMT, precipitated hydrous Fe^{3+} repel incoming HDTMA^+ molecules, lowering their concentration and/or affecting their orientation at interlayer gallery. As a result of this, they displayed lower d_{001} spacing, as listed in Figure 4.4. Concentration exceeding CEC values were also previously reported in some cases of Cu^{2+} and Fe^{3+} , but were argued to be a result of multi-nuclei complexes or colloidal particle formation⁴.

Table 4.3 Reported metal ion concentrations (in CEC, meq/100 g of clay) for cation exchanged clays.

Metal-ion exchanged	Obtained Results	Reported Results
Pristine clay	92	80 ² , 121 ¹¹
Na^+	83	73 ¹¹
Mg^{2+}	85	166 ¹¹
Al^{3+}	131	74 ²
Fe^{3+}	265	198 ²

4.2.3 Thermal Decomposition

4.2.3.1 Thermal Decomposition of MI-clays

Brønsted Acidity in MI clays

Depending on ionic strength of cations, dehydration temperatures of different MI-clays varied as seen from Figure 4.5. The stronger the ion-dipole interactions, the higher are the dehydration temperatures. All MI-clays show intense derivative weight loss peak below 150 °C associated with free surface water evolution. Beyond this temperature, MI-clays show prominent dehydration peaks up to temperatures as high as 350 °C. For example, MgMMT shows a strong shoulder between 170-210 °C; while the trivalent cation exchanged clay, FeMMT, shows much higher dehydration peak in between 180-260 °C. In case of concentric hydration spheres for polyvalent metal hydration complexes, inner hydration sphere is formed of water molecules, which are coordinately bonded with compensating cation through cation-dipole interaction. The outer hydration sphere consists

of water molecules that are not directly bound to cation but have hydrogen-bonding with the inner sphere. Binding energies for inner and outer hydration spheres are reported as 19 kcal/mole and 10 kcal/mole, respectively²⁰⁻²¹. Therefore, it can be argued that the dehydration of outer hydration shell starts at a lower temperature in comparison with inner shell, resulting in the observed broadening of dehydration peaks in polyvalent cations. It should be noted that as water molecules in the hydration shell experience weakening of O–H bond, this generally results in higher Brønsted acid characteristics for complexes. This Brønsted acidity, however, is a function of interlayer water and it drops sharply beyond clay dehydration temperatures. However, NaMMT does not show prominent mass loss as other MI-clays until 400 °C. It only displays minor mass loss around 265-360 °C. But the nature of water that is responsible for this is not clear.

Figure 4.5 Mass loss rate curve for MI-clays: presence of water coordinately bonded with interlayer cations.

Apart from dehydration temperature, cations also affect the quantity of bound water, which can be as high as 5.48 wt.%¹¹. In case of MI-clays, bound water content is calculated based on their respective dehydration mass loss peaks. They are found to be 1.13 wt.%, 1.54 wt.% and 1.25 wt.% for MgMMT, AlMMT and FeMMT, respectively. In combination with high bound water content, the Brønsted acidity can play a significant role in the decomposition of organic matter. The strength of Brønsted acidity as a function of polarizing power of

exchangeable cations vary in the order of $H^+ > Al^{3+}, Fe^{3+} > Mg^{2+} > Na^+$. This is further supported by the reported acid dissociation constants (Table 4.1).

Lewis Acidity in MI clays

Beyond complete dehydration, exchange cations regain ionic state while at exchange positions, which otherwise were stabilized by hydration water below 300-350 °C. These exposed and partially bound reactive metal ions generate Lewis sites^{7,22}. Hence, depending on inherent reactivity of exchange cations, their presence in ionic state can significantly increase overall Lewis acidity of MI-clay. This in turn will affect thermo-catalytic decomposition of polymer matrix and oxidation stability of carbonaceous char residue.

4.2.3.2 Thermal Decomposition of OMI-clays

Effect of Brønsted Acidity

To further corroborate and extend the above results, decomposition of organic modifier, HDTMA-Br, was studied under oxidative and inert conditions (Figure 4.6). As expected, HDTMA-Br showed comparatively quicker decomposition under oxidative conditions. Onset temperature (where the mass loss reached 5 wt.%), $T_{5\%}$, was lowered from 275 °C (in N_2 atmosphere) to 230 °C; while peak decomposition temperature, T_p , reduced from 298 °C to 242 °C. Other than temperature shifts, decomposition mechanism also varied with test atmospheres. As compared to one-step decomposition at 300 °C under inert conditions, a two-step decomposition pattern was observed for oxidative conditions. The first mass loss was observed at 250 °C yielding 10 wt.% residue as a result of oxidative attack on aliphatic chain in $HDTMA^+$ followed by complete mass loss through oxidation at 550 °C. Interestingly, these temperature regimes corresponding to onset of mass loss for organo-modifier overlap with MI-clay dehydration temperatures (Figure 4.5). This further increases the importance of Brønsted acid character of MI-clays towards organo-modifier decomposition.

TG curves of OMI-clays under oxidative and inert atmospheres are shown in Figure 4.7. Mass loss observed from TG analysis for all clays under both atmospheres are tabulated in Table A1 in Appendix A. It is known that thermal decomposition of $HDTMA^+$ modified clays experience two-stage decomposition process under inert conditions. Stage one

typically occurs around decomposition temperature of neat surfactant (250-290 °C) and is associated with loss of surface adsorbed surfactant molecules. Second stage mass loss is observed at temperatures (~450 °C) much higher than actual decomposition temperature of surfactant. This loss is attributed to decomposition of surfactant molecules, which are intercalated between the clay layers and can be used to quantify intercalated surfactant. Higher ionic bond strength between intercalated surfactant and clay is considered to be a prime reason for this increase in thermal stability²³. However, a different pattern is observed when sample is tested under oxidative conditions. Although OMI-clays show similar mass loss trend below 300 °C, no prominent mass loss was observed between 300 °C and clay dehydroxylation temperature of ~550 °C. It is argued that intercalated surfactant under oxidative conditions forms carbonaceous residue, analogous to pristine HDTMA-Br, which completely oxidizes at temperatures incidentally similar to clay dehydroxylation temperatures.

Figure 4.6 TG curves for HDTMA-Br in air and nitrogen atmosphere.

Although overall decomposition onset for all OMI-clays is in line with widely accepted Hoffmann elimination mechanism (Scheme 4.1)²⁴, they show some distinctive features as a result of their corresponding Brønsted acidities and possible catalytic activity of dehydrated metal ions. OAIMMT not only showed quickest peak decomposition (260 °C under nitrogen and 268 °C in air) but also showed a unique two-step mass loss between

260-295 °C, irrespective of test atmosphere. This effect may be attributed to the combination of three distinct phenomena, Brønsted acidity, catalytic effect of dehydrated Al^{3+} and Hoffman elimination. Figure 4.8A clearly indicates overlap for $T_{5\%}$ for OAlMMT

Figure 4.7 TG curves for HDTMA⁺ modified clay samples in air (A) and nitrogen (B) atmospheres.

and peak dehydration temperature of AlMMT which confirms conditions favoring (Brønsted) acidolysis of HDTMA⁺. Although similar overlap was observed in case of FeMMT-OFeMMT pair (Figure 4.8B), presence of one derivative peak at 271 °C instead of twin peaks similar to AlMMT-OAlMMT pair indicate the characteristic difference

between Al^{3+} and Fe^{3+} system. Relatively sharp mass loss in case of OFeMMT may be due to simultaneous effects of Brønsted acidity, catalytic effect of dehydrated Fe^{3+} ion on HDTMA^+ and Hoffman elimination. In the case of MgMMT, dehydration was almost complete below 210°C and $T_{5\%}$ for OMgMMT (not shown separately). Hence, it may be inferred that the effect of Brønsted acidity is negligible in this case owing to the absence of hydration water. Further, it should also be noted that Mg^{2+} is relatively less reactive as compared to Al^{3+} or Fe^{3+} and therefore, the catalytic decomposition of quaternary ammonium ions with saturated long chain is absent. Possible mechanism accounting for Brønsted acidity effect in case of OAlMMT and OFeMMT is depicted in Scheme 4.2 where water from hydration spheres around Al^{3+} and Fe^{3+} act as a nucleophile which then abstracts acidic beta H^+ from HDTMA^+ to form carboanion and hydronium ion (H_3O^+). Subsequent rearrangements lead to formation of tertiary amine and alkene similar to Hoffman elimination. The negative charge, thus, generated on clay surface is neutralized by proton from H_3O^+ balancing the reaction. This additional effect of Brønsted acidity arising from hydration water in case of OAlMMT and OFeMMT is responsible for their quicker and distinctive thermal decomposition patterns while generating same end products.

Scheme 4.1 Hoffman elimination mechanism for all OMI-clays.

Scheme 4.2 Effect of Brønsted acidity on decomposition of HDTMA^+ in OAlMMT and OFeMMT.

Figure 4.8 TG curves for MI-clay and OMI-clay samples in air atmosphere; AIMMT (A) and FeMMT (B).

Further, it was observed that except for OFeMMT, each OMI-clay showed similar (11-16 wt.%) mass loss between 260-300 °C irrespective of test atmosphere, whereas OFeMMT demonstrated mass loss of 6-7 wt.%. This variation in case of OFeMMT was related to lower quantity of surface adsorbed HDTMA⁺ as seen from derivative weight loss peak at 270 °C for OFeMMT under inert atmosphere, which is also consistent with XRD and ICP-AES results. Nonetheless, in both atmospheres, AIMMT and FeMMT showed quicker onset of decomposition of surface adsorbed HDTMA⁺ owing to their inherent ionic nature and catalytic activity. However, OMgMMT showed slightly delayed peak decomposition

temperature, T_p , (297 °C) in inert atmosphere as compared to ONaMMT (291 °C). This might be of particular importance to polymer/clay nanocomposites as under fire conditions, surfactant and matrix decomposition occurs in oxygen-deprived atmosphere, essentially, anaerobic conditions. This will be discussed further in following chapters.

Effect of Lewis Acidity

Lewis acidity affects three different processes, (i) kinetics of carbonaceous residue formation around 450 °C under oxidative conditions, (ii) oxidation stability of carbonaceous residue generated at temperatures above 550 °C and (iii) dehydroxylation temperatures of MI-clays at temperatures upside of 550 °C.

Processes (i) and (ii) will be explained in detail in the following sections. Process (iii) deals with clay dehydroxylation temperatures, essentially signifying loss of hydroxyl groups from octahedral layer in clay structure. Depending on Lewis acid characteristics of metal ions and their interactions with surface hydroxyl groups on clay surface, dehydroxylation temperatures of MI-clays varied (Figure 4.5). For OMI-clays, similar temperatures are noted under inert conditions; but under oxidative atmosphere, they exhibited substantially lower dehydroxylation temperatures (Figure 4.7A). An average drop of 15 °C was observed for all OMI-clays except for OFeMMT, which displayed a significant drop of 55 °C. These variations clearly suggest the combined effect of catalytic oxidation of carbonaceous residue from organic decomposition as well as catalytic attack on clay surface by different metal ions. Amongst Na^+ , Mg^{2+} , Al^{3+} and Fe^{3+} , Fe^{3+} has greater ability to catalytically oxidize carbonaceous residue and catalytically destroy the clay structure by assisting in dehydroxylation. This results in the formation of amorphous meta-montmorillonite¹⁰. In the following sections, clay residues at 450 °C and 750 °C are analyzed by FT-IR and XRD techniques to establish the effect of Lewis acidity.

4.2.4 Spectroscopic Analysis of MI-clays and OMI-clays residues

4.2.4.1 Fourier Transform Infrared Spectroscopy

FT-IR of MI-clay residues (burnt at 750 °C, Figure 4.9) displayed prominent reduction in peak intensities associated with OH-stretching (~ 3640 , $\sim 3450 \text{ cm}^{-1}$) and OH-bending

vibrations ($\sim 1645\text{ cm}^{-1}$) signifying the loss of surface water and water coordinated with interlayer cations²⁵. FeMMT residue is an exception as OH-stretch peak intensities are largely unchanged. The reasons for this are still unclear and require further investigation. Nevertheless, the shifts observed in bending vibration peak from $\sim 1645\text{ cm}^{-1}$ to ~ 1608 and $\sim 1622\text{ cm}^{-1}$ in AlMMT and FeMMT, respectively, suggest strong associations of metal ion (present at interlayer positions) with structural oxygen from dehydrated clay surface²⁶. In case of OMI-clay residues (burnt at $450\text{ }^{\circ}\text{C}$), intensities at $\sim 3640\text{ cm}^{-1}$ and $\sim 3450\text{ cm}^{-1}$ decreased as expected due to dehydration (Figure 4.10). Besides, a peak shift from original $\sim 1645\text{ cm}^{-1}$ towards lower wavenumber was observed, similar to MI-clay. However, a sharp increase in peak intensity at $1615\text{-}1633\text{ cm}^{-1}$ is observed attributable to carbonaceous material consisting of C=C. New shoulder peaks observed around $1420\text{-}1480\text{ cm}^{-1}$ associated with $-\text{CH}_2-$ are progressively stronger in the order of $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+}$. Considering the presence of these absorption peaks at $1615\text{-}1633\text{ cm}^{-1}$ and $1420\text{-}1480\text{ cm}^{-1}$, it can also be argued that aromatic structures are formed in accordance with decomposition mechanism suggested by Bellucci et al. for long chain alkyl ammonium cation under oxidation²⁷ (Scheme 4.3). However, this mechanism does not account for formation of carbonyl groups either evolved as volatiles reported previously²⁴ or as observed in present case of OMI-clays.

Scheme 4.3 Oxidative decomposition mechanism for alkyl fragment from organic modifier as proposed by Bellucci et al²⁷.

Figure 4.9 FT-IR spectra for MI-clays and their residues tested in air at 750 °C.

Figure 4.10 FT-IR spectra for OMI-clays and their residues tested in air at 450 °C and 750 °C.

Xie et al. reported the generation of linear and branched aldehydes as observed from pyrolysis/GC-MS at 400 °C in case of MMT modified using trimethyl octadecylammonium chloride²⁴. In the current work, in OMI-clay residues at 450 °C, shoulder peaks around 1710-1735 cm⁻¹, generally associated with presence of C=O, are progressively stronger in the order of Na⁺ < Mg²⁺ < Al³⁺ < Fe³⁺. This confirms the deviation from proposed hydrogen abstraction mechanism by Bellucci et al. under oxidative conditions. It also demonstrates the influence of metal ions in the generation of carbonyl groups in OMI-clay residues. It is important to note that Xie et al. although confirmed the generation of aldehyde groups, they attributed their formation to catalytic oxidative reaction between decomposing organic matter and oxygen from clay under confined lamellar conditions (experienced in collapsed clay structures)²⁴. In current study, to investigate the role of oxygen from test atmosphere, OFeMMT was taken as representative sample as it displayed strongest shoulder corresponding to C=O. From Figure 4.11 it is evident that the shoulder for C=O is absent when test was performed under inert condition. This consolidates the influence of oxygen from test atmosphere. As a result, peroxy-based mechanism (Scheme 4.4) is proposed, which yields similar polyaromatic char products as reported before. In addition, carbonyl groups in volatiles or in residue can be generated.

Figure 4.11 FT-IR spectra for residues of OFeMMT tested in air and nitrogen at 450 °C.

Formation of large quantities of highly reactive peroxy radicals under oxidative condition is crucial in determining the carbonaceous residue content. Higher are the quantities of these alkoxy, peroxy radicals, greater is the possibility for alkyl radical formation and their subsequent recombination, thus, lowering volatilization. Significantly lower quantities of such peroxy radicals can form under pyrolytic conditions as source of oxygen being surface adsorbed oxygen or surface hydroxyl groups on clay. As a result, essentially volatilization of organic matter predominates over radical recombination. The limited quantity of alkoxy radicals formed may yield volatile aldehydes as reported earlier.

Possible role of metal ion on rate of generation of carbonaceous residue under oxidative conditions is depicted in Scheme 4.5. Presence of metal ions can accelerate the rate of decomposition of hydroperoxide generating oxy or peroxy organic radical²⁸. This process is further accelerated at higher temperatures. Metal ion can either oxidize by donating one electron to hydroxyl radical or reduce by accepting one electron from proton radical, generating corresponding ions. Although this phenomenon can occur under any atmosphere, intuitively it should be more prominent under oxygen atmosphere due to abundance of alkyl hydroperoxide groups. It is known that higher valency ions show more prominent effect which might be correlated to stronger C=O absorption peak in their corresponding OMI-clay residue IR spectra. Hence, presence of metal cations can uniquely affect the rate of generation of carbonaceous residue starting at 400 °C based on their inherent catalytic characteristics.

Benson suggested that oxidative decomposition of alkyl chains by forming peroxy groups is more prominent at temperatures below 200 °C²⁹⁻³⁰. At temperature above 250 °C hydrogen abstraction by oxygen molecule becomes more prominent (Scheme 4.3, for example). However, presence of noticeable C=O absorption peaks and aldehydes suggest that the overall oxidative decomposition mechanism is influenced by (i) confinement effect from partially collapsed clay, (ii) catalytic effect from dehydrated metal ions and (iii) Lewis acid sites from clay edges.

Scheme 4.4 Proposed peroxy-based decomposition mechanism for alkyl fragment from organic modifier between 400-500 °C.

Scheme 4.5 Effect of metal ions on decomposition of hydroperoxides yielding highly reactive organic oxy or peroxy radicals²⁸.

Although exact nature of this carbonaceous matter is currently not investigated, but it can be concluded that presence of different metal ions at exchange positions alter the decomposition mechanisms of organic modifier. By comparing the IR spectra for MI-clay residues and OMI-clay residues at 750 °C in Figure 4.9 and 4.10, it is evident that the peak intensities at 1615-1633 cm⁻¹ are lowered and additional shoulders (1420-1480 cm⁻¹ and 1710-1735 cm⁻¹) are absent. This confirms the loss of carbonaceous matter when continued heating above 450 °C and up to 750 °C.

4.2.4.2 X-Ray Diffraction Spectroscopy

To further substantiate the role of Lewis acidity, XRD analysis for residues was carried out. For comparison purpose, interlayer spacing for pristine NaMMT and its residues at 450 °C and 750 °C were presented in Figure 4.12. Apparently, 450 °C seems to be sufficient for complete dehydration of NaMMT resulting in collapse of platelet structures. The interlayer spacings changes from 12.1 Å to 9.8 Å. Further heating up to 750 °C, beyond its dehydroxylation temperature range of 550-675 °C, had no impact on the final d₀₀₁ of NaMMT residue. But residues of all OMI-clays at 450 °C displayed only partial collapse (interlayer spacings changes from ~18 Å to 13 Å) (refer Figure 4.13A). This in conjunction with TGA results confirm presence of carbonaceous matter between interlayer of clay platelets. However, absence of any peaks corresponding to well-structured carbon suggests that the carbonaceous matter formed is of amorphous nature or its content is below the

detection limit. Figure 4.14 depicts schematic representation of formation of residual carbonaceous matter through thermal decomposition of OMI-clays.

Figure 4.12 XRD patterns for residues of pristine NaMMT tested under air atmosphere.

Interesting effects on stability of carbonaceous matter were observed for OMI-clays while studying XRD patterns for their residues at 750 °C (Figure 4.13B). Despite the near complete collapse of all residues as a result of oxidation of carbonaceous matter there seems to be minor variations in their final d_{001} spacing (shown in inset). These variations could be attributed to metal ions present in different OMI-clays and their catalytic effects on delaying the oxidation of carbonaceous matter. Amongst OMI-clay residues, OFeMMT achieved complete oxidation/dehydroxylation by 750 °C as evident from the overlapping d_{001} peaks for residues of NaMMT (~ 9.8 Å) and OFeMMT (~ 10 Å). Thus, it was suggested that catalytic nature of Fe^{3+} can significantly reduce the final char yield by assisting oxidation. A shift in d_{001} to ~ 10.6 Å for ONaMMT, OMgMMT and OAlMMT as against ~ 9.8 Å for NaMMT is a result of presence of residual carbonaceous content. It can be concluded that Mg^{2+} and Al^{3+} ions from these clays retard oxidation of said carbonaceous content, in turn resulting in incomplete oxidation (even up to 750 °C). The delay in oxidation can be correlated to Figure 4.7A, where peak mass loss rate and the tail in its broad temperature peak between 550-750 °C is quite evident for OMI-clays. Song et al.³¹ also reported a noticeable improvement in performance of charring catalyst through

introduction of magnesium. Magnesium was believed to improve the utilization of nickel, a known carbonizing catalyst.

In order to verify the complete loss of HDTMA^+ when heated up to 450°C as seen from the TG results for inert atmosphere (Figure 4.7B), a representative sample, OFeMMT, and its residues at 450°C and 750°C were analyzed using XRD. Complete collapse of clay platelets representing absence of carbonaceous matter in residues was observed for clay residue at 450°C , thus, verifying the reason provided. Corresponding XRD curves comparing samples tested in air and nitrogen and residues at 450°C and 750°C are given in Figure 4.15.

Figure 4.13 XRD patterns for residue of HDTMA^+ modified clay samples tested in air at 450°C (A) and 750°C (B).

In short, it can be concluded that final char content is governed by inherent concentrations of Mg^{2+} , Al^{3+} and Fe^{3+} in MMTs as they affect its Lewis acid character. For example, Fe^{3+} rich NaMMT reduces the char content, while the sample containing higher Mg^{2+} or Al^{3+} gives opposite effect. Thus, it becomes important to compare ion percentage from MMT used in different studies before generalizing any effects. Generally, owing to much lower contents of these ions in MMTs than those used in this study, their effect on decomposition of polymer matrix is easily overlooked.

Figure 4.14 Schematic representation of formation of residual carbon at clay interlayers affecting d_{001} spacing for OMI-clay residues at 450 °C. Exact temperature above 750 °C for complete collapse depends on oxidation stability of residual carbon in presence of different metal ions (Na^+ , Mg^{2+} , Al^{3+} or Fe^{3+}).

Figure 4.15 XRD patterns for OFeMMT and its residues tested in air and nitrogen at 450 °C (A) and 750 °C (B).

Finally, to further consolidate TGA and XRD results, CHNS technique was employed for OMI-clays and their residues at 450 °C and 750 °C. Their carbon content (%) are tabulated in Table 4.4. It is quite evident that clay residues at 450 °C have significant carbon content whereas clay residues at 750 °C display only trace amounts as a result of loss due to oxidation, supporting the argument made in previous section.

Table 4.4 Carbon content (%) in OMI-clays and their residues at 450 °C and 750 °C as noted from CHNS technique. (Average values from triplicate results with standard deviations).

Temperature (°C)	ONaMMT	OMgMMT	OAlMMT	OFeMMT
25	32 ± 3	27 ± 4	32 ± 8	18 ± 2
450	15 ± 5	8 ± 1	14 ± 4	7 ± 4
750	0.5 ± 0.1	0.7 ± 0.3	0.6 ± 0.6	0.4 ± 0.1

4.3 Summary

A better understanding was achieved regarding the catalytic effects of individual metal ions (Mg^{2+} , Al^{3+} and Fe^{3+}), otherwise inherently present in varied proportions in MMT lattice, on the thermal decomposition of organic modifier, HDTMA^+ . The catalytic activity was seen to be a combined effect of Brønsted and Lewis acid characters associated with these metal ions. Significant findings include:

- Difference in Brønsted acidity, as a result of water coordinated with different interlayer metal ions, govern the onset of HDTMA^+ decomposition.
- Lewis acidity for OMI-clays can affect the rate of generation of carbonaceous content in residue depending on inherent metal ion characteristics following the mechanism proposed.
- Lewis acidity for OMI-clays affects the oxidation stability of carbonaceous content in residue. Although both Al^{3+} and Fe^{3+} exchanged clays demonstrated lower decomposition onset temperatures ($T_{5\%}$), Al^{3+} showed more pronounced effect on initial stages of HDTMA^+ decomposition. OMgMMT showed delayed peak decomposition for HDTMA^+ under inert conditions owing to its lower catalytic action towards HDTMA^+ .
- Significant reduction in MMT dehydroxylation temperatures were observed to be dependent on Lewis acid character varying amongst OMI-clays.
- XRD analysis for residues indicate that Fe^{3+} ions from OFeMMT predominantly influenced oxidation stability of carbonaceous content while presence of Mg^{2+} and Al^{3+} resulted into delayed oxidation of carbonaceous matter.

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Chapter 5

Thermo-oxidative Decomposition Behavior of Polyamide 6 Nanocomposites with Metal-ion Exchanged Clays

This chapter focuses on evaluating the effects of metal ion exchanged clays on thermo-oxidative and combustion properties of Polyamide 6. Microstructural characterization, gas- and condensed-phase analyses provide insights into organo-metallic interface and subsequent effect on decomposition products. Unique effects of each metal ion is established in terms of combustion parameters. Finally, decomposition mechanism is proposed for Polyamide 6 which is prone to catalysis by metal ions.

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5.1 Introduction

The interaction of metal ions with PA6 is rather complex. Some metal ions like Fe^{3+} , Cu^{2+} and Zn^{2+} coordinate directly with carbonyl oxygen from amide link (direct coordination); while Mg^{2+} and Ca^{2+} coordinate with compounds facilitating their hydrogen bonding with carbonyl oxygen from amide linkages (indirect coordination) as represented in Figure 5.1A¹⁻³. Metal-amide complexes may in turn alter crystal structure of PA6 by hindering hydrogen bonding⁴. Complexes with certain metal ions (like Cu^{2+} and Zn^{2+}) increase the electrophilic nature of carbonyl carbon towards (amide) hydrolysis even under neutral conditions⁵. The reported tautomeric structures for metal-amide complex (Figure 5.1B)⁶ could influence β -hydrogen abstraction.

Figure 5.1 (A) Structure of PA6-metallo complex depending on metal ion¹⁻³ (B) Tautomer for metal ion-amide linkage⁶.

Mortland⁷ suggested that the formation of metal-oxygen bond will result in more single-bond character to CO bond while higher double-bond character for CN bond. This leads to lowering in CO stretching frequency which is proportional to electrophilic nature of metal ion. This in other words means that highly electrophilic metal ions like transition metals

promote formation of C=N in Figure 5.1B. Further, metal ions can coordinate with carbonyl compounds with amide/imide linkages like oxamide⁸ or ϵ -caprolactam⁹. Figure 5.2 indicates intermediate (carbonyl) decomposition products commonly generated during PA6 thermo-oxidation that can potentially coordinate with metal ions on clay surface. Strength and degree of this coordination depend on factors like spatial restriction for reorientation of ligand molecule/segment, position of coordinating segments (i.e. along chain length or at terminal ends), electronegativity of metal ion, and conjugation.

Figure 5.2 Potential coordination complexes at organo-clay interface between metal ion and carbonyl compounds generated during PA6 thermo-oxidation.

It is well known that PA6 follows peroxy-based decomposition mechanism under thermo-oxidative conditions generating reactive alkoxy- and peroxy- moieties during initial stages of decomposition. Metal ions can accelerate the generation of these intermediate reactive moieties, and also influence oxidative stability of the char (depending on their redox

potential, concentration and chelation)^{5, 10-12}. Following work focusses on evaluation of combustion properties of PA6 when incorporated with MI-clays and OMI-clays.

5.2 Results & Discussion

5.2.1 Crystal Phase & Microstructure

It is known that polyamides seek to maximize the number of hydrogen bonds within and between polymer chains. This process requires polyamide chains to adopt either a fully extended or a twisted configuration determining the resulting crystal form, monoclinic α - or pseudo-hexagonal γ -phase. However, with the incorporation of clay platelets (particularly, montmorillonite), many studies have reported that a γ -phase is favoured instead of α -form¹³. This was believed to be a result of chain conformation change (pointing to the extent of dispersion of clay layers in the matrix), limiting the formation of hydrogen-bonded sheets of polyamides. In line with this, even in the current work, strong γ phase peaks (10.7° and 21.3°) for PA6/OMI-clay composites are observed suggesting good dispersion of OMI-clay in PA6 matrix. Diffraction patterns for all composites are shown in Figure 5.3. TEM micrographs shown in Figure 5.4 further confirm this. PA6/MI-clay composites, however, displayed prominent diffraction peaks corresponding to α phase (20.5° and 24°) indicating limited dispersion of MI-clays in PA6. To further corroborate these results, DSC tests are carried out and the results are shown in Figure 5.5. It is evident that there is no change in melting temperature of PA6/MI-clay composites as compared to neat PA6, suggesting predominance of high melting α phase. PA6/OMI-clay composites, however, exhibited the presence of both α phase and low melting γ phase, supporting the above XRD results.

Figure 5.3 XRD patterns of PA6/MI-clay microcomposites (A) and PA6/OMI-clay nanocomposites (B).

Nonetheless, the prominence of α or γ might not be a direct indicator of dispersion. Li et al.¹⁴ showed that the addition of fibrillar multi-walled carbon nanotubes to polyamide favor α -phase instead of γ (even with well dispersed nanotubes). However, they also observed that with amino-functionalization of multi-walled carbon nanotubes, γ -form was preferred over α . This shows that stronger interaction could force PA6 chains out of hydrogen-bonded sheets of the α -form and promote crystallization in the γ -form. Similarly, the effect of metal cations on this process was also discussed in a few studies, which showed that amide-metal complexation is a major parameter influencing hydrogen bonding and thereby,

Figure 5.4 Representative TEM images of PA6/OMI-clay nanocomposites (5 wt.% loading); PA6/ONaMMT (A), PA6/OMgMMT (B), PA6/OAlMMT (C), and PA6/OFcMMT (D).

crystallinity (and melting point). Ciferri et al.¹⁵ have reported that the addition of calcium chloride (Ca^{2+} is alkaline earth metal similar to Mg^{2+}) to PA6 lowered the melting temperature of PA6. Moreover, the % reduction was dependent on metal ion content (Table 5.1). In similar studies, it was noted that amide-metal complexation (PA6/Fe^{3+} or PA6/Cr^{3+}) will result in perturbed hydrogen bonding, in turn decreasing crystalline content (Table 5.1) and higher content of low melting (γ phase) crystallites^{4,16}. Influence of metal ions becomes

more pronounced with thermal aging as reported by Cerruti et al.¹⁷ for PA6,6/metal salt composites. Marked differences in melting point as a result of aging under oxidative conditions (Figure 5.6) highlight that PA6,6 chains undergo relaxation-like rearrangements to increase the coordination with metal ions. This reduces the inter-chain hydrogen bonding causing lower melting temperature.

Table 5.1 Reported DSC results for PA6/metal halides confirming influence of metal ions on crystallographic properties of PA6.

Reported by	Specimen	Salt Conc. (wt.%)	Melting Point, T_m (°C)	Melting Enthalpy, ΔH_m (cal/g)	% Crystallinity
Ref ¹⁵	PA6	-	225	16.4	Not reported
	PA6/CaCl ₂	1	214	13.6	Not reported
		3	212	11.3	Not reported
		5	206	9.0	Not reported
Ref ⁴	PA6	-	225	15.2	31.4
	PA6/FeCl ₃	5	210	12.2	25
		12.5	191	7.6	15.7

Figure 5.5 Second heating cycle curves from DSC for PA6/MI-clay (A) and PA6/OMI-clay (B) composites.

It is interesting to see that PA6/OMI-clay nanocomposites show this behavior with successively stronger γ phase peak ($\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+}$) indicating the influence of metal ions on crystallization behavior is in accordance with previously reported studies. Absence of this in PA6/MI-clay composites suggests steric hindrance experienced by polymer chains in intercalated morphology that limits the complexation during crystallization. Correlating these results with XRD, it can be argued that γ phase development is a function of two different factors, physical dispersion (delamination) of clay and nature of interaction between metal ion and neighboring polymer chains. Difference in interactions amongst metal ions with polymer melt might lead to variations in final γ -phase content as well.

Figure 5.6 Influence of metal ion on melting temperature of PA6,6 with aging under oxidative conditions¹⁷.

5.2.2 Combustion Properties

Combustion properties of neat PA6 and its composites obtained from cone calorimeter are listed in Table 5.2. With OMI-clays, time-to-ignition (TTI) values of nanocomposites improved (over PA6/MI-clay composites) and this is attributable to lower concentrations of residual exchangeable metal ions on OMI-clay surfaces, as discussed and confirmed in our earlier study¹⁸. Better dispersion of clay platelets in PA6/OMI-clay nanocomposites

compared to PA6/MI-clay composites is another factor that can affect TTI values. Among all the samples, PA6/AlMMT composite displayed quickest ignition time of 83 s. Even with OAlMMT, TTI value is still 92 s suggesting the dominance of catalytic effect of Al^{3+} . Similar (catalytic) activity was also reported in polypropylene samples filled with Al-POSS where TTI was reduced by 19 s compared to neat polypropylene¹⁹. In short, comparing TTI values of all samples, it is clear that pre-ignition reactions depend on combined effects of type/nature of metal ions on clay particles and the physical barrier (more detailed discussions on these aspects in later sections).

Table 5.2 Cone calorimeter results of neat PA6 and its composites with MI-clays and OMI-clays.

Specimen	TTI (s)	pHRR (kW/m ²)	Avg. HRR (kW/m ²)	THR (MJ/m ²)	Char (%)	TSR (m ² /m ²)	TSP (m ²)
PA6	140	840	298	97	0	108	0.96
PA6/NaMMT	94	826	349	148	12.4	427	3.77
PA6/MgMMT	85	535	261	113	34.2	586	5.18
PA6/AlMMT	83	566	263	113	28.5	425	3.76
PA6/FeMMT	100	543	295	147	17.6	737	6.52
PA6/ONaMMT	116	369	257	147	11.9	1133	10.02
PA6/OMgMMT	114	327	229	151	10.0	1087	9.61
PA6/OAlMMT	92	368	254	154	10.6	1035	9.15
PA6/OFeMMT	107	397	253	161	6.2	1354	11.97

Beyond TTI, the influence of MI-clays and OMI-clays is also evident on HRR, % char, and smoke parameters (TSP and TSR). pHRR values, as expected, showed a dependence on dispersion of clay platelets in the matrix; relative reductions of up to 36 % in pHRR values are obtained with PA6/MI-clay samples and up to 61 % with PA6/OMI-clay nanocomposites compared to neat PA6 (Figure 5.7). Further, PA6/MgMMT composite gave highest char of ~34 % followed by PA6/AlMMT with ~28 % and PA6/FeMMT with ~17 %. These results are also in line with our previous work where it was found that Mg^{2+} and Al^{3+} delayed the oxidation of carbonaceous matter, whereas Fe^{3+} catalyzed the oxidation process¹⁸. Similar trend is seen with PA6/OMI-clay nanocomposites. These values of % char clearly point to enhanced crosslinking as a result of complex formation²⁰.

Even in a recent study, it was reported that when Ba^{2+} (alkaline earth metal like Mg^{2+}) was incorporated into sodium alginate fibres, a high char value of 34.2 % was obtained (in TGA under air atmosphere until 900°C)²¹. Without the divalent cation, only 0.63 % char was obtained.

Figure 5.7 HRR curves of PA6 and its composites with MI-clays (A) and OMI-clays (B).

It was observed from Figure 5.8A that both PA6 and PA6/NaMMT begin to emit smoke around 20 s. However, there is still a delay of 46 s in TTI of PA6 compared to PA6/NaMMT. Rest of the PA6/MI-clay composites displayed higher and different TSP onset times in the order of Al^{3+} (30 s) < Mg^{2+} (112 s) < Fe^{3+} (125 s). When compared with their lower TTI it

is suggested that volatiles generated by MI-clay composites are possibly low molecular weight or require lower activation energy for complete oxidation. As a result, they are not registered as smoke but as CO₂ (product of complete combustion) as evident from their CO₂ evolution profile shown in Figure 5.9A. A delay of 40-50 s for CO evolution onset observed from Figure 5.9A-B indicates the occurrence of partial combustion on account of higher rate of volatile generation as sample progresses towards flashover point (pHRR). Apart from TSP onset the difference in overall TSP profile clearly indicates compositional variation of smoke as influence by metal ion on clays.

Figure 5.8 TSP profiles for PA6 and its composites with MI-clays (A) and OMI-clays (B).

Figure 5.9 CO and CO₂ emission profiles for PA6/MI-clay composites and PA6/OMI-clay composites. CO₂ production is shown in (A) and (C) while CO production is shown in (B) and (D).

Even though PA6/OMI-clay composites exhibit similar TSP onset, they continue to show a delay of ~50-80 s as compared to neat PA6 (Figure 5.8B). Nonetheless, the effect of metal ions on TSP onset and overall TSP profile is less evident in modified clay composites, which can be attributed to lower concentrations of metal ions in these systems. Similar to PA6/AlMMT, PA6/OAlMMT showed quickest CO₂ and CO generation (Figure 5.9). As compared to PA6/MI-clays, the delay between CO₂ and CO generation is marginally lower (~30-50 s) suggesting slightly higher rate of volatile generation leading to early incomplete combustion.

PA6/FeMMT composite, despite showing similar reduction in pHRR values as PA6/MgMMT and PA6/AlMMT composites, registered higher values for THR, TSR and TSP. Same observation could be deduced for PA6/OFeMMT sample compared to other PA6/OMI-clay nanocomposites. Moreover, with same THR value as PA6/AlMMT,

PA6/MgMMT produced ~6 % more char and also registered ~28 % higher TSR and TSP. This again indicates that these cations are playing an active and unique role in PA6 decomposition process, possibly, altering decomposition kinetics and/or mechanism. In one of the early studies on metal-catalyzed polymer oxidation⁸, it was reported that addition 0.5 wt.% metal stearate to PP (which incidentally follows peroxy-based thermo-oxidation similar to PA6) resulted in different oxygen uptake rates in the order of $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Mg}^{2+} >$ control PP. Activation energy for auto-oxidation was also lower for metal-containing PP by ~25 kJ/mol than neat PP (125.5 kJ/mol). It was hypothesized that there may be correlation between catalytic activity of metal salt and decomposition of hydroperoxide in line with the current observations.

5.2.3 Thermo-oxidative Decomposition Behavior

Onset temperature at 5 % mass loss ($T_{5\%}$), temperature at 50 % mass loss ($T_{50\%}$) and peak temperature for decomposition step (T_P) as obtained from TGA under oxidative conditions are summarized in Table 5.3 and the TGA curves are shown in Figure 5.10. Interestingly, Al-rich composites showed the lowest $T_{5\%}$ in their respective group similar to TTI values, confirming its catalytic reactivity towards PA6 matrix. Interestingly, $T_{5\%}$ values of PA6/MI-clay and corresponding PA6/OMI-clay nanocomposites are similar. For PA6/MI-clay composites, $T_{50\%}$ and T_P are similar to that of neat PA6, but in the presence of organically modified clays, the values are slightly higher. For example, in the case of OMgMMT composite, there is ~30 °C increment in T_P and ~19 °C in $T_{50\%}$. This is despite clear differences in mass loss rate profiles of MI-clay composites (in particular) compared to neat PA6. This suggests a similarity in kinetics and probable dissimilarity in mechanisms in PA6/MI-clay composites; and vice-versa in PA6/OMI-clay nanocomposites (similar mechanisms but dissimilar kinetics).

Based on the thermo-oxidative decomposition data of MI-clays and OMI-clays¹⁸, these results seem to be a consequence of combined effects of Lewis acidity, clay dispersion and confinement. In PA6/MI-clay composites, polyamide chains that are *confined* in the interlayers of clay platelets will have a higher probability of exposure to metal ions (see Figure 5.11). This either affects the stability of intermediate decomposition products or

results in the formation of different decomposition products. Further significance of interlayer confinement can be derived from work of Sonobe et al.²². They observed formation of highly stacked structure of carbonaceous matter ($d_{002} = 0.337$ nm) between clay platelets for inherently graphitizing as well as non-graphitizing polymer. It was suggested that molecular confinement in two dimensional space facilitated carbonization reaction by virtually making it independent of nature of polymer.

Table 5.3 $T_{5\%}$, $T_{50\%}$ and T_P as obtained from TGA thermograms for PA6 and its composites.

Specimen	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_P (°C)
PA6	437	501	504
PA6/NaMMT	432	505	513
PA6/MgMMT	429	500	508
PA6/AlMMT	422	499	508
PA6/FeMMT	439	501	511
PA6/ONaMMT	430	511	525
PA6/OMgMMT	425	520	534
PA6/OAlMMT	421	507	511
PA6/OFeMMT	434	508	516

In PA6/OMI-clay nanocomposites, delamination results into lower degree of confinement of polymer chains within the intra-gallery region i.e. chains have enough mobility to reorient without spatial restrictions. Though the concentration of metal ions on clay platelets is less, exfoliated morphology could provide an opportunity for enhanced interaction throughout the volume. Depending on the inherent (catalytic) nature of metal ions, it is believed that uniform generation of peroxy and hydroperoxy radical moieties in the condensed phase (of PA6 with OMI-clays) would enhance the recombination reactions. This results in delay of peak decomposition temperatures (i.e., altered decomposition kinetics). Further, lack of steric hindrance near the clay surface provides favourable conditions for surface metal ions to form coordinate complexes with near-by peptide linkages or carbonyl groups. This in turn affects metal ions reactivity similar to inhibitory action of certain chelating agents. For example, Osawa⁸ observed that the oxidizing effect of Cu^{2+} was reduced as a result of its coordination with oxamide and its derivatives.

Moreover, stable coordination and prolonged proximity of (intermediate decomposition) compounds around clay surface might result in localized crosslinking, *shielding* the clay surface.

Figure 5.10 TG curves for PA6 and its composites with MI-clays (A) and OMI-clays (B).

Another important observation is the small mass loss peak around 565 °C for PA6/NaMMT and PA6 composites with FeMMT and OFeMMT. It is hypothesized that this is due to the catalytic-oxidation effect of Fe^{3+} on carbonaceous residue. This in fact supports the argument justifying lower % char for PA6/FeMMT and PA6/OFeMMT composites. To

verify these arguments, condensed phase analysis using FT-IR and XRD, and gas phase analysis using FT-IR are carried out and discussed below.

Figure 5.11 Schematic of structural collapse of PA6/MI-clay and PA6/OMI-clay composites. Intercalated systems pose spatial restrictions on PA6 chains confining them within the galleries of platelets. This could influence the formation and conformational stability of coordinate complexes. Possible complexes are reported in Figure 5.2.

5.2.4 Condensed Phase Analysis

5.2.4.1 Isothermal Study between 325 - 475 °C

To understand the early stages of decomposition of PA6 and development of surface char, all samples are isothermally heated for 5 min in the temperature regime of 325-475 °C with a 25 °C step and ATR FT-IR spectra is taken from the surface of residues. Progressive decomposition and difference in residue appearance with increase in temperature is evident from Figure 5.12A. Representative image of surface char and underneath material is shown in Figure 5.12B. Due to similarity, images and their corresponding spectra included here are of composites rich in Fe^{3+} only (Figures 5.13 and 5.14). Data for other composites are presented as Figure A1-A2 in Appendix A.

Figure 5.12 Digital images for residues of PA6, PA6/FeMMT and PA6/OFeMMT composites after isothermal tests between 325 - 750 °C (A). Image B shows the ruptured surface char exposing material underneath.

Figure 5.13 reveals the following spectral features and peak positions for neat PA6: weak (shoulder) peaks at 1712 cm^{-1} and 1762 cm^{-1} pointing to the formation of carbonyl moieties (aldehydic, ketonic or carboxylic carbonyl); and isocyanate peak between $350\text{--}400\text{ }^{\circ}\text{C}$, but it is unclear if this peak continues to exist beyond $400\text{ }^{\circ}\text{C}$ as it is overlapped by stronger nitrile group peak from $425\text{ }^{\circ}\text{C}$. In PA6 composites, the evolution of nitrile moieties with temperature is dependent on the type of metal ion (Figure 5.15). This reiterates the significant influence of metal ions on kinetics and/or mechanism.

Figure 5.13 Overlay of ATR FT-IR spectra for isothermally heated PA6 between 325 and 475 $^{\circ}\text{C}$.

In line with widely presumed major functional groups present in decomposition products for PA6¹⁰, differences between FeMMT/OFeMMT reinforced PA6 and neat PA6 in the temperature regime studied are highlighted in Table 5.4 for simple viewing. Protection provided by surface char prevented decomposition of underneath PA6 for test duration of 5 min. As a result, ATR FT-IR performed on under-the-surface layer predominantly displayed PA6 peaks overshadowing any minor variations and peaks corresponding to decomposition products.

Figure 5.14 Overlay of ATR FT-IR spectra for isothermally heated PA6/FeMMT and PA6/OFeMMT composite. Isocyanate peak (indicated by 'a') shifted by 12 cm^{-1} between 325 and 350 °C for PA6/FeMMT, while PA6/OFeMMT display isocyanate peak even at 475 °C; both PA6/FeMMT and PA6/OFeMMT display nitrile peak (indicated by 'b') below their respective $T_{5\%}$ (439 °C and 434 °C); PA6/OFeMMT display strong aliphatic carbon peak at 375 °C indicated by 'c' and development of strong Si-O peak from 450 °C ('d') that is below its $T_{50\%}$ (508 °C).

Table 5.4 FT-IR bands observed as a result of isothermal heating of PA6 and its Fe-based composites.

Absorption range, cm^{-1}	Assignments	Analysis
2950-2830	$-\text{CH}_3$, $-\text{CH}_2-$ aliphatic carbon, stretch	Only PA6/FeMMT display these strong bands in the range of 2950-2830 cm^{-1} and only between 350 and 400 °C suggesting accelerated generation of aliphatic carbon moieties in condensed phase.
2250-2240	$\text{N}=\text{C}=\text{O}$ in isocyanate, anti-sym. stretch	Isocyanate peaks for PA6/FeMMT remain inconclusive due to possible overlapping with broad nitrile peak. However, a distinct weak isocyanate for PA/OFeMMT can be observed at 475 °C due to absence of nitrile peak at that temperature, hence it is suggested that isocyanate moieties are stable even at 475 °C.
2230-2210	$\text{C}=\text{N}$ in nitrile, stretch	Strength of nitrile peaks in both PA6/FeMMT and PA6/OFeMMT is stronger even at temperatures of 375 °C.
1606-1775	$\text{C}=\text{O}$ in carbonyl moieties, stretch	After deconvolution of the spectra obtained at 375 °C in the range of 1900-1550 cm^{-1} , it is clear that PA6/FeMMT shows a shift of ~22 cm^{-1} from 1628 to 1606 cm^{-1} indicating back-bonding of Fe^{3+} -amide linkage complex (Figure 5.16). Similarly, shifts of ~11 and 13 cm^{-1} are also observed in the carbonyl peaks to higher wavenumbers 1723 and 1775 cm^{-1} . This might be due to the generation of different carbonyl moieties than those formed in neat PA6. In PA6/OFeMMT nanocomposite, there is no presence of any peak corresponding to $\text{C}=\text{O}$ above 1760 cm^{-1} . In polyamides, bands observed at 1735, 1725, 1710 and 1700 cm^{-1} are ascribed to imides & cyclic ketones, saturated aldehydes, dimeric carboxylic acid and α,β -unsaturated carboxylic acid, respectively ¹⁷ .
1150-1050	$\text{Si}-\text{O}-\text{Si}$ in MMT, stretch	This peak appears for PA6/OFeMMT at temperatures as low as 450 °C before $T_{50\%}$ (508 °C) is reached. This confirms that clay migration for exfoliated morphologies start at temperatures lower than those for intercalated morphologies ²³ (like PA6/FeMMT).

Figure 5.15 Variation in peak intensities corresponding to nitrile group for PA6/MI-clay composites between 325 and 475 °C. Intensity was measured using temporary base line in the range of 2300-2100 cm⁻¹.

Figure 5.16 Deconvoluted ATR FT-IR spectra in the range of 1900-1550 cm⁻¹ from the surface char of PA6 and its Fe-based composites after isothermal heating at 375 °C.

5.2.4.2 Isothermal Study at 750 °C

By comparing FT-IR and XRD results of residues obtained from PA6/MI-clay and PA6/OMI-clay composites after isothermal heating at 750 °C (Figure 5.17), a couple of interlinked differences are evident: (i) $-\text{CH}_3$ and $-\text{CH}_2-$ (stretching) peaks (though very small) at ~ 2925 and 2850 cm^{-1} ; and (ii) intensity and breadth variation in diffraction peaks in the $6 - 9^\circ$ range and at 27.5° . They suggest compositional concentration changes of carbonaceous residue entrapped between collapsed clay platelets. Sonobe et al.²² reported that nitrile group coordinated with (interlayer) Ca^{2+} from CaMMT are more stable than the free group at 400 °C. Taking this into account, it is suggested that interaction of different metal ions with condensed phase decomposition products may eventually result in different composition of carbonaceous matter. For instance, peak between $6 - 9^\circ$ is a direct indication of oxidizing capacity of each cation during late stages of charring. As we have reported earlier¹⁸, Fe^{3+} enhances oxidation of carbonaceous matter explaining the significantly less intense peak at 7° for both PA6/FeMMT and PA6/OFeMMT residues. The nature of this carbonaceous matter is represented by the peak at 27.5° , which is generally ascribed to (002) plane in graphitic structure and is consistently observed in polymer/clay nanocomposite residues²⁰. Yermiyahu et al.²⁴ studied the adsorption of anionic dye congo-red by different MI-clays, their thermo-oxidation behaviour and subsequent formation of carbonaceous matter (which they referred as “charcoal”) in interlayer. They observed that two types of “charcoal” were formed, one with low temperature stability and other with high temperature stability. It was suggested that nature of exchange metal ion determines the ratio between these two types of “charcoal”. Amount of high temperature stable “charcoal” increased with increasing the acidity of exchange cation i.e. $\text{Fe}^{3+} > \text{Al}^{3+}$. But in current study PA6/AlMMT shows more prominent graphitic peak than PA6/FeMMT. This might be associated with overall decomposition reactions and different combination of decomposition product formed.

Figure 5.17 FT-IR spectra (A, C) and XRD curves (B, D) of PA6/MI-clay and PA6/OMI-clay composites isothermally heated at 750 °C.

In case of PA6/OMI-clay residues, they do not show expected reduction in peak intensities associated with --OH stretching (~ 3640 , $\sim 3410\text{ cm}^{-1}$) and --OH bending vibrations ($\sim 1645\text{ cm}^{-1}$) associated with dehydroxylation of clay. This signifies minimum loss of surface and coordinated water even at 750 °C. This is an indication of clay shielding as described earlier. That is, depending on the interaction and inherent catalytic activity of cation, PA6 can decompose preferentially around the clay platelet generating a coat of carbonaceous residue. This shield could delay clay dehydroxylation and prohibit the interaction of interlayer cations with neighbouring organic matter. Some other minor differences among the samples suggesting metal ion migration in montmorillonite are explained in Section A1.1 in Appendix A.

5.2.5 Gas Phase Analysis

5.2.5.1 Condensate Study at 500 °C

Collected condensates for PA6 and PA6/MI-clay composites showed subtle differences as shown in Figure 5.18. An obvious difference was observed between 3600-3200 cm^{-1} . PA6/MgMMT displayed least peak intensities in this range while PA6/FeMMT showed multiple shoulder suggesting multiple overlapping peaks. Relevant groups that display peaks in this region are $-\text{NH}$ in secondary amines, $-\text{OH}$ in oximes and $-\text{NH}_2$ in primary amines/amides/aromatic amines. It is presumed that these peaks do not indicate H_2O evolution during sample preparation as it will escape and will not stay back in condensate solution; while ACN from filter paper was also vaporized at 110 °C removing any uncertainty. Most prominent peak between 1660-1640 cm^{-1} is primarily attributed to $\text{C}=\text{O}$ in primary amides (amide I band), $\text{N}-\text{H}$ in primary amides (amide II band) but can also possibly indicate $\text{C}=\text{O}$ in β -diketones, tertiary amides, β -ketone esters and NH_3^+ in amino acids.

Figure 5.18 Overlay of ATR FT-IR spectra for condensate collected from isothermally heating PA6 and PA6/MI-clay composites at 500 °C.

Peaks at 2950-2850, ~1490 and ~980 cm^{-1} corresponding to $-\text{CH}_3$, $-\text{CH}_2-$ in aliphatic compound, CH_2 scissor vibration in aliphatic compounds and $\text{HC}=\text{CH}-$ in trans

disubstituted alkenes prominently shown by PA6/MgMMT alone suggest that condensable gases consist of significant amount of aliphatic compounds. Intensity variations between $1556\text{--}1549\text{ cm}^{-1}$ are associated with --NO_2 in aliphatic and aromatic compounds, --NH in secondary amines and triazine ring stretch. Although FT-IR technique is limited in the identification of exact molecules especially in mixtures, it is quite evident that these condensable gaseous products have different molecular combination.

5.2.5.2 TG-IR Analysis

A four-stage evolution process for CO_2 is seen from the 3D TG-IR plot of neat PA6, Figure 5.19, inset A. By correlating this data with TG results discussed earlier, it is evident that the first stage corresponds to $T_{5\%}$, second and third stages to oxidation of decomposition products while the final stage is a result of oxidation of char. Inset B highlights absorbance signals of evolved products. Apart from the peaks corresponding to CO , CO_2 , H_2O and primary amines, strong signals at ~ 1640 and 2890 cm^{-1} corresponding to cyclo-ketones (cyclopentanone and cyclohexanone) and ϵ -caprolactam, respectively, are observed.

Figure 5.19 3D TG-IR spectrum of PA6. The arrows in inset A indicate the steps corresponding to evolution of CO_2 . Inset B highlight absorbance peaks for different groups evolved.

This assignment was made considering gas chromatography coupled with mass spectroscopy results of Michal et al.²⁵ They reported that cyclopentanone and cyclohexanone constitute ~46 % of total evolved gases for PA6 under thermo-oxidative condition. Expectedly, only 1.2 % was registered to ϵ -caprolactam. However, array of peaks seen in Figure 5.19 in the range of 1730-1760 cm^{-1} also suggest formation of other carbonyl groups like aldehyde or carboxylic acid.

Comparing TG-IR data of PA6 with PA6/MI-clays (Figure 5.19 and 5.20), differences are apparent in (i) 3000-4000 cm^{-1} region, in which, traditionally, peaks are associated with –OH, –NH and CO_2 ²⁶; and (ii) around 2350 cm^{-1} (CO_2 evolution profile). Peak intensity in the 3000-4000 cm^{-1} range successively reduced for MI-clay composites in the order of $\text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Fe}^{3+}$. Interestingly, this reduction overlaps with increase in Lewis acid character from Na^+ to Fe^{3+} . This signifies greater coordination character. As a result, intermediate decomposition products like acrylamide imide attain certain stability that are otherwise prone to thermal dissociation without accumulation in PA6.²⁷ This influences decomposition kinetics. The presence of confined environment within the intercalated PA6/MI-clay composites as discussed in previous sections, might as well provide favourable conditions for enhancing the interfacial interaction between metal ions on clay surface and constrained matrix/intermediate decomposition products. It has also been reported that these confined conditions resulted in same product with different conformation, which otherwise, was not energetically favourable.²⁸

Absence of profound differences between PA6 and PA6/NaMMT (Figure 5.19 and 5.20A), suggest that Na^+ does not significantly alter the decomposition mechanism of PA6, which highlights restricted capability of Na^+ (on clay surface) to form coordinate complex.²⁹ However, Na^+ influenced oxidation stability of carbonaceous matter giving additional CO_2 peak at 570 $^\circ\text{C}$, similar to Fe^{3+} , and stronger than the one observed in neat PA6. It was observed that oxidation of PA6 at 400 $^\circ\text{C}$ in the presence of ‘Na-salts’ gave 70 % less HCN and 15-35 % more ammonia.³⁰ This was attributed to the reaction of sodium ions with HCN inhibiting HCN evolution by forming NaCN. However, there was no evidence of NaCN in condensed phase, casting questions on the hypothesis put forth. This is not observed in the present case illustrating the differences in reactivity (or restricted ability) in the two cases. For PA6/AlMMT, a noticeable shoulder around 450 $^\circ\text{C}$ in Figure 5.20C suggests that Al^{3+}

Figure 5.20 3D TG-IR spectra of PA6/NaMMT (A), PA6/MgMMT (B), PA6/AlMMT (C), and PA6/FeMMT (D). CO₂ (stretch) signals are indicated with arrows. For PA6/NaMMT and PA6/FeMMT composites, peaks at 570 and 565 °C, respectively, are due to oxidation of carbonaceous char as seen from Figure 5.10 and 5.22. Presence of only one CO₂ peak in PA6/AlMMT and PA6/MgMMT composites at ~525 °C indicates that Mg²⁺ and Al³⁺ do not influence oxidation of carbon content in residue beyond 675 °C. This is also confirmed by FT-IR analysis (Figure 5.17A).

might have accelerated the rate of decomposition (oxidation) implying its influence on reaction kinetics. This observation is in line with early decomposition temperature and early ignition time of PA6/AlMMT sample. PA6/FeMMT composite, apart from showing strongest 2930 cm⁻¹ peak amongst PA6/MI-clay composites, also displayed noticeable peaks within 900-1000 cm⁻¹, 1300-1390/1430-1470 cm⁻¹ and 3000-3100 cm⁻¹ corresponding to various groups *viz.* =C-H (bend) in trans di-substituted alkenes, aliphatic C-H (rock/bend) and aromatic C-H (stretch)/ unsaturated =C-H (stretch), respectively

(pointed out in the inset of Figure 5.20D). This indicates that PA6/FeMMT generates higher quantities of unsaturated aliphatic and/or aromatic compounds and also explains its smoke characteristics (Table 5.2).

Figure 5.21 3D TG-IR spectra for PA6/ONaMMT (A), PA6/OMgMMT (B), PA6/OAlMMT (C) and PA6/OFeMMT (D).

TG-IR spectra for PA6/OMI-clay nanocomposites are shown in Figure 5.21. Except for twin peak in CO₂ evolution profile for PA6/OFeMMT, rest all composites showed very similar single peak, no other observable difference was noted apart from peak CO₂ evolution temperatures. Supporting the theory proposed earlier suggesting restricted interaction of interlayer cations with neighboring decomposing PA6 chains, as a result of shielding effect on metal ions. This may result into similar decomposition pattern for all PA6/OMI-clays giving similar TG-IR contour plots. PA6/OFeMMT continue to show

second peak at 565 °C, although with much lower intensity, thus, it may be argued that catalytic activity of Fe^{3+} was subdued due to surface coat. Lower concentration and comparatively lower catalytic activity of Na^+ as compared to Fe^{3+} may possibly explain the disappearance of second peak in CO_2 emission profile otherwise observed at 570 °C in case of PA6/NaMMT.

Referring to Figure 5.22 there are two important observations for PA6/FeMMT that can be associated with its decomposition mechanism; (1) very sharp maxima for 2930 cm^{-1} curve and (2) distinct maxima in 1750 cm^{-1} curve around 480 °C overlapping with onset of oxidation as seen from shoulder in 2358 cm^{-1} curve, indicates early generation of aliphatic C-H and C=O containing compounds. The evident shift in peak temperatures indicate the

Figure 5.22 Absorption profile for IR with increase in temperature. Wavenumbers 2950, 2358 and 1750 cm^{-1} are markers of aliphatic group, CO_2 and carbonyl group, respectively.

influence of metal ions on generation of different compounds, conservatively associated to decomposition kinetics.

5.2.6 Thermo-oxidative Decomposition Mechanism

Levchik et al.¹⁰ reviewed several thermo-oxidative decomposition reactions that were proposed for neat PA6. Although it is anticipated that presence of clay deviates the decomposition path of matrix polymer, overall decomposition mechanism (in this case, peroxy-based) remains unchanged as it principally depends on polymer backbone structure. Influence of the presence of metal ions (on clay surface) on relevant mechanisms of PA6 are given in Schemes 5.1 and 5.2. As reported in our previous investigation¹⁸, metal ions have preferential reactivity towards peroxy groups. They can, either oxidize by reducing hydroperoxide group into more reactive peroxy group or reduce by oxidizing hydroperoxide group into another reactive alkoxy group. This indicates that presence of metal ions might help maintain a larger pool of highly reactive peroxy- (I) and/or alkoxy- (II) groups in condensed phase at least during initial stages of decomposition (Scheme 5.1). According to observations made from condensed phase analysis, plausible pathways for generation of nitrile and isocyanate groups are suggested in Scheme 5.2. However, concentration of hydroxyl moiety (III) in Scheme 5.2 is dependent on concentrations of (I) and (II). Hence, role of metal ions in generation of intermediaries (I), (II) and (III) will dictate the early generation of carbo-nitrogenous compounds in condensed phase as seen from Figure 5.14.

Based on cone calorimeter results, it is hypothesized that Mg^{2+} and Al^{3+} facilitate preferential formation of oligomeric alkyl radicals at a rate higher than at which they are fragmented (and are air-borne) resulting in significantly higher quantities of unsaturated compounds in condensed phase. This (along with trapping of volatiles by clay barrier) can facilitate recombination and cross-linking resulting in higher char content as seen from Table 5.2. It is suggested that depending on their stereo specificity, Mg^{2+} , Al^{3+} and Fe^{3+} will preferentially produce either ordered or amorphous carbonaceous matter as observed from Figure 5.17B. However, the oxidative stability of this could not be precisely evaluated in the current work. Further understanding of mechanisms is possible if the evolved gases

during cone calorimeter testing are evaluated, which will be the focus of a future work and is beyond the scope of current study.

Scheme 5.1 PA6 decomposition mechanism identified for possible influence of metal ions for accelerated generation of peroxy-/alkoxy- group in condensed phase for PA6/MI-clay nanocomposites. Reversible reactivity of metal ions can maintain the pool of reactive oxy- and peroxy- moieties, creating the environment for possible alternate route of decompositions.

Scheme 5.2 Possible routes for generation of carbo-nitrogenous residues from intermediate product. The generation and quantity of starting hydroxyl-moiety directly depends on role of metal ions as depicted in Scheme 5.1.

Even for PA6/OMI-clay nanocomposites, contour plots are similar (Figure 5.21), and differ from neat PA6. This suggests that these materials also follow the decomposition scheme as PA6/MI-clay composites. The much lower quantities of metal ions in OMI-clays and possible shielding of clay platelets resulted in indistinguishable effect between different metal ions. Subsequently, decomposition mechanism becomes independent of cation towards peak decomposition stage and thereon on.

5.3 Summary

The work presented in this Chapter advances our knowledge of fundamental cause of clay catalysis and the role of different cations on thermo-oxidative stability and combustion properties of PA6/clay nanocomposites. This knowledge is significant to overcome limiting aspect of clays making them a viable stand-alone flame retardant. Notably,

- All exchange metal ions (Mg^{2+} , Al^{3+} and Fe^{3+}) displayed profound effects on PA6/clay composites' decomposition kinetics and mechanism. Combination of their Lewis acidity and physical barrier (as determined by clay dispersion in the matrix) were the governing factors.
- Condensed- and gas-phase analysis provided a qualitative insight into composition of decomposition intermediaries as influenced by clay-polymer interactions (specifically, metal ion-organic interactions).
- Al^{3+} -rich composites showed accelerated decomposition; Fe^{3+} reduced oxidation stability of char and influenced smoke generation; and Mg^{2+} registered highest char suggesting better thermo-oxidation stability.
- Primary decomposition reactions prone to be influenced by redox nature of metal ions were identified for PA6.

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Chapter 6

Thermo-oxidative Decomposition Behavior of Polyamide 6 Nanocomposites with Structurally Different Clays

The primary focus of this chapter is to determine the influence of metal ions that are located at structural locations in clay lattice on the thermo-oxidative decomposition of PA6. For this purpose, different naturally occurring clays belonging to the same expandable smectite family and individually rich in specific metal ions (of interest) were chosen. They are MMT, Hec, and Nnt rich in octahedral Al^{3+} , Mg^{2+} , and Fe^{3+} , respectively. As before, comparative and thorough condensed and gas phase analysis at different size scales is carried out. Even here in the case of structural ions, it is established that each clay displays different effect on decomposition of PA6 which in turn depends on principle metal ion present in their octahedral position.

6.1 Introduction

Work from previous chapters has decisively established unique effect displayed by each metal ion (Mg^{2+} , Al^{3+} , Fe^{3+}) during decomposition of organic matter (surfactant and PA6) while occupying the exchange position in MMT. This chapter explores further into the effect of same ions while they are inherently situated at structural positions in clay lattice. Accordingly, three natural clays, MMT, Hec and Nnt, all belonging to expandable 2:1 smectite group and each individually rich in octahedral Al^{3+} , Mg^{2+} , and Fe^{3+} , respectively, (refer Table 6.1 for compositions) are selected. As shown in Figure 6.1, each of these clays have one octahedral sheet sandwiched between silica tetrahedral sheet on either side with hydroxyl and apical oxygen at sheet interfaces.

Figure 6.1 Composition and spatial arrangement schematic of $\frac{1}{2}$ unit cell for MMT (A), Hec (B) and Nnt (C)¹.

Table 6.1 Clay compositions (as obtained from supplier data sheet).

Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	CEC
MMT	57.7	19	4.2	< 0.01	2.14	-	92
Hec	34.7	0.69	0.02	0.25	15.3	23.4	43.9
Nnt	57	3.4	37.42	-	0.34	2.67	69.7

MMT and Nnt have dioctahedral structures while Hec have a trioctahedral structure (refer to Table A3 in Appendix A for better understanding). Charge deficit primarily occurs at octahedral layer for MMT and Hec in contrast to Nnt where charge deficit is due to isomorphous substitution in tetrahedral layer² which can also be seen from Figure 6.1.

In clay lattice, structural cations are relatively stable as they are ionically bonded with oxygen, hydroxyl group, and neighboring cation. Consequently, they show lower chemical reactivity as compared exchange cations. However, structural cations present at edges and (crystallographic) defect sites are partially bonded. They show higher reactivity and are considered to be principle catalytic sites³. The structure of each clay (in particular, their octahedral ion) also provides information on intensity of acidity of –OH groups at edge and defect sites⁴. For instance, Liu et al. reported the pKa values for –OH groups present at edge and defect sites of MMT which are bonded with Si, Al or Mg, refer to Table 6.2⁵. It is evident that acidity of edge groups is highly dependent on octahedral cation.

Table 6.2 pKa values reported for different edge groups located in MMT⁵.

Edge groups	pKa values
≡Si–OH	7.0
≡Al–OH ₂ –OH	8.3
≡Mg–(OH) ₂	13.2

The basal surface of each clay is composed of siloxane bonds making them extremely stable whereas broken bonds at edges and defect sites are more reactive owing to unbalanced charge stabilization of metal ion and have a tendency to form inner-sphere complexes with protons and cations⁶. It was reported that octahedral cations significantly

influence structural transformations in various natural clays with the rise in temperatures. Structural transformations can change clay acidity (reduction in Brønsted acidity and increase in Lewis acidity⁷) or migration of structural metal ions within crystal lattice to crystallographic cavities or outward towards interlayer region⁸⁻⁹. In general, intensity of effect of such transformations on clay-organic matter interactions depends on,

- the composition of tetrahedral and octahedral layers i.e. charge distribution throughout the clay⁹,
- unbalanced cations at edge and defect sites¹⁰,
- oxygen and hydroxyl groups at edge and defect sites¹⁰
- nature and reactivity of interlayer cation¹¹.

As experimental details are already covered in Chapter 3, here on focus will be on result analysis for thermal behavior of clays and their PA6 nanocomposite under thermo-oxidation and combustion conditions.

6.2 Results and Discussion

6.2.1 Structural Analysis of Different Clays and Organic Modification of Clays

Experimental trials judged the applicability of organic surfactant, HDTMA⁺, for all three clays. Based on their CEC values, different ratios of clay/HDTMA-Br were used. All clays were modified following the same protocol. XRD curves of the organically modified clays shown in Figure 6.2B confirmed successful intercalation. This was of particular advantage because of two reasons; (1) dispersion quality primarily depends on matrix-surfactant interaction, so using the same surfactant for all three clays would ensure similar dispersion profiles in PA6 and (2) use of same surfactant reduces the complexity in decomposition of the matrix as a result of surfactant-matrix interaction. Organically modified clays were also assessed using FT-IR (Figure 6.3) technique. As expected, all organically modified clays displayed prominent markers corresponding to aliphatic C-H (2850-2950 cm⁻¹) from HDTMA⁺.

Figure 6.2 XRD pattern for clays before (A) and after (B) organic modification using cation exchange process (prefix O for clays in image B correspond to organically modified).

Figure 6.3 FT-IR spectra for clays prior-to and after organic modification using cation exchange process.

6.2.2 Thermal Decomposition of Clays

TG analysis of neat clays was carried out to understand their dehydroxylation characteristics. As mentioned in previous chapters, dehydroxylation onset temperatures mark the beginning of the loss of structural OH groups which, alternatively, indicate that

Brønsted acidity remains prominent until that temperature. The strength of this Brønsted acidity depends on the amount of structural –OH groups present in the crystal lattice and can be correlated to mass loss during dehydroxylation of clays. These dehydroxylation characteristics are governed by metal ions present in octahedral locations. Klopogge et al. reported that –OH groups migrate from octahedral layer to siloxane layer during heating to form new surface silanol sites that are eventually lost during dehydroxylation. Corresponding migration temperatures are dependent on octahedral cation e.g. in Mg-smectites like Hec formation of silanol was observed above 250 °C¹² while in Al-smectites like beidellite, silanol were observed above 400 °C¹³. This further signifies the importance of –OH content which can eventually affect acid-base character of clay, *in situ*. Dehydroxylation also depends on bond strengths between octahedral cations with neighboring –O– and –OH groups. With different structural compositions, each clay is expected to display unique dehydroxylation characteristics as seen from Figure 6.4.

MMT and Hec display high dehydroxylation temperatures, 500-680 °C and 600-800 °C, respectively, whereas Nnt undergoes dehydroxylation at much lower temperatures (320-500 °C). The presence of divalent Mg²⁺ in octahedral layer of Hec is expected to produce a more stable structure as compared to trivalent ions like Al³⁺ (in MMT) or Fe³⁺ (in Nnt) because of its high electronegativity difference with oxygen. High electronegativity difference for Mg–O (2.13) and Li–O (2.46) in Hec forms strong ionic bond whereas Al–O (1.83) and Fe–O (1.61) in MMT and Nnt, respectively, exhibit polar-covalent nature³. Additionally, it is known that clays with a high concentration of Fe³⁺ in octahedral layer register lower dehydroxylation temperature¹⁴, and lower than other dioctahedral phyllosilicates with different trivalent octahedral metal ions e.g. in Al³⁺ in MMT¹⁵. This is precisely observed in Figure 6.4 as well. It is argued that presence of octahedral Fe³⁺ forms five- and six-coordinated centers during dehydroxylation. This reduces dehydroxylate stability so much that it may even partially disintegrate the clay lattice before completion of dehydroxylation¹⁴. Incidentally, as discussed in Chapter 4 section 4.2.3.2, FeMMT also registered lower dehydroxylation temperatures as compared to NaMMT by 55 °C. This indicates that, irrespective of its location, Fe³⁺ lowers the thermal stability of clay lattice by lowering its dehydroxylation temperature.

Figure 6.4 TG curves for different clays highlighting their dehydroxylation temperatures and corresponding mass loss in the form of water.

The amount of water loss due to dehydroxylation of clay is critical and can be directly correlated to its Brønsted Acidity. Hec losses ~20 wt.% water compared to 5 wt.% for MMT. These losses are initiated at high temperatures (500 °C for MMT, 600 °C for Hec) likely beyond $T_{50\%}$ for most of the polymers including PA6. This suggests that Hec retains high amounts of -OH up to 600 °C maintaining its acidity which can significantly influence PA6 decomposition. Incidentally, this makes Hec an efficient catalyst for reactions involving amide bond formation^{3, 16}. Bujdak et al. suggested that high ionic nature of Mg-O and Li-O in Hec makes octahedral oxygen more negatively charged, which in turn facilitates favorable spatial orientation of amino acid zwitterions along the edges and defect sites with exposed octahedron. This promotes condensation reaction yielding amide bonds^{3, 16}. Compared to Hec, 5 wt.% loss for MMT indicates lower Brønsted acid character for MMT. Nnt, on the other hand, even with similar ~5 wt.% water loss during dehydroxylation, is more influential because of its low dehydroxylation temperature. As mentioned earlier, generation of H_2O between 300-500 °C is of particular importance as it overlaps with typical decomposition onset for organic surfactants and various condensation polymers including PA6.

6.2.3 Thermal Decomposition of Organically Modified Clays

TG analysis (Figure 6.5A) revealed that all organically modified clays irrespective of their composition display similar two-step pyrolytic decomposition where first step (180-350 °C) typically correspond to decomposition of surface adsorbed surfactant while second step (350-500 °C) correspond to decomposition of intercalated surfactant molecules.

Figure 6.5 TG curves for organically modified clays under pyrolytic (A) and oxidative (B) conditions.

Under oxidative conditions, unlike pyrolysis, initial step corresponds to decomposition of surface adsorbed surfactant leading to carbonization of intercalated surfactant preventing second step decomposition. This carbonized matter eventually oxidized between 500-700 °C depending on the clay. However, the oxidation temperature and corresponding dehydroxylation temperature of clays seem to overlap. This suggests that (Lewis acidity of) dehydroxylated octahedral metal ions at edges and defect sites interact with carbonaceous matter influencing their oxidation.

As compared to dehydroxylation temperatures of unmodified clays (Figure 6.4), organically modified clays showed certain variations e.g. under oxidative conditions, MMT dehydroxylation peaks at 640 °C whereas OMMT dehydroxylation peaks at 622 °C. Similarly, for Hec and OHec (under air purge) dehydroxylation peaks at 746 and 723 °C, respectively. The exact reason for this behavior is unknown. However, Yariv et al. argued that this reduction might be associated with the reaction of interlayer carbonaceous matter with nascent water molecules¹⁷. Low dehydroxylation temperatures for Nnt make it difficult to analyze decomposition of ONnt. This is evident from an overlap of temperatures for decomposition of intercalated surfactant and dehydroxylation in Figure 6.5A. A similar issue was encountered under oxidative conditions for ONnt. However, distinguishable peaks at 465 and 510 °C indicate the possible distinction between oxidation of carbonaceous matter and dehydroxylation. However, it is necessary to use other characterization techniques like XRD and FT-IR in corroboration with TGA observations to have more clarity. Consequently, because of their overlapping regime with PA6 decomposition as a particular case, residue analysis is performed for Nnt and ONnt as discussed in next section.

6.2.4 Residue Analysis for Nontronite Clays

FT-IR for Nnt, ONnt, and their residues are shown in Figure 6.6. Extremely weak peaks corresponding to –OH group at 3600-3200 cm⁻¹ and 1640 cm⁻¹ in Nnt residue at 500 °C confirm the near-complete dehydroxylation as observed in its TG curve (Figure 6.4). Nnt continues to maintain its platelet structure even after dehydroxylation as seen from Figure 6.7A. This is in tandem with reported observations for smectites. According to these

observations, smectites do not lose their structural integrity with the loss of hydroxyl groups and do not show any observable changes in their XRD pattern until the onset of phase change¹⁵. So, at a temperature as high as 750 °C, Nnt continues to maintain its platelet shape. When Nnt was further heated up to 875 °C, characteristic peaks corresponding to β -cristobalite were observed in XRD pattern¹⁸. This follows the high-temperature phase diagram (Figure 6.8) reported by Grim et al. for Nnt¹⁵.

Figure 6.6 Residue FT-IR spectra of Nnt (A) and ONnt (B) when heated under an oxidative atmosphere.

Figure 6.7 Overlapping of XRD patterns for Nnt (A), ONnt (B) and their residues when heated under an oxidative atmosphere at different temperatures.

FT-IR spectra of ONnt residues at 400 °C and 500 °C were studied to distinguish between temperatures regimes for oxidation of carbonaceous matter and dehydroxylation of clay. The presence of strong markers of aliphatic carbon (FT-IR peaks at 2800-2950 and ~1490

cm^{-1}) in ONnt residue at 400 °C and its subsequent absence in residue at 500 °C confirms oxidation precedes dehydroxylation.

Contrary to Nnt, ONnt continues to show strong FT-IR peaks corresponding to structural hydroxyl groups at 500 °C. This is suspected to be a consequence of chemical interaction between clay and oxidizing carbonaceous matter (prior to 500 °C). According to previously reported mechanism¹¹, HDTMA⁺ follow peroxy-based decomposition between 400-500 °C that leads to the generation of radical rich carbonaceous matter. Additionally, Carvalho et al¹⁹ have provided experimental evidence for radical trapping behavior of structural Fe^{3+} following Fe^{3+} to Fe^{2+} transformation in Nnt (Figure 6.9). Hence, it is suggested that presence of radical rich carbonaceous matter (prior to 500 °C) may lead to a reduction of octahedral Fe^{3+} . This reduction will increase localized octahedral charge²⁰ deviating from behavior otherwise experienced by neat Nnt. This could potentially delay the dehydroxylation or may even prevent complete loss of $-\text{OH}$ beyond 500 °C. This can also eventually alter phase transition reactions and kinetics as compared to Nnt providing a possible answer for the continued presence of (although low intensity of) FT-IR peaks for structural hydroxyls in ONnt residue at 750 °C and generation of β -cristobalite at 750 °C itself as seen from XRD pattern (Figure 6.7B). Development of strong shoulder at $\sim 1205 \text{ cm}^{-1}$ unique to the ONnt residue at 750 °C confirms certain unknown structural change not seen in neat Nnt residues.

Although the overall explanation is supported by clay mineralogy reports to a best possible extent, the author acknowledges the potential limitation of provided explanations. However, for the scope of current work, there is enough observational evidence pointing towards inter-dependency of Nnt and organic matter decomposition which has to be considered.

With basic understanding achieved for thermal behavior of clays and their organically modified counterparts, focus, here-after, will remain on polymer/clay composites, their morphological and decomposition behavior as influenced by different clays.

Figure 6.8 Phase changes in Hec, MMT, and Nnt upon heating¹⁵. Origin of clays: MMT from Crook County, Wyoming, Hec from Hector, California and Nnt from Manito, Washington.

Figure 6.9 Radical trapping behavior and conversion of octahedral Fe^{3+} to Fe^{2+} as demonstrated by the evolution of threshold energy (E_t). PMMA is a radical source. Transformation of Fe^{3+} corresponds to peak decomposition temperature of PMMA with a maximum number of radicals present. “ r ” denotes Fe-O bond length¹⁹.

6.3 PA6/Clay Nanocomposites

6.3.1 Combustion Properties

Combustion data obtained for different PA6 composites are tabulated in Table 6.3 and corresponding HRR curves are shown in Figure 6.10. All PA6/clay microcomposites ignited early (by 40 – 50 s) as compared to neat PA6. As compared to PA6/MMT, PA6/Hec showed early ignition by 4 s while PA6/Nnt showed ignition delay of 5 s. Although differences in TTIs were observed amongst themselves, the magnitude of these difference was very low. One reason might be lower number active sites in the clay i.e. very low ratio of total active sites (edges and defect sites combined) to the large relatively benign (Si-O-Si) planar surface. Other reason might be due to partial stabilization of exposed metal ions at edges and defect sites because they still continue to remain part of clay lattice. This can prevent them from showing the noteworthy effect as seen in the case of MI-clays where same metal ions were free to interact with matrix without spatial restrictions. It is interesting to note that PA6/Nnt displayed highest TTI than its counterparts because it was expected that hydrolysis assisted by Nnt dehydroxylation would rather reduce the TTI much lower than PA6/MMT or PA6/Hec. Delay in ignition suggests generation of volatiles entities which require much larger pool (causing time delay) to reach minimum fuel concentration for ignition. Evolution of gaseous entities with high molecular weights or those requiring higher activation energies for sustained oxidation and flame can also delay ignition. Since exact reason is yet to be understood, it is proposed that overall PA6 decomposition mechanism has been altered by the presence of Nnt due to combined effect of dehydroxylation of Nnt clusters, confinement effect analogous to PA6/MI-clay composites and Fe^{3+} - Fe^{2+} transformation capability displayed by Nnt.

Concurrent with observation from previous chapter, incorporation of organically modified clays showed higher TTI as compared to their micro composite counterparts. This is mainly attributed to better dispersion and significantly higher polymer/clay interface facilitating better barrier effect and more uniform catalysis across the bulk. With no reduction in overall Brønsted acidity and Mg^{2+} concentration in Hec upon organic modification, a similar magnitude of difference in TTI for PA6/MMT – PA6/Hec (- 4 s) and PA6/OMMT – PA6/OHec (- 6 s) is no surprise. However, PA6/ONnt did not display an increase in TTI,

on the contrary, it showed early ignition by 15 s than PA6/Nnt. It is argued that, contrary to PA6/Nnt, superior delamination (higher interfacial area between PA6 and dehydroxylating ONnt) along with enhanced dispersion of ONnt throughout the matrix would promote hydrolysis to greater extent. It would also accelerate the generation of peroxy radical pool causing rapid localized fragmentation. Thus, resulting in early ignition. Presence of decomposing HDTMA^+ at Nnt surface can significantly affect PA6-Nnt interaction especially during early stages of decomposition.

Figure 6.10 HRR curves for PA6/clay (A) and PA6/Oclay (B) composites.

Table 6.3 Cone calorimeter results of neat PA6 and its composites with clays.

Specimen	TTI (s)	pHRR (kW/m ²)	aHRR (kW/m ²)	THR (MJ/m ²)	Char (%)	TSR (m ² /m ²)	TSP (m ²)
PA6	140	840	298	97	0	108	0.96
PA6/MMT	94	826	349	148	12.4	427	3.77
PA6/Hec	90	661	181	145	19.2	624	5.51
PA6/Nnt	99	604	314	82	4.9	609	5.39
PA6/OMMT	116	369	257	147	11.9	1133	10.02
PA6/OHec	110	433	222	143	15.1	843	7.45
PA6/ONnt	84	382	287	125	6.8	1489	13.17

pHRR is principally governed by platelet size, quality of dispersion and distribution of clay platelets. With the difference in their chemical composition, differences in interfacial interactions between surface siloxane groups and PA6 is expected. In a similar work, Mrayed et al. studied the influence of atomic configuration of MMT on interactive forces between PA6 and MMT surface²¹. Based on Mg/Al ratio in MMT and location of substitution, it was reported that resultant atomic charge on basal oxygen plane from siloxane tetrahedra can significantly alter binding energies and bond length between PA6/clay surfaces as shown in Table 6.4. Higher polymer-clay interaction can lead to relatively different quality of dispersion amongst clay microcomposites. This is evident from the differences in their pHRR. Starting interlayer distance for Hec clay is 14.9 Å as seen from Figure 6.2A, which might have assisted in certain degree of intercalation resulting into lower pHRR for PA6/Hec.

On the other hand, Nnt has lowest d_{001} (11.2 Å) as compared to MMT (12.1 Å) and Hec (14.9 Å), so it is expected that PA6/Nnt to display prominent phase-separated behavior which will limit the reduction in its pHRR. Yet, PA6/Nnt showed a highest reduction in pHRR (more than PA6/Hec). It is associated with (comparatively) superior degree of dispersion and distribution of Nnt in PA6 on account of its interfacial interaction with PA6. However, dehydroxylation of Nnt is also a crucial factor changing the decomposition mechanism, thus, affecting pHRR. This aspect will be addressed in further detail in the following the discussion.

Table 6.4 Interfacial interaction between PA6 and MMT clay: binding energy and bond length (predicted using density functional theory)²¹ as influenced by Mg/Al ratio and location of substitution.

System	No. of atoms in Octahedral layer		No. of atoms in Tetrahedral layer		Binding Energy (kcal/mol)	Bond length (Å)
	Al	Mg	Al	Mg		
1	16	-	16	-	74	1.613
2	15	1	16	-	126	1.582
3	15	1	15	1	373	1.551
4	16	-	14	2	373	1.544

In nanocomposites, dispersion and distribution are also dependent on PA6-surfactant interaction and amount of surfactant. OMMT has highest surfactant content (~31 wt.%) as seen from Figure 6.5 whereas OHec and ONnt have ~20 and ~15 wt.% HDTMA⁺, respectively (due to temperature overlap additional mass loss due to dehydroxylation of Nnt is taken into account). Still, PA6/OMMT and PA6/ONnt shows similar pHRR. This again suggests that higher interaction between ONnt with PA6 lead to superior dispersion. OHec, with a highest d_{001} value of 18.4 Å, showed the lesser magnitude of reduction in pHRR. This contradicts to what is expected. A possible explanation for this behavior is that the interfacial interaction between OHec with PA6 might have resulted in volatiles that require little activation energies for complete combustion, and in turn increasing oxygen consumption.

THR and % char primarily depend on decomposition mechanism of the matrix. Residue images are shown in Figure 6.11. PA6/Hec displayed the highest char of ~19.2 %, which is ~7 % higher as compared to PA6/MMT even with similar THR. This provided preliminary evidence that Hec and MMT interact differently with PA6. That is, there is a possible difference in their decomposition reactions while maintaining similar total heat evolved. This is further supported by higher TSP and TSR (~31 %) for PA6/Hec than PA6/MMT. THR for PA6/Nnt composite is more complex as it is resultant of simultaneous matrix decomposition and Nnt dehydroxylation. As mentioned earlier, Nnt upon dehydroxylation generates 5 wt.% water i.e. 0.25 wt.% in PA6/Nnt. Despite the small content, the released water might assist in the hydrolysis of PA6, but in the process can

result in the generation of different volatile entities, which have different (in this case, lower) combustion enthalpies. The exact reason is however, yet to be established. Further, the absence of any carbonaceous matter in char highlights complete oxidation of organic matter. Hence, it is confirmed that fundamental reactivity of clay principally depends on its structural composition. This further supports the importance of polymer-clay interaction which not only affects physical barrier formation by retarding volatile migration, but also matrix decomposition mechanism in general.

In the case of nanocomposites, again, PA6/OHec and PA6/OMMT exhibited similar THR. Also, their THR values are similar to their respective micro-composites. Even PA6/OHec showed higher char (15.1 %) than PA6/OMMT (11.9 %). This suggests that, apart from better dispersion that lowered their pHRR values, PA6/OHec and PA6/OMMT do not deviate much from their respective microcomposites. This suggests that reactions having similar net heat of evolution have occurred. However, PA6/OHec and PA6/OMMT had completely different TSP and TSR values signifying a change in decomposition mechanism. PA6/ONnt, on the other hand, showed significantly higher THR as compared to PA6/Nnt. Although there was little carbonaceous matter in the residue, considerably higher values for TSP and TSR suggests that dispersion of ONnt has influenced the hydrolysis-assisted decomposition of PA6 matrix to generate different volatiles with much higher oxidation enthalpies. Hence, it is suggested that overall decomposition mechanism depends on the structural reactivity of clay as well as clay dispersion, in general.

6.3.2 Thermo-oxidative Decomposition Behavior

Mass loss temperatures for PA6/clay nanocomposites are summarized in Table 6.5, and corresponding TGA curves are shown in Figure 6.12.

All composites displayed lower onset temperatures than neat PA6. PA6/MMT and PA6/Hec displayed similar onset temperatures but more interestingly showed similar MLR profiles which when correlated to their difference in % char, TSP and TSR values from cone calorimeter test, suggests that they have similar volatilization kinetics i.e. similar decomposition kinetics but different mechanism. This variation is attributed to the difference in nature of the interaction between PA6 and Hec/MMT surfaces. The basicity

Figure 6.11 Residue images for PA6 (A) and PA6/clay composites (B-G) as obtained from cone calorimeter test. Brownish residue for Nnt composites signify oxidized octahedral Fe^{3+} in residual clay.

of the surface siloxane plane depends on octahedral layer composition. In trioctahedral smectites (like Hec), bridging oxygen is coordinated to four atoms i.e. one Si^{4+} in the tetrahedral layer and three Mg^{2+} in octahedral layers. Whereas, in dioctahedral clays (like MMT & Nnt), the bridging oxygen is coordinated to three atoms, one Si^{4+} in the tetrahedral layer and two Al^{3+} in octahedral layers. With one lone pair, electron density at the non-bonding orbital of the oxygen sustains. As a result, the basic strength of the O-plane of

dioctahedral clays is higher than that of trioctahedral clays²². This is in tandem with a report by Chou et al.²³ which focused on organic matter-clay interactions. The difference in interaction was observed for MMT and Hec while interacting with a same organic molecule. Based on a mismatch in lattice parameters for MMT ($a_0 = 5.17$ Å and $b_0 = 8.95$ Å) and Hec ($a_0 = 5.25$ Å and $b_0 = 9.18$ Å), it was suggested that Hec possesses higher O–O distance on account of the expansion of its unit cell. Hence, based on basic-strength and physical aspect of bond lengths, it is expected that Hec and MMT will display different interaction strengths and possess certain selectivity towards organic molecules¹³. On similar lines, it is proposed that PA6/MMT and PA6/Hec will have different interfacial interactions regarding molecular arrangements at the surface for PA6 segments and intermediate decomposition products, possibly with different configurations. This can lead to deviation in decomposition reactions but incidentally with similar mass loss pattern.

Figure 6.12 TG curves for PA6/clay composites.

Table 6.5 $T_{5\%}$, $T_{50\%}$ and T_P as obtained from TGA thermograms for PA6/clay composites.

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_P (°C)
PA6	437	501	504
PA6/Mmt	432	505	513
PA6/Hec	433	497	500
PA6/Nnt	383	454	462
PA6/OMmt	430	511	525
PA6/OHec	424	517	524
PA6/ONnt	379	450	457

PA6/Nnt continue to remain complex on account of parallel processes i.e. PA6 hydrolysis promoted by Nnt dehydroxylation in addition to its thermo-oxidative decomposition. Additionally, the interfacial interaction between PA6 and Nnt is significantly different because there is one unique difference between Nnt and MMT (or Hec). The isomorphous substitution site for Nnt is in its tetrahedral layers instead of the octahedral layer as in the case of MMT (or Hec). This lead to a difference in their basic character for surface siloxane planes. Surface siloxane group typically have very weak basic character. Si-O form strong σ bond along with π bond between vacant d orbital of Si and lone pairs of electrons from O. This reduces basicity of Si-O-Si lowering the tendency for surface siloxane group to donate an electron pair to acidic groups as in the case of MMT (or Hec). However, substitution of Al^{3+} for Si^{4+} in Si-tetrahedral layer (as in the case of Nnt) and lack of ability for Al^{3+} to form π bond disrupts the electronic cloud in Si-O-Al imparting it with directionality towards O. As a result, localized basicity is induced. The strength of this basicity depends on the extent of isomorphous substitution of Al for Si in the tetrahedral layer.²⁴ Hence, in addition to hydrolysis, interfacial interactions play a crucial role in PA6/Nnt decomposition i.e. affecting nature of volatile evolved. This also explains higher TTI in the case of PA6/Nnt counter-intuitively with lower decomposition onset (~ 50 °C than PA6/MMT or PA6/Hec).

The difference in MLR profile between PA6/Hec and PA6/OHec as seen from Fig 6.12C, D suggests different kinetics and/or mechanism of decomposition. Mg^{2+} being a structural component, the organic modification cannot alter the composition of Hec. This confirms previous proposal that dispersion of clay as influenced by organic treatment of clay

significantly alters the matrix decomposition. Specific surface area presented by Hec tactoids in PA6/Hec is much lesser than (largely) delaminated Hec platelets in PA6/OHec. Superior dispersion (intercalation/exfoliation) in PA6/OHec will promote enhanced interaction of organic matter with surface siloxane plane and unbalanced Mg^{2+} , $-\text{O}^{(-)}$ and $-\text{OH}$ at edge and defect sites without spatial restrictions. So, more pronounced peroxy-based decomposition of PA6 is expected to lower $T_{5\%}$ (424 °C) for PA6/OHec compared to 433 °C for PA6/Hec. Better dispersion also leads to higher number of possibly peroxy sites throughout the condensed phase which, in turn, facilitates possible recombination reactions altering the decomposition mechanism of PA6 resulting in two prominent mass loss maxima. The stark difference between MLR profile for PA6/OMMT and PA6/OHec supports the observation made for their TSP and TSR values which suggested a difference in their decomposition mechanism.

PA6/ONnt continued to display similar MLR profiles as PA6/Nnt despite their significantly different combustion properties like THR, TSP, and TSR, which are all dependent on condensed phase reactions. This change in decomposition mechanism between PA6/Nnt and PA6/ONnt was not seen from their TG MLR profile which suggests that they have similar volatilization kinetics. In the case of PA6/ONnt, as mentioned earlier, the superior dispersion influences hydrolysis-assisted decomposition. The presence of surfactant also affects PA6-Nnt interfacial interaction especially with similar temperature regime for Nnt dehydroxylation, decomposition of intercalated surfactant and PA6 decomposition onset. As a consequence, deviating the decomposition mechanism from that of PA6/Nnt. It is proposed that different entities of intermediate products and volatiles are generated with lower molecular weight or lower activation energy for oxidation with higher oxidation enthalpies. This leads to lower TTI, higher THR and smoke parameters as observed for PA6/ONnt (as compared to PA6/Nnt). Upon continued heating, eventual dehydroxylation will result in unbalanced Fe^{2+} or Fe^{3+} at edges and defect. They could readily interact with surrounding carbonaceous matter accelerating their oxidation to 500-540 °C (similar to oxidation of carbonaceous matter in ONnt before 500 °C, Figure 6.6 B) which otherwise oxidize between 550-650 °C in the case of neat PA6.

Alternatively, a synergistic effect between the peroxy-based mechanism for PA6 and radical trapping phenomena demonstrated by Nnt may result into dramatic increase in the

pool of hydroperoxy- groups and protons following scheme 4.5 in Chapter 4 (repeated here for easy reference). Aggressive oxidation of organic molecules demonstrated by Fe^{2+} and Fe^{3+} through Fenton-like reactions are well documents²⁵ and is hereby used to suggest their possible reactivity towards PA6 decomposition. This can not only accelerate decomposition of PA6 but also potentially overshadow any effect of dispersion leading to similar MLR profiles and T_P for PA6/Nnt and PA6/ONnt.

Scheme 4.5 Effect of metal ions on the decomposition of hydroperoxides yielding highly reactive alkoxy- or peroxy- radicals.

Results for PA6/ONnt, however, contradicts with the result for PMMA/Nnt¹⁹. PMMA/Nnt showed an increase in decomposition onset by $\sim 100^\circ\text{C}$ under oxidative conditions as illustrated in Figure 6.13. This increase is with respected to neat PMMA which inherently has lower decomposition temperatures ($\sim 150^\circ\text{C}$) as compared $\sim 430^\circ\text{C}$ for PA6 used in current study. Here, Nnt affects onset of PA6 while in their case it is interacting with rapidly decomposing PMMA. This highlight the importance of understanding of thermo-oxidative stability for base matrices while making cross-comparison between two different systems. Effect of backbone structure can be further highlighted by comparing maximum hydroperoxide concentration for PP and PA6 at 120°C as reviewed by Richaud et al.²⁶ (Table 6.6).

Table 6.6 Hydroperoxide concentration in polymers prone to peroxy-based decomposition²⁶.

Polymer	T ($^\circ\text{C}$)	[POOH] _{Max} (mmol/l)
PP ²⁷	120	800
PA6 ²⁸	120	7

Figure 6.13 TG curves for PMMA/Nnt clay nanocomposites¹⁹.

6.3.3 Condensed Phase Analysis

6.3.3.1 Isothermal Study at 400 °C

The isothermal study was carried out to evaluate chemical changes happening in PA6/clay composites at 400 °C. ATR FT-IR was performed on the surface char of heated composites. Two most prominent observation made are a peak at 2230-2210 cm^{-1} (Figure 6.14) and the shifts in carbonyl peaks as shown in Figure 6.15. Interestingly, PA6/Nnt continue to display a relatively strong peak at 2230-2210 cm^{-1} ($\text{C}\equiv\text{N}$ in nitrile) similar to PA6/FeMMT. This suggests that ferric ion irrespective of its location preferentially promotes the generation of intermediate decomposition compounds with nitrile groups. High molecular weight compounds with nitrile groups will remain in condensed phase while smaller nitrogenous molecule would evolve to the gas phase.

Figure 6.14 ATR FT-IR for PA6/clay composites (A) and PA6/Oclay composites (B) at 400 °C.

Figure 6.15 Deconvolution of FT-IR spectra between 1900-1500 cm⁻¹ for isothermally heated samples at 400 °C; PA6 (A), PA6/clay composites (B-G).

The cumulative shift in carbonyl peaks between PA6 and its clay composites highlight the change in mixture composition of different carbonyl moieties in the surface char layer. Reported assignments for various carbonyl moieties generated during PA6 thermo-oxidation are $\sim 1750\text{ cm}^{-1}$ for aliphatic carboxylic acids, $\sim 1735\text{ cm}^{-1}$ for esters, $\sim 1725\text{ cm}^{-1}$ for aldehydes and $\sim 1715\text{ cm}^{-1}$ for ketones²⁸. Moreover, similarities are drawn between PA6/clay composites and their corresponding PA6/exchanged clay counterparts to check the effect of location of the metal ion. The overall direction of peak shift to lower wavenumbers (as compared to neat PA6) for PA6/Hec and PA6/Nnt is same as that of PA6/MgMMT and PA6/FeMMT. This indicates that clays rich in Mg^{2+} and Fe^{3+} (irrespective of their position) yield carbonyl moieties with similar structures in condensed phase.

6.3.3.2 Isothermal Study at 500 °C and 750 °C

Further investigation was carried out particularly for PA6/Nnt and PA6/ONnt composite residues to explore their condensed phase reactions that register unexpected THR from cone calorimetry. The possible effect of dehydroxylation was analyzed using XRD (Figure 6.16) and FT-IR (Figure 6.17). For better understanding XRD of residues at 500 °C and 750 °C are overlapped for Nnt, ONnt, and their PA6 composites.

Amongst PA6 composites, it was observed that at 500 °C PA6/Nnt shows a minor diffraction peak at 7° corresponding to partial collapse while a stronger diffraction peak at 9° suggests the complete collapse of clay platelets. On the other hand, PA6/ONnt showed an only peak corresponding to a partial collapse. This is expected because, in the case of PA6/Nnt due to poor intercalation, Nnt would remain in clusters which can readily collapse. However, minor peak at 7° suggests intercalation to a certain extent which can partially explain the reduction in pHRR for PA6/Nnt. On the other hand, because of superior dispersion in PA6/ONnt, exfoliated clay platelets continue to remain separated while the matrix is decomposing, which is also a reason for the significant reduction in pHRR.

From Figure 6.16B, it is interesting to see that PA6/Nnt and PA6/ONnt residues at 750 °C displays diffraction peaks similar to those from ONnt residue and not from Nnt residue. This confirms the fact that presence of organic matter indeed changes internal reactions in

Nnt clay. The presence of β -cristobalite peaks at 750 °C signify accelerated destruction of platelet structure and in turn suggests that phase diagram (as shown in Figure 6.8) for Nnt does not continue to hold valid in the presence of organic matter.

Figure 6.16 XRD of residues at 500 °C (A) and 750 °C (B) when heated under oxidative atmosphere

Figure 6.17 FT-IR spectra of residues at 500 °C (A) and 750 °C (B) when heated under oxidative atmosphere

FT-IR spectra for PA6/Nnt and PA6/ONnt residues at 500 °C display peaks corresponding to structural $-\text{OH}$ group ($3600\text{--}3200\text{ cm}^{-1}$ and $\sim 1640\text{ cm}^{-1}$) confirming the previous discussion made for ONnt. However, those peaks are absent in their residues at 750 °C. So, comparing $-\text{OH}$ group peaks between residues of PA6/Nnt, PA6/ONnt and ONnt it is suggested that nature of structural modifications taking place inside Nnt platelet depend on the polarity of surrounding decomposing organic matter. Decomposing PA6 will create

larger radical pool than HDTMA⁺. Consequently, Fe³⁺-Fe²⁺ transformation reaction are expected to be more pronounced in the presence of decomposing PA6. Additionally, the strength of shoulder observed between 1205-1230 cm⁻¹ further confirm the occurrence of structural differences between ONnt and PA6 composites.

Unfortunately, residue analysis did not yield any insights explaining the difference seen in combustion properties of PA6/Nnt and PA6/ONnt. However, considering the scope of the current Chapter, it does provide sufficient evidence for structural changes occurring in Nnt especially in the presence of organic matter suggesting polymer decomposition and structural changes in clay are interlinked.

6.3.4 Gas Phase Analysis – Condensate Study at 500 °C

The major difference observed in collected condensate between PA6 and its composites are highlighted with arrows in Figure 6.18. The peaks between 3650-3200 cm⁻¹ are typically ascribed to -NH in secondary amides, -OH in oximes and -NH₂ in primary amines, amides, and aromatic amines. So the variation can be associated with a difference in concentrations of compounds containing these groups. PA6/Nnt displayed prominent peaks at 2260, 2140 and 1960 cm⁻¹ which respectively correspond to C≡N in nitriles/N=C=O in isocyanates/C≡C in disubstituted alkynes, C≡N in isonitriles/C≡C in mono-substituted alkynes and substituted benzene rings. This is in line with the observation made in previous section 6.3.3.1 suggesting the evolution of low molecular weight nitrogenous compounds eventually captured in condensate FT-IR.

Intensity differences for peaks at 1548-1555 and 1482 cm⁻¹ amongst the all clay composites and neat PA6 clearly highlight the compositional variations in the condensate. Shifts in peak between 1548-1555 cm⁻¹ may be associated to -NO₂ in aliphatic compounds, -NO₂ in aromatic compounds, -NH in secondary amines and triazine ring stretch. The peak at 1482 cm⁻¹ can either be -NH in secondary amides or benzene in aromatic compounds. Further, very prominent peak at 978 cm⁻¹ for PA6/Nnt can be associated with HC=CH- in trans disubstituted alkenes.

Further detailed characterizations using GC-MS or TGA-MS is necessary to identify specific compounds present in the condensates. However, the current focus is to establish

the difference in chemical composition of volatiles evolved during decomposition of different PA6/clay systems which eventually highlights the influence of the structural composition of clay on PA6 decomposition.

Figure 6.18 Overlay of FT-IR spectra for condensate collected from isothermally heating PA6 and PA6/clay composites at 500 °C.

6.3.5 Thermo-oxidative Decomposition Mechanism

Decomposition mechanisms of PA6 in the presence of clay are proposed in Scheme 6.1. These take into account the interaction site between organic matter and clay, i.e., whether at edge/defect site or clay surface. At edges/defect sites, unbalanced metal ions are exposed and are in direct contact with neighboring decomposing organic matter. While at clay surface, the siloxane plane (with random defect sites having surface hydroxyl group) completely shields/prevent any organo-metallic contact. Scheme 6.2 depicts possible conformational changes in dienes near clay surface.

As a special case with low dehydroxylation temperature for Nnt, preferential hydrolysis of PA6 as shown in Scheme 6.3 can be expected. This will rapidly reduce the molecular weight during initial stages of decomposition through the non-radical pathway. These PA6 fragments can undergo typical peroxy-based mechanism. However, the Fe^{3+} - Fe^{2+} transformation of Nnt can potentially change the kinetics/mechanism of decomposition.

The influence of Fe^{3+} - Fe^{2+} transformation selectivity towards certain oxidation reactions especially during early stages of PA6 decomposition are proposed in Scheme 6.4. Accessibility of Fe^{3+} by organic matter is important and governs the extent of influence. In the case of PA6/Nnt, Fe^{3+} present at edges and defect sites of microscopic tactoids may present limited reactive sites whereas increased sites on account of delamination and superior dispersion in PA6/ONnt may alter the chemical composition of condensed phase (and in turn change the combustion properties like TTI, THR, TSP, as observed). The relatively larger concentration of H^+ may accelerate decomposition reactions.

Scheme 6.1 Possible decomposition reactions in condensed phase during early stages of PA6/clay nanocomposites. It is postulated that presence of metal ions at edges or defect sites will promote decomposition of alkoxy- radical yielding alkyl radical whereas over the surface of clays where organic matter is in direct contact with surface siloxane plane, the majority of decomposition products may have amide- or nitrile- terminal groups. For reactions proposed near edges, the source of hydrogen is mainly organic whereas surface hydroxyl groups from broken sites in siloxane plane can additionally act as hydrogen donor sites.

Scheme 6.2 Clay surface or edges can act as proton donor sites to adsorbed diene. This could potentially change the conformation of the end product. The addition of proton to diene forming carbo-cation site followed by hydrogen-migration converting secondary carbocation to relatively stable tertiary carbocation site. With continued combustion/heating, loss of proton can result into diene with different conformation. This reaction is supposed to take place at relatively later stages of combustion (post peak mass loss) during which condensed phase contains relatively lower molecular weight chain fragments or molecules as hydrogen-migration is possible only at short-range.

Scheme 6.3 Hydrolysis of PA6 chain as a result of water evolved during dehydroxylation of Nnt.

Scheme 6.4 Proposed reactions which can potentially be influenced of Fe^{3+} - Fe^{2+} transformation selectivity of Nnt especially during early stages of PA6 decomposition. Fe^{2+} will eventually oxidize to Fe^{3+} at temperatures above $400\text{ }^\circ\text{C}^{14}$. [Note that these reactions can also be applied to other clays like MMT with Al^{3+} as octahedral cations but may not apply to Hec on account of its high water content (Brønsted acidity) which may overshadow direct participation of Mg^{2+}].

Finally, it should be noted that with current limitations in testing and characterization technique at high temperatures, it is difficult to evaluate condensed phase products especially during early stages of decomposition. The presence of high molecular weight polymer restricts the use of off-line techniques like NMR or MS. Further, the majority of intermediate decomposition products will have similar atomic composition making it virtually impossible to differentiate between isomers. FT-IR provides certain insights in

different bonds present in condensed phase and, hence, was utilized in the current study. The objective of this work is achieved, which was set to show the differences in PA6 decomposition in the presence of clays each individually rich in one particular metal ion in octahedral position.

6.4 Summary

This Chapter provides an insight into the decomposition of polyamide 6 matrix in the presence of different natural clays rich in specific cations. In short,

- Natural clays with higher basic nature of surface siloxane groups or having transition metal ions as structural component present superior compatibility with polar PA6 matrix.
- The structural composition of clay influences the organic matter-clay interactions. Nature, reactivity and oxidation state of octahedral metal ion governs the interface interactions, which eventually affect the decomposition of organic matter like surfactant and PA6 matrix.
- Polarity of organic matter can significantly influence phase transition reactions in Fe^{3+} rich Nnt clay affecting their dehydroxylation temperatures.
- Mg^{2+} rich Hec registered the highest char suggesting improved thermo-oxidation stability.
- Fe^{3+} rich Nnt reduced the oxidation stability of carbonaceous matter/char and influenced smoke generation. It also showed the generation of nitrogen-rich compounds.

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Chapter 7

Controlling the Interfacial Interactions Between Clay and Host Polyamide 6 Matrix

Previous chapters have provided thorough knowledge of catalytic effect of clay on the thermo-oxidative decomposition of PA6, particularly ignition. This chapter focuses on controlling the interfacial interactions between clay and PA6 to restrict or entirely prevent direct matrix-clay interface. Accordingly, organically modified clay was coated with high-temperature-resistant polymers, viz. PEI and PI before melt compounding with PA6. Huge reductions in HRR are seen even with coated clays as in previous chapters. More importantly, early ignition of composites was avoided confirming the impact of matrix-clay interface. This simple solution provides a potential solution for the major issue of early ignition in polymer/clay nanocomposites.

7.1 Introduction

As shown in previous chapters, interface interactions between clay surface and matrix play a crucial role, especially during pre-ignition stages¹. One approach to confirm this phenomenon is to prevent direct physical contact between the surface of clay platelets and surrounding polymer matrix. There are reports on coating of clay surfaces (which are inherently highly hydrophilic) with various water-soluble polymers like PVA², polypyrrole³, polyethyleneglycol⁴. However, these polymers have poor thermal stability compared to PA6. To prove the current hypothesis, it is essential to use high-temperature-resistant polymers that maintain the protective coating on clay during compounding and also while PA6 matrix thermally decomposes. Accordingly, polymers like PI and PEI with high glass transition temperatures ($T_g > 220$ °C) and melting points ($T_m > 300$ °C) are chosen. Their structures are shown in Figure 7.1. These are polar polymers, and so shows affinity towards PA6. Therefore, dispersion and distribution of coated clay could be achieved.

Figure 7.1 Repeat units for PEI and PI used in the following study.

PEI (used in the current study) can be solubilized in organic solvents, unlike PI, which is known for its insolubility. So instead of using PI directly, its precursor, PAA was dissolved in organic solvent and is used for coating clay platelets. This is followed by imidization resulting in PI coating on clay. The rationale behind using two different polymers is to compare the effectiveness of two coating methodologies, i.e., solution blending-precipitation (for PEI) and solution blending-imidization-precipitation (for PI).

The author would like to highlight that this study is dedicated to confirming the influence of clay-matrix interface on combustion and overall feasibility of clay coating process.

Consequently, full system optimization and fine-tuning of the coating methodologies is deliberately not considered. Working with readily available PAA solution and organic solvent soluble PEI gave an opportunity to establish the proof-of-concept. As a future work, optimization with regards to use of PAAs with different repeat units and use of MI-clays to improve PAA/clay interaction could be made. This can facilitate superior exfoliation of clays in the non-aqueous solvent during coating process eliminating the current need of organically modified clays (as starting material).

For detailed experimental procedures concerning clay modification, testing and characterization, please refer to Chapter 3.

7.2 Results and Discussion

7.2.1 Clay Coating Analysis

SEM micrographs highlight the differences in surface morphology of PEI and PI-coated organoclay (Figure 7.2). It is expected that precipitation of PEI from solution on organoclay will lead to non-uniform coverage, whereas imidization of PAA over organoclay will have more uniform coverage as seen from Figure 7.2C. Tyan et al.⁵ has previously reported that addition of p-phenylenediamine modified MMT enhanced imidization kinetics of PAA (same as the one used in the current study) by dramatically reducing imidization temperature from 300 °C to 250 °C without affecting the structure of PI, thus, formed. This was attributed to the heterogeneous surface provided by clay platelets promoting dehydration and imide ring closure reactions.

Powder FT-IR provided confirmation of the presence of PEI and PI in coated clays (Figure 7.3). Coated clays display prominent markers from both coating polymers and clay. Detailed peak assignments are listed in Table 7.1. XRD data shown in Figure A4 in Appendix A indicates the absence of complete exfoliation of clay in either case, which is expected considering high ratio of clay to coating polymers (1:1). Low temperatures employed during PEI coating process prevented loss of surface adsorbed surfactant in C30B. However, imidization temperatures of 230 °C used for PI-C30B displayed decomposition of surface adsorbed surfactant molecules lowering the inter-platelet distances as seen from decreased d_{001} .

Figure 7.2 Representative SEM images of clays: (A) C30B, (B) PEI-C30B, (C) PI-C30B.

Figure 7.3 FT-IR spectra comparing C30B, coating polymer and coated clay: PEI-system (A) and PI-system (B).

Table 7.1 FT-IR bands assignments for C30B, coating polymers (PI, PEI)⁶⁻⁷.

Absorption range, cm ⁻¹	Assignments	Material
2950-2830	–CH ₃ , –CH ₂ – aliphatic carbon, stretch	C30B
1800	Imide I C=O, anti-sym. stretch	PI, PEI
1740-1720	Imide II C=O, sym. stretch	PI, PEI
1610-1600	C=C in aromatic, stretch	PI, PEI
1500-1490	aromatic ring stretch	PI, PEI
1390-1380	Imide III C–N, stretch	PI, PEI
1250	Tertiary C aliphatic	PEI
1230-1210	C–O–C aromatic ether	PI, PEI
1150-1050	Si–O–Si in MMT, stretch	C30B
~730	Imide IV C-N ring deformation	PI, PEI

7.2.2 Decomposition Behavior of Coated Clays

Thermal stability of C30B and coated clays were analyzed using TGA under oxidative conditions (Figure 7.4). It was observed that both PEI-C30B and PI-C30B displayed a gradual mass loss starting from 100 °C until 450 °C. This behavior can be attributed to the removal (desorption) of solvent molecules that are trapped during the synthesis procedure and/or fragmentation of some (excess) surface adsorbed surfactant molecules from C30B. However, absence of any FT-IR bands corresponding to solvents refutes the possibility of residual solvent in the system after the coating process. Fine-tuning of the coating process can potentially solve this issue. Nearly overlapping mass loss for neat polymers and corresponding coated clays confirm the presence of polymers.

Figure 7.4 TG curves for C30B, coated clays and corresponding coating polymers under oxidative condition.

7.2.3 Combustion Properties

Combustion study was carried out to evaluate the effectiveness of physical barrier enclosing clay surface on ignition characteristics of PA6/clay nanocomposites. As expected, PA6/C30B showed early ignition by 59 s compared to neat PA6 (Table 7.2 and Figure 7.5). Coated clay systems displayed significant improvement in ignition resistance and the ignition times are similar to neat PA6. This provides confirmation that clay-matrix interaction plays a major role in ignition characteristics of PCNs. Apart from the physical

barrier, chemical properties of PEI and PI cannot be overlooked. It is hypothesized that especially during pre-ignition stages chemical inertness of PEI and PI prevent them from interacting with decomposing PA6. This allows the matrix to follow decomposition mechanism similar to neat PA6, which leads to similar ignition times.

Figure 7.5 HRR curves for PA6 and its nanocomposites as obtained from cone calorimeter when exposed to a flux of 35 kW/m².

Table 7.2 Cone calorimeter results of neat PA6 and its composites with coated clays.

Specimen	TTI (s)	pHRR (kW/m ²)	Avg. HRR (kW/m ²)	THR (MJ/m ²)	Char (%)	TSR (m ² /m ²)	TSP (m ²)
PA6	140	840	298	97	0	108	0.96
PA6/C30B	81	338	250	142	13.1	1148	10.15
PA6/PEI-C30B	133	554	399	122	7.6	1696	15.00
PA6/PI-C30B	139	396	272	128	9.4	1542	13.63

Apart from maintaining the ignition time, coated clay based nanocomposites have also exhibited a huge reduction in pHRR (Figure 7.5 and Table 7.2). PA6/PEI-C30B registered 34 % reduction in pHRR value compared to neat PA6, whereas PA6/PI-C30B registered 52 % reduction, much similar to 60 % reduction for PA6/C30B nanocomposite. These

different values can be attributed to differences in their microstructures (coating uniformness, dispersion and distribution of coated clay particles/platelets in PA6 matrix (Figures 7.2 and 7.6). As evident, PA6/PEI-C30B composite showed some big clusters of clay in addition to some finely dispersed clay. This suggests that solution precipitation technique resulted in non-uniform coating i.e. forming clusters of coated clay rather than coated clay platelets, eventually resulting in inferior dispersion of coated clay particles.

On the other hand, the solution-imidization-precipitation technique employed for PI seem to generate uniform coating over the clay surfaces (ranging from single platelet to stack of 5 platelets, as seen from TEM images) which in turn facilitate superior dispersion. The affinity of PEI and PI will also affect the dispersion characteristics. However, the conclusion can be drawn only when PEI coating is also made via a solution-imidization-precipitation technique using appropriate polyamic acid. On a similar note, one of the previous studies⁸ reported PEI/clay nanocomposites produced from *in situ* imidization of PAA (for PEI) and organically modified MMT (with an aliphatic chain of twelve carbon). Even with 10 wt.% clay loading (as against 100 wt.% clay loading in the current system) not many single layers were seen. It was concluded that *in situ* imidization produced an intercalated-exfoliated system in PEI matrix.

Lower THR and char values for coated clay systems as compared to PA6/C30B composite also confirm that clay indeed acts as a catalyst which alters the decomposition mechanism of neighboring matrix. Although valid during pre-ignition stages, PA6 may not continue to follow decomposition mechanism of neat PA6 during later stages of combustion (post-ignition). This is quite evident from higher THR values for coated system as compared to neat PA6.

Figure 7.6 Representative TEM images of clays: PA6/C30B (A), PA6/PEI-C30B (B) and PA6/PI-C30B (C). 10 wt.% loading of coated clay.

7.2.4 Thermo-oxidative Decomposition Behavior

Thermo-oxidative decomposition results are concurrent with ignition time results from cone calorimeter. Higher onset decomposition temperatures ($T_{5\%}$) for PA6/PEI-C30B and PA6/PI-C30B composites are observed as compared to PA6/C30B system as shown in Figure 7.7 and Table 7.3. However, no significant difference was observed in their $T_{50\%}$

value suggesting the similar rate of mass loss post-decomposition onset. This highlights that coated clays are influential only during initial stages of decomposition.

Figure 7.7 TG curves of PA6 and its composites with C30B and coated clays. Inset shows MLR corresponding to oxidation of char from PA6 and decomposition of coating polymer.

Table 7.3 $T_{5\%}$, $T_{50\%}$ and T_P as obtained from TGA thermograms for PA6 and its composites with coated clays.

Specimen	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_P (°C)
PA6	353	455	462
PA6/C30B	360 (+ 7)	445	451
PA6/PEI-C30B	380 (+ 27)	452	458
PA6/PI-C30B	384 (+ 31)	454	453

7.3 Summary

This piece of work successfully validates the sub-hypothesis 2 proposed in section 1.3 of Chapter 1 according to which interface interaction between clay platelet and the polymer matrix is responsible for early ignition in PCNs. Further, the coating on clay surface has been achieved with simplistic approaches like solution mixing. To the best of author's

knowledge, this is the first-ever report that has provided experimental evidence of direct influence of clay surface on polymer decomposition. Preventing direct contact using a physical barrier like high-temperature resistant polymer coating is a simple solution to a major issue of early ignition.

With 52 % reduction in pHRR without early ignition, use of coated clays has shown a way forward for PCN systems for FR applications. However, an increase in cost due to coating with specialty polymer and smoke characteristics need to be explored further for real-time use.

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Chapter 8

Clay Catalysis and Fire Retardancy of Polymer/Clay

Nanocomposites: *A Complete Overview*

This chapter summarizes the idea behind this thesis based on the set hypothesis and obtained results (discussed thus far). Supplementary test data are provided to prove specific points to further strengthen the overall argument made. Lastly, continuing questions are briefly discussed with strategies for future work.

8.1 General Discussion

8.1.1 Importance of Thermo-oxidative Study

Ignition is a fire triggering step. Ignition occurs when volatiles reach critical concentration necessary to sustain combustion in the presence or absence of external ignition source. Upon ignition, the fraction of the heat of combustion fed back to the condensed phase must be greater than its heat of gasification so as to maintain a pool of combustible volatiles for sustained flame. For any given material, this condition can be related to the mass loss rate at ignition.

Thermal decomposition of polymers can proceed by external heat alone, or with the combined action of external heat and oxygen. Most of the polymers show accelerated thermal decomposition in the presence of oxygen, lowering the minimum decomposition temperatures. During pre-ignition stages, thermo-oxidative decomposition is most prominent, particularly at the surface. While under steady flame (post-ignition), irrespective of ventilation conditions, condensed-phase decomposition continues under oxygen-deprived or rather anaerobic conditions, with oxidation taking place mainly in the gas phase¹. Hence, it is perceived that continuous mass loss during combustion (post-ignition) happens via pyrolysis². So to evaluate ignition characteristics, it is necessary to assess the decomposition behavior of polymer under oxidative rather than pyrolytic conditions³. Support for this argument can be drawn from results presented for a kinetic modeling study done by Dabrowski et al.⁴. They highlighted that role played by oxygen is very crucial in the stabilization of protective surface (char) barrier in case of charring polymers like PA6 and PA6/clay nanocomposite during initial stages of thermal decomposition.

According to experimental evidence provided by Fina et al.⁵, decomposition of neat polymer and PCN follows a different route, especially during pre-ignition stages. Neat polymers (PET and PA6) displayed involvement of bulk (matrix) in the generation of volatiles which ascertains the dominance of pyrolytic decomposition of the bulk material. However, when incorporated with clay, it was seen that ignition for PCNs took place as soon as the surface temperature reached polymer decomposition temperature whereas neat polymers when attained polymer decomposition temperature showed a delay before

ignition. This was attributed to clay-assisted catalysis that triggers oxidation of volatiles as soon as they are generated at the surface. This certainly highlights the importance of surface chemistry for PCNs to elucidate their ignition characteristics. To further confirm charring behavior under thermo-oxidative conditions, a simple isothermal test using TGA was carried out for neat PA6 and PA6/clay composite. The isothermal test was conducted at 350 °C corresponding to surface temperatures reported by Fina et al. (381 ± 6 °C for PA6 and 340 ± 22 °C for PA6/clay nanocomposite) at ignition. Corresponding mass loss profiles are shown in Figure 8.1. Key highlights from this study are,

1. Confirmation of charring phenomena for PA6 & PA6/clay composite only under a thermo-oxidative condition.
2. Under the oxidative condition, PA6 show subtle differences in mass loss rates as test proceeds after 20 min while PA6/clay display continuous profile. Under the pyrolytic condition, their difference in initial decomposition profile is much more evident. This shows that incorporation of clay changes the decomposition profile during early stages irrespective of surrounding environment.
3. Influence of clay on retardation of decomposition rate is very evident under pyrolytic condition.

Figure 8.1 Mass loss profiles for PA6 and PA6/clay composite under oxidative and pyrolytic conditions using isothermal TGA study at 350 °C.

It is noted that post-ignition, combustion will predominantly follow anaerobic decomposition which affects THR, % char, TSP, and TSR from cone calorimeter. The changes observed in these values with the incorporation of different clays brings out the essence of this work which deals with the influence of clay composition on PA6 combustion in totality.

8.1.2 Metal-ion Influenced Clay Catalysis

Combustion is a complex process that involves simultaneous heat and mass transfer. Altering either of them can significantly change the combustion behavior of the material. The presence of nano-dispersed clay platelets creates a physical barrier retarding the volatile evolution from condensed phase, and at the same time, the barrier restricts the heat feedback loop. This affects two of the three arms of fire triangle (heat-fuel-oxygen). Altering the decomposition of polymer matrix at molecular level and utilizing the inherent catalytic nature of clays can provide additional resistance to combustion which forms the basis of this work.

Metal ions present in clay structure (Mg^{2+} , Al^{3+} , and Fe^{3+}) are very crucial. Their inherent chemical nature and combinations thereof impart uniqueness to each clay regarding Brønsted and Lewis acidity as governed by their dehydration and dehydroxylation characteristics. Hence, evaluation of the effect of these metal ions on the decomposition of PCN can reveal valuable information regarding clay catalysis and its effect on combustion properties (as summarized in Figure 8.2).

The similarity in general trend in combustion properties for PA6/MI-clays and corresponding PA6/clay composites clearly suggests that effect of a particular metal ion at exchange position in clay can be extrapolated to its effect when situated at structural location (with an assumption that all clays belong to the same family, have similar dimensions). MgMMT has more surface Mg^{2+} ions which can freely interact with surrounding organic matter as compared to restricted interaction between partially bound Mg^{2+} present at edges and defect sites in Hec. So there is the difference in their intensities for catalytic reactivity. PA6/Hec showed higher THR, lower char and higher smoke release rate as compared to PA6/MgMMT. This clearly indicates that higher concentration of free

Mg²⁺ ions (like in the case of MgMMT) can be more efficient in restricting exothermic reactions taking place during combustion of PA6 yielding more char and minor smoke. Similar pattern is seen between PA6/AlMMT - PA6/MMT and PA6/FeMMT – PA6/Nnt. However, PA6/Nnt showed lowest THR as opposed to the highest value shown by PA6/FeMMT amongst their respective groups. This signifies the importance of overall clay structure and resulting properties. Low dehydroxylation temperature for Nnt additionally affects PA6 decomposition, changing the condensed phase reactions, which in turn display altered total reaction enthalpies.

Figure 8.2 Cross-comparison to observe trends among different metal ions and to evaluate the effect of their position in clay on PA6/clay composite combustion.

The effect of concentration of metal ion is also validated by investigating the combustion properties of PA6 with organically modified clays (OMI-clays and Oclays) and comparing to their respective unmodified versions. With organic modification, only OMI-clays show a reduction in concentration in (exchangeable) metal ions while their concentration remains unaffected in Oclay (being at structural locations). As expected, the noticeable effect demonstrated by PA6/MI-clays virtually vanish for PA6/OMI-clays while PA6/Oclays continue to show the same trend. With the same number of Mg²⁺ sites in Hec and OHec,

as expected, similar THR values were observed. Marginal drop from ~19 % to ~15 % observed for PA6/OHec as against drop from ~34 % to ~10 % between PA6/MgMMT and PA6/OMgMMT confirms the importance of concentration of metal ion sites. This points to the conclusion that superior properties can be achieved if the concentration of reactive Mg^{2+} is maintained high even after organic modification. The presence of Fe^{3+} always resulted in highest smoke and lowest char irrespective of the location of Fe^{3+} or organic modification of Fe-rich clays. This clearly suggests that Fe^{3+} is associating smoke and charring characteristics of PA6/clay nanocomposites with the inherent catalytic reactivity of Fe^{3+} ion from clay.

Figure 8.3 Cross-comparison to observe trends among different metal ions and to evaluate the effect of their concentration and position in organically modified clay on PA6/clay nanocomposite combustion.

Although effects of metal ion have been established on different stages of combustion and decomposition, it is interesting to see the cumulative effect of all metal ions, thus, validating the acquired results. This forms a motive for the first supporting experiment as discussed below.

8.1.3 Supporting Experiments

8.1.3.1 Ripidolite Experiment

Ripidolite (Rip) is a naturally occurring clay which is equally rich in all metal ions studied in this work (Table 8.1). So it is expected that PA6/Rip composite should display trend for all metal ions. Striking points from cone calorimeter data for PA6/Rip composites as shown in Table 8.2 are as follows,

- PA6/Rip produced the high char consistent with previous observations for PA6 composites with Mg-rich clays.
- It yielded the lowest smoke as compared to other PA6/clay composites (PA6/Hec, PA6/MMT, and PA6/Nnt). Low smoke is analogous to Al-rich clays (refer Figure 8.2).
- It has highest TTI, also consistent with Fe-rich clay composites (refer Figure 8.2).
- It has low THR which might be combined effect of all metal ions.

Table 8.1 Ripidolite clay compositions⁶.

Clay	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	CEC
Rip ^{a,b}	25.8	18.3	4.1	21.3	20.3	-	2

^a Rip used in this study was CCa-2 (Flagstaff Hill, El Dorado County, CA, USA) and was obtained from The Clay Minerals Society, Source Clay Minerals Repository, USA.

^b Unlike MMT, Hec, and Nnt, which belong to expandable smectite family, Rip belong to non-expanding chlorite family.

Table 8.2 Cone calorimeter results of PA6 composites with ripidolite.

Specimen	TTI (sec)	pHRR (kW/m ²)	THR (MJ/m ²)	Char (%)	TSR (m ² /m ²)	TSP (m ²)
PA6	140	840	97	0	108	0.96
PA6/Rip	108	739	111	28.3	336	2.97
PA6/ORip	108	728	127	34.8	304	2.69

Rip being non-expanding and with very low CEC, its organic modification was expected not to aid in its dispersion in PA6, which was precisely observed as no reduction in pHRR was seen. However, ORip contained 2 wt.% of HDTMA⁺ as seen from TG curves in Figure A5 in Appendix A. This must have facilitated in better and uniform distribution of ORip throughout PA6 that resulted in deviation observed in THR, % char and TSP values for PA6/ORip.

Hence, it is proven that metal ions from clay structure play a major role PA6 decomposition. Different clay compositions can help achieve different properties depending on metal ion concentrations.

8.1.3.2 Confinement Effect – Validation

Confinement effect is a physical effect where constraint volume is created between two adjacent platelets. Idealized image correlating constrained volume and clay platelet size is shown in Figure 8.4. To validate the confinement effect (as proposed for PA6/MI-clay composites), new PA6 composites were made with milled clays with reduced clay platelet size (area). Starting size is 200 μm while milled clay size is 71 μm (as determined by sieve mesh size).

Figure 8.4 Schematic diagram showing the effect of the size of clay platelet of constrained volume of polymeric chains and resultant confinement effect. Smaller clay platelets display short range spatial restrictions for polymeric mobility in intercalated regions.

Table 8.3 shows the result obtained for PA6 composites with milled clays. The absence of char improvement, higher smoke characteristics as compared to PA6/MgMMT confirm the effect of confinement on overall decomposition mechanism in condensed phase. Further, higher pHRR for milled clay composites highlights the importance of strong surface barrier as developed by interlocking platelets, an effect that vanished for very small platelet size.

Table 8.3 Cone calorimeter results of neat PA6 and its composites with MI-clays and milled MI-clays.

Specimen	pHRR (kW/m ²)	Char (%)	TSR (m ² /m ²)	TSP (m ²)
PA6	840	0	108	0.96
PA6/NaMMT (200 μm)	826	12.4	427	3.77
PA6/MgMMT (200 μm)	535	34.2	586	5.18
PA6/NaMMT (71 μm)	973	5.7	889	7.86
PA6/MgMMT (71 μm)	833	7.2	1010	8.94

Clay size are in parenthesis.

8.2 Conclusions

This research addressed an outstanding and major issue related to combustion properties of PA6/clay nanocomposites yielding novel and fundamental insights, which are highlighted as follows:

1. In the first study of its kind, a systematic analysis has been carried out to understand the effect of different metal ions (Mg^{2+} , Al^{3+} , and Fe^{3+}) present in clay lattice on the decomposition and combustion properties of PCNs. A performance matrix (Figure 8.5) is generated to associate their effects with different stages and crucial aspects of decomposition, viz. ignition, total heat release, smoke generation, and char formation. The performance matrix also incorporates the impact of location of metal ions in clay lattice. Depending on end properties required for PCN, this matrix can be used to identify appropriate clay composition. For example, optimum ratio and/or concentration of Mg^{2+} and Al^{3+} can make clay act as a char promoter. On the other hand,

Al^{3+} , Fe^{3+} or their combinations can provide an accelerated decomposition of PCN from the viewpoint of the end-of-life.

Performance Matrix

Property	Trend	Location
Decomposition onset (time, temperature) (Higher the better)	$\text{Mg} < \text{Al} < \text{Fe}$ $\text{Al} < \text{Mg}$	Structural Interlayer
Decomposition (total enthalpy) (Lower the better)	$\text{Fe} < \text{Al} = \text{Mg}$ $\text{Fe} > \text{Al}$	Structural Interlayer
Smoke generation (Lower the better)	$\text{Fe} > \text{Mg} > \text{Al}$	Both
Char formation (Higher the better)	$\text{Fe} < \text{Al} < \text{Mg}$	Both

Figure 8.5 Performance matrix associating effect of each metal ion with different stages of decomposition and combustion of PA6/clay nanocomposite.

2. It is established that both clay composition and clay dispersion, are equally important as they govern the interfacial interaction between matrix and clay surface.
3. For the first time using coated clays, an experimental confirmation is provided which directly links early ignition with the interfacial interaction between polymer matrix and clay surface.

It should be noted that the fire retardancy behavior of clay-polymer is highly system dependent. Polarity of polymer, backbone rigidity, side chains, inherent charring behavior, clay composition, clay surface, clay surfactants, etc. are some parameters to consider before extrapolating this study or drawing parallel lines to another system.

8.3 Future Work

1. On clay catalysis, an outstanding question is quantification and identification of volatiles generated during pre-ignition stages. In the current work, qualitative differences were observed using spectrometric data. However, exact information on the molecular identity of volatiles generated can help elucidate condensed phase reactions.
2. Synthesis of synthetic clay or layered di-hydroxides (LDHs) with precise control on chemical composition for superior FR properties. For example, synthesis of clays with an increase in Mg^{2+} content to make clay act as a char promoter. However, considering ripidolite experiment, it might be more advantageous to synthesize clay or LDH with an optimized combination of metal ions targeting multiple properties like pHRR, THR, smoke generation, and char.
3. With no early ignition and similar reductions in heat release rates, coated clay systems show significant potential. It is also advantageous to explore the use of NaMMT as a base clay for clay coating instead of organically modified clay. This can eliminate the use of surfactants which, otherwise, display low thermal stability. This can also prevent the generation of acidic H^+ site on clay surface during surfactant decomposition and essentially prevent possible autotransformation. On the other hand, superior dispersion of clay can be achieved by choosing appropriate high-temperature-resistant polymer for clay coating with reference to the polymer matrix.
4. End-of-life degradation using PCNs:
Harvesting catalytic activity of particular metal ions can also accelerate the disintegration of the polymer matrix. It can significantly impact plastic recycling. For example, the effect of Fe^{3+} - and Ni^{2+} - exchanged MMT was evaluated on degradation (weight loss) of polyethylene-thermoplastic starch (PE-TPS) composite. It was observed that under accelerated conditions (300-400 nm wavelength, 50 W/m² UV irradiance, 60 °C and 50 % humidity) presence of NiMMT rapidly disintegrated PE-TPS composite. On a similar line, based on matrix used, MMT exchanged with

different metal ions can be explored, which can act as decomposition accelerator (Figure 8.6).

Figure 8.6 Effect of different MI-clays on degradation of PE-TPS composite.

- Another important aspect that deserves a thorough investigation is the effect of interaction of metal ions (present on clay) with polymer chains during melt compounding. This will influence not only crystallization kinetics of PA6 but also the extent of evolution of different crystal phases.

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APPENDIX A: Auxiliary Details

Table A1 TG analysis for OMI-clays in air and nitrogen.

Specimen	ONaMMT		OMgMMT		OAIMMT		OFeMMT	
	T (°C)	% wt loss	T (°C)	% wt loss	T (°C)	% wt loss	T (°C)	% wt loss
Air	283	15.6	278	15.2	268	7.1	271	6.3
	-	-	-	-	293	9.4	-	-
	400-500	4.1	-	-	-	-	300-430	3.9
	620	9.6	609	13.2	606	12.9	565	14.3
Res at 450 °C	81.8		84.8		83.5		89.9	
Res at 750 °C	69.7		71.3		70.4		74.9	
Nitrogen	291	14.3	297	12.4	260	7.3	273	6.9
	-	-	-	-	289	7.9	-	-
	431	12.4	432-460	11.7	435	12.0	423	11.4
	-	-	550	3	-	-	-	-
	596	2.4	613	2	589	2.4	618	2.9
Res at 450 °C	73.5		75.3		74.3		80.8	
Res at 750 °C	68.2		69.4		69.6		76.7

Figure A1 Surface ATR FT-IR for PA6/NaMMT (A), PA6/MgMMT (B) and PA6/AlMMT (C) composites.

Figure A2 Surface ATR FT-IR for PA6/ONaMMT (A), PA6/OMgMMT (B) and PA6/OAIMMT (C) nanocomposites.

A1.1 Metal-ion Migration in Montmorillonite upon Heating

It is necessary to understand the fundamental vibrations in montmorillonite (key FT-IR absorption frequencies are reported in Table A2). MgMMT system was chosen as a representative system to provide complete comparison between FT-IR spectra for MgMMT, residues of MgMMT and OMgMMT and residues of PA6/MgMMT and PA6/OMgMMT composites (Figure A3).

Figure A3 FT-IR for MgMMT system, (a) dried MgMMT at 110 °C, (b) MgMMT residue at 750 °C, (c) OMgMMT residue at 750 °C, (d) PA6/MgMMT residue at 750 °C, and (e) PA6/OMgMMT residue at 750 °C.

R. Tettenhorst¹ reported that upon heating above certain temperatures interlayer cations migrate into the vacant regions of tetrahedral and octahedral layers which subsequently affect the stretching vibration of Si-O_{basal}-Si bond that can be detected using FT-IR. This migration was confirmed by observing shifts in FT-IR bands corresponding to Si-O_{basal} to higher frequencies and decreasing intensity of band corresponding to Al-OH-Al. It is understood that clay sourced from different parts of world have different composition. As a result, minor differences in original bands positions are expected. However, the shifts in

FT-IR bands upon heating are expected to be of similar nature. Accordingly, the shifts observed for band at $\sim 1120\text{ cm}^{-1}$ to higher wavenumber as much as up to $\sim 1135\text{ cm}^{-1}$ for composite residues, possible shift of $\sim 1015\text{ cm}^{-1}$ band to overlap with broad band at 1030 cm^{-1} and diminished band $\sim 915\text{ cm}^{-1}$ can be argued to signify migration of interlayer cation into silica skeleton. Following another reported work by Calvet et al.², the shift observed in diminished band from ~ 915 to $\sim 940\text{ cm}^{-1}$ support the migration of Mg^{2+} into silica skeleton. Migration of cations as big as Cu^{2+} into hexagonal holes upon heating Cu^{2+}MMT up to $350\text{ }^{\circ}\text{C}$ has also been reported³. Bakandritsos et al.⁴ reported reduction of intercalated Fe^{3+} to Fe^{2+} and its simultaneous migration to octahedral vacant locations. Although the determination of extend of migration is beyond the scope of this work, it is important to note that size as well as oxidation state of migrated cation can influence its association with structural oxygen. This subsequently could result in strong shoulder at $\sim 1200\text{ cm}^{-1}$, in the order of $\text{Na}^{+} < \text{Mg}^{2+} < \text{Al}^{3+} < \text{Fe}^{3+}$.

Table A2 FT-IR band assignments for MMT

Typical absorption frequencies, cm^{-1}	Assignments
~ 3640	OH-stretching
~ 3400	OH-stretching
~ 1645	OH-bending
$\sim 1120, \sim 1045, \sim 1015$	Si-Obasal-Si
~ 1080	Si-Oapical-Si
~ 915	Al-OH-Al
~ 880	Al-OH-Fe
~ 840	Al-OH-Mg
~ 525	Si-O-Al (bend)

Further, the exact nature of structural bonds corresponding to new band at $\sim 530\text{ cm}^{-1}$ or reason for absence of band at $\sim 725\text{ cm}^{-1}$ in case of PA6/OMgMMT is yet to be identified. However, there are convincing evidences that organic modification of clay induces certain structural modifications in clay otherwise absent at higher temperature. Since these bands are absent in residue for OMgMMT, it appears to occur exclusively in presence of organic polymer matrix.

Lastly, it is important to apprehend the influence of structural composition of clay on migration of interlayer cations. Purnell et al.⁵ observed that for montmorillonite originated from Texas, cations like Ni^{2+} , Co^{2+} and Zn^{2+} displayed migration phenomena upon heating respective cation exchanged clays. This was reported to be in complete contrast to bentonite clay originated from Wyoming region. This is a very crucial observation and potentially highlights the possible influence of inherent clay chemistry upon polymer matrix decomposition.

Table A3 Classification of clay based on their $\frac{1}{2}$ unit cell formula.

Clay	$\frac{1}{2}$ Unit cell formula	Classification
MMT	$(\text{Na}_{0.4}) [\text{Al}_{1.6} \text{Mg}_{0.4}] [\text{Si}_4] \text{O}_{10} (\text{OH}_2)$ ----- $1.6 + 0.4 = \mathbf{2}$	Diocahedral
Hec	$(\text{Na}_{0.4}) [\text{Mg}_{2.6} \text{Li}_{0.4}] [\text{Si}_4] \text{O}_{10} (\text{OH}_2)$ ----- $2.6 + 0.4 = \mathbf{3}$	Triocahedral
Nnt	$(\text{Na}_{0.4}) [\text{Fe}^{\text{III}}_2] [\text{Si}_{3.6} \text{Al}_{0.4}] \text{O}_{10} (\text{OH}_2)$ ----- $\mathbf{2}$	Diocahedral

Nomenclature

(exchange cation_a) [Octahedral cation_b] [Tetrahedral cation_c] Oxygen_d (Hydroxyl group_e)

where;

a, b, c, d and e are their ratio in $\frac{1}{2}$ unit cell

Figure A4 XRD pattern for C30B and coated clays.

Figure A5 TG curves for Rip and ORip under inert conditions. Heating rate of 20 °C/min.

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APPENDIX B: Publications & Presentations

List of Journal Publications:

1. I. S. Zope, A. Dasari and G. Camino. Elucidating the catalytic effect of metal ions in montmorillonite on thermal degradation of organic modifier. *Mater. Chem. Phys.* **2015**, 157, 69-79.
2. I. S. Zope, A. Dasari, F-G Guan and Z-Z. Yu. Influence of metal ions on thermo-oxidative stability and combustion response of polyamide 6/clay nanocomposites. *Polymer*. **2016**, 92, 102-113.
3. J. New*, I. S. Zope*, S. N. Abdul Rahman, X. L. W. Yap and A. Dasari. Physiological comfort and flame retardancy of fabrics with electrostatic self-assembled coatings. *Mater Des.* **2016**, 89, 413-420.
(* First co-authors. Contribution: Conception, designing and optimization of coatings, thermal and flame retardant property measurement, partial manuscript writing and making all images).

List of Book Chapters:

1. I. S. Zope, A. Dasari. *High-Temperature-Resistant Polymer Nanocomposite*, In: A. Dasari, J. Njuguna (Eds.), *Functional and Physical Properties of Polymer Nanocomposites*, John Wiley & Sons Ltd, Singapore, **2016**, pp. 183-202.

List of Oral Presentations:

1. I. S. Zope, A. Dasari. Understanding the role of clay catalysis in combustion of polymer/clay nanocomposites. 29th International Symposium on Polymer Analysis and Characterization, Singapore, 2016.

List of Poster Presentations:

1. I. S. Zope, A. Dasari. Polymer/clay Nanocomposites – Eco-benign Fire Retardant System. Society of Plastics Engineers (SPE) Asean Seminar, Singapore, 2016.
(Best Poster Award)
2. I. S. Zope, A. Dasari. Composites with superior fire retardancy for structural applications. Innovative Composites Summit, JEC Composites, Singapore, 2014.