A Thesis

entitled

Preparation and Characterization of Polyethylene Terephthalate/Montmorillonite
Nanocomposites by In-situ Polymerization Method

by

Rohan Labde

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requirements for the Master of Science Degree in Chemical Engineering

__________________________
Dr. Saleh A. Jabarin, Committee Chair

__________________________
Dr. Maria Coleman, Committee Member

__________________________
Dr. Isabel Escobar, Committee Member

__________________________
Dr. Patricia Komuniecki, Dean
College of Graduate Studies

University of Toledo
May 2010
Polymer nanocomposites are prepared by dispersing small quantities (0.5-10% by weight) of nano-sized particles which have high aspect ratios (100-1500) and high surface area (in excess of 750-800 m${^2}$/g) into the polymer matrices. Polymer nanocomposites offer improvements over conventional composites in mechanical, thermal and barrier properties without substantially increasing the density or affecting the light transmission properties of the base polymer.

The objective of this project is to develop a new process for preparation of polyethylene terephthalate (PET)/montmorillonite (MMT/Na⁺MMT) nanocomposite and to characterize it. During the study, we tried to disperse natural clay (Na⁺MMT) in PET polymer monomers by different methods. Natural MMT clay has been chosen to prepare PET nanocomposites because previous studies with organoclay have shown that organically modified clays get thermally degraded at PET preparation and processing temperatures (~280°C) and because of degradation, PET nanocomposites do not show
expected improvement in properties. PET nanocomposites were prepared by dispersing pristine MMT (Na⁺MMT) clays into ethylene glycol (esterification-ES clay addition) and bishydroxy ethylene terephthalate (polycondensation-PC clay addition). Thermal, mechanical and barrier properties of these nanocomposites have been studied in comparison to those of neat PET.

Differential scanning calorimetry (DSC) results were used to study thermal properties and it was observed that regardless of weight percentage of Na⁺MMT clay in PET matrices, there were no significant changes in glass transition temperatures (Tg) or melting temperatures (Tm) of the nanocomposites compared to neat PET. It was observed, however, that crystallization rate had increased at higher clay loading because of agglomeration of clay in the PET polymer matrices. For 0.5 wt% ES clay addition PET nanocomposite, tensile strength and tensile modulus observed to be increased by 85% and 92% respectively compared to that of neat PET. As clay percentage increased further, decrease in mechanical properties was noticed because of agglomeration of clay. Compared with neat PET, 0.5 wt% ES clay addition nanocomposite showed 30-40% increase in oxygen barrier properties. Different theoretical models were used to calculate values of tensile modulus and oxygen permeation for given clay content in the PET matrix and compared with experimental values of PET/ Na⁺MMT nanocomposites. It is concluded that the ES clay addition method resulted into better dispersion of Na⁺MMT clay into the PET matrices than the PC clay addition method. It is very easy and efficient method to prepare PET/Na⁺MMT nanocomposites and results into the nanocomposites having better properties than that of neat PET without organic modification of natural MMT.
Dedicated to my family and Dr. S.A. Jabarin
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TABLE OF CONTENT

ABSTRACT ........................................................................................................ iii

ACKNOWLEDGEMENT .................................................................................. vi

TABLE OF CONTENT ..................................................................................... vii

LIST OF FIGURES .......................................................................................... xi

LIST OF TABLES ............................................................................................ xvi

CHAPTER

1. INTRODUCTION ....................................................................................... 1

1.1 Polyethylene Terephthalate (PET) ........................................................ 1

1.2 The Manufacture of PET ........................................................................ 4

1.3 Need for Polymer Nanocomposites ..................................................... 6

1.4 Importance of high aspect ratio of fillers ............................................ 7

2. CLAY MINERALS AND THEIR ADVANTAGES .................................... 10

2.1 Structure of Clay Minerals .................................................................. 10

2.1.1 Layered Structure of Na⁺MMT Clays ............................................. 11

2.2 Modification of Na⁺MMT Clays ............................................................... 12

2.3 Advantages of Polymer Nanocomposites ........................................... 13

2.3.1 Permeability Models for Polymer Nanocomposites ....................... 15
2.3.2 Tensile Property Models for Polymer Nanocomposites

3. PROCESSING TECHNIQUES AND LITERATURE REVIEW OF PET/CLAY BASED NANOCOMPOSITES

3.1 In situ Polymerization

3.2 Solution Process

3.3 Melt Blending/Intercalation

3.4 Previous work on PET Nanocomposites at Polymer Institute, University of Toledo

3.5 Research Objective

4. EXPERIMENTAL

4.1 Materials

4.2 Optical Microscopy

4.3 Melt Intrinsic Viscosity Measurement

4.4 Single Screw Brabender Extruder

4.5 Density and Crystallinity Measurement

4.6 Thermal Analysis

4.6.1 Differential Scanning Calorimeter

4.6.2 Thermal Gravimetric Analysis

4.7 Mechanical Property Analysis

4.7.1 Instron Tester

4.8 Morphological Analysis

4.8.1 Wide Angle X-ray Diffraction
4.8.2 Transmission Electron Microscopy ...............................................47
4.9 Oxygen Permeability Test..............................................................49

5. RESULTS AND DISCUSSIONS .......................................................51
5.1 Natural Clay (Na⁺MMT) Selection for PET Nanocomposites ..............51
5.2 Dispersion of Na⁺MMT clay in PET Monomers ...............................53
  5.2.1 Dispersion of Na⁺MMT Clay in EG .......................................53
  5.2.2 Dispersion of Na⁺MMT Clay in BHET .................................57
5.4 Preparation of PET/Na⁺MMT Nanocomposite ...............................60
  5.4.1 ES Clay Addition Method ...................................................62
  5.4.2 PC Clay Addition Method ...................................................62
5.5 Chemicals and Their Usage ..........................................................63
5.6 Intrinsic Viscosity Measurement by RDA III .................................64
5.7 Thermal Analysis of PET/Na⁺MMT Nanocomposites ......................65
  5.7.1 Thermal Characterizations by DSC ....................................65
    5.7.1.1 DSC measurement 1 ..................................................65
    5.7.1.2 DSC measurement 2 ..................................................71
    5.7.1.3 DSC measurement 3 ..................................................78
    5.7.1.3.1 Non-isothermal Crystallization Behavior .....................83
  5.7.2 Thermal Stability Analysis by TGA .....................................89
5.8 Density and Crystallinity of Neat PET and PET/Na⁺MMT Nanocomposites ..93
5.9 Mechanical Properties of Neat PET and PET/Na\textsuperscript{+}MMT Nanocomposites ……96

5.9.1 Comparison between Experimental Mechanical Properties of Neat PET
And PET/Na\textsuperscript{+}MMT Nanocomposites………………………………………………96

5.9.2 Theoretical Calculation and Comparison of Tensile Modulus of
PET/Na\textsuperscript{+}MMT Nanocomposites……………………………………………………104

5.10 Morphological Analysis……………………………………………………………..107

5.10.1 Basal Space Measurement by Wide Angle X-ray Diffraction ………………107

5.10.1.2 WXRD Paradox………………………………………………………………………109

5.10.2 Morphological Analysis of PET Nanocomposite by Transmission Electron
Microscopy………………………………………………………………………………..112

5.11 Barrier Properties of Neat PET and PET/Na\textsuperscript{+}MMT Nanocomposites………117

5.11.1 Oxygen Permeability of PET/ Na\textsuperscript{+}MMT Nanocomposites………………117

5.11.2 Theoretical Calculation of Permeability of PET/Na\textsuperscript{+}MMT Nanocomposites..120

6. CONCLUSIONS AND RECOMMENDATIONS……………………………………124

6.1 Conclusions…………………………………………………………………………124

6.2 Recommendations……………………………………………………………………127

7. REFERENCES………………………………………………………………………………128
LIST OF FIGURES

Figure 1.1a: Esterification of Terephthalic acid (TPA) ........................................... 4
Figure 1.1b: Ester interchanges of Dimethyl Terephthalate (DMT) ....................... 5
Figure 1.1c: Polycondensation of BHET to produce PET under proper reaction conditions ........................................................................................................... 5
Figure 1.2: Plot of the function describing the ration surface area to volume (A/V) vs. aspect ratio (a) for cylindrical particles with a given volume. (a = L / W) ............... 8
Figure 1.3: Effect of clay platelet’s aspect ratio on relative permeability coefficient of polyimide nanocomposites ................................................................. 9
Figure 2.1: Chemical structure of montmorillonite clay ........................................ 11
Figure 2.2: Modification of clay by long chain ammonium ion ............................ 12
Figure 2.3: Different types of clay platelets dispersion in polymer ................. 14
Figure 2.4: Tortous Path model of polymer nanocomposites ............................ 15
Figure 4.1: Schematic representation of DSC equipment ................................. 40
Figure 4.2: Q500 TGA instrument and platinum pan used for thermal stability analysis ......................................................................................................................... 42
Figure 4.3: Schematic representation of X-ray diffraction ............................... 45
Figure 4.4: The schematic layout of components in a TEM ........................... 48
Figure 4.5: TEM sample support mesh "copper grid" ..................................... 49
Figure 4.6: Oxygen Permeability Test ASTM D 3985 ................................. 50
Figure 5.1a: Clay dispersion in water by ultrasonification

Figure 5.1b: Na\textsuperscript{+}MMT clay dispersion in water after 6 hours magnetic stirring

Figure 5.1c: Na\textsuperscript{+}MMT clay dispersion in water after 6 hours magnetic stirring and dispersion kept for overnight

Figure 5.1d: Viscous mixture obtained after removal of water from water-clay-ethylene glycol mixture

Figure 5.2: Direct clay dispersion in melt BHET

Figure 5.3: XRD results for Na\textsuperscript{+}MMT, BHET-clay dispersion and pure BHET

Figure 5.4: BHET intercalation in clay platelets

Figure 5.5: In-situ polymerization reactor system used to prepare PET and PET/Na\textsuperscript{+}MMT clay nanocomposites

Figure 5.6: DSC thermographs for neat PET and ES 0.5 wt% clay addition PET nanocomposite obtained by following procedure for measurement 1 to calculate initial crystallinity

Figure 5.7: DSC thermographs for neat PET, ES 2 wt% clay addition, PC 2 wt% and 5 wt% PET nanocomposites obtained to calculate initial crystallinity of the extruded films

Figure 5.8a: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and various wt% of ES clay addition PET/ Na\textsuperscript{+}MMT nanocomposites (step 6-reheating thermograms)
Figure 5.9a: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and ES 0.5% clay addition PET/ Na⁺ MMT nanocomposites (step 8- different cooling rates)…………………………………………………………………………………………………74

Figure 5.9b: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and ES 2 wt% clay addition PET/ Na⁺ MMT nanocomposites (step 8- different cooling rates)…………………………………………………………………………………………………75

Figure 5.9c: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and PC 2 wt% clay addition PET/ Na⁺ MMT nanocomposites (step 8- different cooling rates)…………………………………………………………………………………………………76

Figure 5.10a: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of ES clay addition PET/ Na⁺ MMT nanocomposites (step 4- cooling from 300 °C to 40 °C at 10°C/min)………………………………..79

Figure 5.10b: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of ES clay addition PET/ Na⁺ MMT nanocomposites (step 6- Reheating from 40°C to 300°C at 10°C/min)…………………..80

Figure 5.10c: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of PC clay addition PET/ Na⁺ MMT nanocomposites (step 4- cooling from 300 °C to 40 °C at 10°C/min)…………………………………81

Figure 5.10d: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of PC clay addition PET/ Na⁺ MMT nanocomposites (step 6- Reheating from 40°C to 300°C at 10°C/min)…………………………………82
Figure 5.11a: TGA graphs for PET and ES 0.5% and 2% wt clay addition PET/ Na$^+$MMT nanocomposites obtained by heating polymer samples from room temperature to 800 °C with constant heating rate (20°C/min).................................................................................................................90

Figure 5.11b: TGA graphs for PET and PC 0.6% and 2% wt clay addition PET/ Na$^+$MMT nanocomposites obtained by heating from room temperature to 800 °C with constant heating rate (20°C/min).................................................................................................................90

Figure 5.12: Change in the density with respect to wt% of clay in ES and PC clay addition nanocomposites.................................................................................................................................94

Figure 5.13: Picture of neat PET and PET/ Na$^+$MMT nanocomposites films..................................................................................................................................................................................95

Figure 5.14a: Comparison of tensile strengths of neat PET and ES clay addition nanocomposites..........................................................................................................................................................99

Figure 5.14b: Comparison of tensile strength of neat PET and PC clay addition nanocomposites..........................................................................................................................................................100

Figure 5.15a: Comparison of tensile modulus of neat PET and ES clay addition nanocomposites..........................................................................................................................................................102

Figure 5.15b: Comparison of tensile modulus of neat PET and PC clay addition nanocomposites..........................................................................................................................................................102

Figure 5.16: XRD pattern of Na$^+$MMT and ES0.5wt% clay addition nanocomposite…107

Figure 5.17: XRD pattern of Na$^+$MMT, Clay-BHET powder, PC 0.6 wt% clay addition nanocomposite..................................................................................................................................................108

Figure 5.18: WAXRD pattern of Na$^+$MMT and EG- Na$^+$MMT clay dispersion.........110
Figure 5.19a: TEM image of low clay loading (0.5 wt%) ES PET nanocomposite (low magnification)………………………………………………………………..113

Figure 5.19b: TEM image of ES 0.5% Clay addition PET nanocomposite………………114

Figure 5.19c: TEM image of PC 0.6% Clay addition PET nanocomposite………………115

Figure 5.20: Comparison of O₂ Permeability of neat PET and PET/ Na⁺MMT nanocomposites (PNC: polymer nanocomposite)………………………………………………………………………..118

Figure 5.21a: Graph of Pc/Pm Vs φ of PET/ Na⁺MMT nanocomposites for “S” = 0 (random orientation)………………………………………………………………………………122

Figure 5.21b: Graph of Pc/Pm Vs φ of PET/ Na⁺MMT nanocomposites for “S” = 1 (parallel orientation)………………………………………………………………………………122
LIST OF TABLES

Table 1.1: Packaging Applications of PET.................................................................3
Table 3.1: Comparison between different organoclays............................................30
Table 4.1: Properties of Na$^{+}$MMT........................................................................35
Table 5.1: Chemical names and their usages used in this research project.................63
Table 5.2: IV values of melt phase polymerized PET/Na$^{+}$MMT nanocomposites......64
Table 5.3: DSC data for measurement 1 for neat PET and ES 0.5 wt% clay addition PET nanocomposite obtained from Fig. 5.1.................................................................68
Table 5.4: Thermal data collected from DSC thermographs of neat PET, ES and PC clay addition nanocomposites.................................................................85
Table 5.5: TGA data obtained from Figures 5.6 for neat PET, ES and PC clay addition nanocomposites.................................................................91
Table 5.6: Density and Volume fraction crystallinity values of PET and PET/Na$^{+}$MMT nanocomposites obtained by using equation 10 and11.................................93
Table 5.7: Mechanical Properties of PET and PET/Na$^{+}$MMT nanocomposites.........96
Table 5.8: Comparison between experimental and theoretical tensile modulus of PET nanocomposite.................................................................105
Table 5.9: Experimental O$_2$ Permeability values of neat PET and PET/Na$^{+}$MMT nanocomposite.................................................................117
Table 5.10: Comparison of experimental and theoretical Pc/Pm values of neat PET and PET/Na\textsuperscript{+} MMT nanocomposites
CHAPTER I

INTRODUCTION

Polymer nanocomposites are prepared by dispersion of fillers which have at least one dimension in nanometer scale into the polymer matrices. Polymer/clay nanocomposites have become an important area studied more widely in academic, government and industrial laboratories due to their potential application in wide variety of fields [1-7]. Polymer nanocomposite materials were first reported as early as 1950 [8]. The preparation of the high performance polymer nanocomposite by Toyota researchers [9-11] instigated a new interest in this research area. This early work of the Toyota group was based on the formation of nanocomposites by in situ polymerization method in which montmorillonite (MMT/ Na⁺MMT) was intercalated with ε-caprolactam.

Polymeric materials have been filled with several inorganic and/or natural compounds [12-17] in order to get property enhancements, e.g, increased stiffness, rigidity and strength, greater dimensional stability, enhanced gas barrier properties and lower water absorption. The property improvements of clay based nanocomposites are due to dispersion of nanoparticles in the polymer resulting in very high surface area for interaction between polymer chains and filler surface.

1.1 Polyethylene Terephthalate (PET):
Polyethylene terephthalate (PET) is a long chain polymer which has found increasing applications within the packaging field. It is a thermoplastic polymer. Its chemical
inertness, and other physical properties, has made it particularly suitable for food and beverage packaging applications [2-4]. The dispersion of clay into PET can result in excellent property improvements in terms of decreasing oxygen permeability in food packaging, increasing flame resistance in textiles, and increasing the mechanical properties such as tensile modulus in injection molded parts. This can be done with less clay content than fillers used in most conventional composites. Conventional fillers have been used to improve properties and reduce cost; however, there are limitations in their application due to phase separation, particle agglomeration, and heterogeneous distribution in the polymer matrices [1-4].

In its purest form, PET is a transparent, amorphous glass-like material. PET can be semi-rigid to rigid depending on its thickness and it is very lightweight. PET was originally patented and exploited by the DuPont [18, 19] during the search for new fiber-forming polymers. Polyester fibers have been used in wide variety of applications and the majority of the world's PET production is for synthetic fibers (in excess of 60%) with bottle production accounting for around 30% of global demand [20]. In the late 1950s PET was developed and used as film in various applications such as video, photographic and X-ray films in addition to uses in flexible packaging, [21]. Later PET was modified and reinforced by micro fillers such as mica and glass which gave PET dimensional stability required for the use in injection molded and extruded materials [13, 16]. In the early 1970s PET was stretched by blow molding, stress blow molding techniques and first oriented three dimensional structures such as bottles were produced from the PET. This development initiated the rapid utilization of PET as a packaging material which is lightweight, tough and has a good barrier properties (Table 1.1) [3, 21, 22].
Table 1.1: “Packaging Applications of PET” [21]

<table>
<thead>
<tr>
<th>PET packaging products</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottles</td>
<td>Beverages, soft drinks, fruit juices, and mineral waters, Especially suitable for carbonated drinks cooking and salad oils, sauces and dressings.</td>
</tr>
<tr>
<td>Wide mouth jars and tubs</td>
<td>Jams, preserves, fruits and dried foods</td>
</tr>
<tr>
<td>Trays</td>
<td>Pre-cooked meals for re-heating in either microwave or conventional ovens, pasta dishes, meats and vegetables</td>
</tr>
<tr>
<td>Films and metalized foils</td>
<td>„Boil in bag” pre-cooked meals, snack foods, nuts, sweets, long life confectionary, ice creams and spreads</td>
</tr>
<tr>
<td>Coatings</td>
<td>Microwave subsectors</td>
</tr>
<tr>
<td>PET product with added oxygen barrier</td>
<td>Beer, vacuum packed dairy products e.g. cheese processed meats, „Bag in Box” wines, condiments coffee, cakes, and syrups.</td>
</tr>
</tbody>
</table>
1.2 The Manufacture of PET: [2, 22-24]

PET is made by the reaction of bifunctional acids and alcohols, in the presence of a metal catalyst. In the PET polymerization, there are two important steps- esterification and condensation. For manufacture of PET, pure terephthalic acid (TPA) and ethylene glycol (EG) are obtained from the crude oil. When EG and TPA are heated together under certain temperature and pressure conditions, they undergo esterification reaction. The first product obtained is a BHET (bis-hydroxyethyl-terephthalate) and water as a byproduct (Fig. 1.1a). The polycondensation reaction of BHET is carried out under high vacuum and around 275 °C temperature to produce PET and EG as a byproduct (Fig. 1.1c). At this stage the PET is a viscous molten liquid. It is then water quenched to form a glasslike amorphous material. PET is also manufactured using another method based on the dimethyl ester of terephthalic acid (DMT) (Fig. 1.1b). The required high molecular weight PET is manufactured by a second polymerization stage carried out in the solid state at lower temperatures called solid state polymerization [25, 26]. This effectively removes all volatile impurities, such as acetaldehyde, free glycols and water. The high molecular weight is essential for good mechanical properties providing dimensional stability, stiffness and creep resistance while, at the same time, giving sufficient flexibility to resist breaking under pressure [2, 21, 25].

![Figure 1.1a: Esterification of Terephthalic acid (TPA)](image)

Figure 1.1a: Esterification of Terephthalic acid (TPA)
Conventional polymers are reinforced with different fillers such as talc, glass and carbon fibers to improve their properties e.g. strength, stiffness and heat resistance [12-16]. Such reinforcement depends on the rigidity and aspect ratio of the fillers, and adhesive strength.
between filler and polymer matrix. In order to improve adhesive strength, surface modification of fillers is carried out by using compatible agents. Conventional micro filler polymer composite often exhibit phase separation and degradation in polymer properties such as ductility, mold ability and surface smoothness of molded products. Such polymer composite are not easy to process as films due to high level of fillers and their size. Therefore, it is expected that the interface deficiency can be reduced by replacing the micro-fillers with extremely small fillers and mechanical and thermal properties of polymer composites can be improved. The emergence of polymer/clay based nanocomposite is largely based on such a consideration in which polymer matrices are reinforced by uniformly dispersed nanoparticles.

1.3 Need for Polymer Nanocomposites:

Polymer nanocomposites are the materials in which nano-sized inorganic particles, typically nano-scale in at least one dimension, are dispersed in organic polymer matrices in order to dramatically improve the performance properties of the polymer. They are a new class of polymer composites that contain relatively small amounts (<10%) of nanometer-sized clay particles. The particles, due to their extremely high aspect ratios (about 100-1500), and high surface area (750-800 m$^2$/g) promise to improve structural, mechanical, thermal and barrier properties without substantially increasing the density or reducing the optical properties of the polymer [2, 27].

Polymer nanocomposites can be prepared from a variety of nanoparticles, including disk-like nanoparticles (clay platelets), spherical and polyhedral nanocomposite (colloidal silica) and nanofibers (nanotubes, whiskers) [28, 29]. We are focusing on clay based polymer nanocomposites because they are to date the most attractive and promising polymer nanocomposites. The layered clays, which can be used to prepare polymer nanocomposites, may be divided into natural clays (montmorillonite, hectorite and saponite) and synthesized clays (fluorohectorite, laponite, and hydrotalcite). Among
them, montmorillonite (MMT) is the most commonly used one for the preparation of polymer nanocomposite [30]. Polymer nanocomposites show many dramatically improved properties together with some novel properties not exhibited by the individual components or their macro and micro counterparts.

1.4 Importance of High Aspect Ratio Fillers:

The surface to volume ratio indicates the quantity of interfacial region compared to bulk material in a polymer composite. The interfacial region in a composite plays a very important role and not only controls new structural arrangement but also is responsible for the efficient transfer of stress across the composite components. Therefore, as the interfacial region increases, chances of potential increase in the material properties also increases.

Figure 1.2 shows a graph of area/volume (A/V) ratio to aspect ratio (a = Length/Width= L/W) for platelet shaped and rod shaped filler.
Figure 1.2: Plot of the function describing the ration surface area to volume \( (A/V) \) Vs. aspect ratio \( (a= L/W) \) for cylindrical particles with a given volume [31]

From the above graph, we can easily conclude that the A/V values increase is much steeper with respect to the aspect ratios for the platelets compared to that of the rods/fibers. While defining “nano” effect on mechanical properties of nanocomposite, Alfred Crosby et al. [32] concluded that clay platelets have significant advantage over rod or spherical shaped fillers at equivalent volume fraction loading. It can be noticed that the area available from the same volume of platelets is much larger compare to that of rods or fibers. When dispersed properly, platelets can have very large surface area available to interact with polymer matrix.

To investigate the effect of size of clay minerals on properties of polymer composite, Kazuhisa Yano et al. [33] prepared polyimide-clay hybrid films. K. Yano et al. [33] concluded that the degree of improvement of the properties of polyimide depend on the
length of clay. As the length of the clay platelets increased with respect to width, the more effectively barrier properties of polyimide were improved as shown in Fig. 1.3.

Figure 1.3: Effect of clay platelet’s aspect ratio on relative permeability coefficient of polyimide nanocomposites [33]

It was concluded that the decrease in relative permeability coefficient was result of tortuous path formed for the permeating molecules because of dispersion of clay platelets in polymer matrix. However, exfoliation of layered platelets and hence preparation of a well dispersed nanocomposites is seriously hampered by the fact that sheet like materials show strong tendencies to agglomerate because of their large surface contact areas.
CHAPTER II

CLAY MINERALS AND THEIR ADVANTAGES

2.1 Structure of Clay Minerals:

Among the large numbers of layered solids, clay minerals especially the smectite group are most widely used for the reinforcement of polymer matrices and thus for the fabrication of polymer nanocomposites because of their unique structure and reactivity together with their high strength and stiffness and high aspect ratio of each platelet. In particular MMT and hectorite are commonly used layered clays.

2.1.1 Layered Structure Na⁺MMT Clays:

MMT clays belong to smectite family. The crystal structure consists of an aluminum octahedron sheet sandwiched between two silicon tetrahedron sheets. Stacking of the layers leads to a Van der Waal’s gap between the layers (Figure 2.1).

In the crystal structure of MMT clays, some of the atoms of aluminum are replaced by magnesium (Mg), lithium (Li) or iron (Fe) by isomorphic substitution. This leads to having overall negative charge on the surface of the sheet layer, which is counterbalanced by exchangeable metal cations residing in the interlayer space, such as sodium (Na), calcium (Ca) [34].
2.2 Modification of Na\(^+\)MMT Clays:

Pristine MMT (Na\(^+\)MMT) clays are hydrophilic in nature and most polymers are hydrophobic or water susceptible in nature. As a result, they are not compatible with each other. However, Pristine MMT clays have unique structure and high intercalation capabilities which allow them to be chemically modified by organic molecules that are compatible with polymers which make them attractive in clay based polymer nanocomposite. Na\(^+\)MMT clays have unique structure with thickness about 1 nm and aspect ratio 100-1500. They also have low layer charges which lead to weak forces between the adjacent layers. This makes interlayer cations exchangeable. These interlayer cations can be replaced by inorganic and organic cations by facile methods, which is an important aspect of their use in polymer nanocomposites fabrication [35, 36, 37].
In clay modification, mostly interlayer cations (Na\(^{+}\), Ca\(^{2+}\)) are replaced by organic bulky ammonium or phosphonium cations [37,38]. This leads to an increase in interlayer spacing and a decrease in clay layer-layer attraction. The quaternary ammonium ions are normally chosen to make clays compatible with polymer resin (Fig. 2.2).

![Modification of clay by long chain bulky ammonium ion](image)

Figure 2.2: Modification of clay by long chain bulky ammonium ion [40]

The molecular structure of ions, such as alkyl chain length, number of alkyl chains and insaturations, is an important factor determining compatibility and thermal stability of polymer/MMT nanocomposites [1, 39]. These modifying agents are getting significant success in preparation of polymer nanocomposite; however, their main shortcoming for PET nanocomposites is their poor thermal stability [1].
2.3 Advantages of Polymer/Clay Nanocomposite: [41]

- Mechanical properties: Increased strength and stiffness, high elongation of the matrix.
- Decreased permeability to gases and water: Increased permeation resistance helps to increase shelf-life of nanocomposite packaged materials
- Transparency: Low loadings and good filler dispersion maintain inherent polymer transparency
- Recyclability: Thermally stable nanofillers are not affected or degraded during processing, physical properties of polymer composites are not seriously affected by recycling
- Flame resistance: Good dispersed nanofillers increase thermal stability, excellent flame resistance
- Transport properties: Density of nanocomposites do not increase too much as percolation at very low loadings in high aspect ratio systems

Depending on the nature of compounding and processing conditions, three types of structure can be formed when clay platelets are dispersed into a polymer (Fig.2.3). Sometimes polymer can not intercalate into the galleries of clay platelets, which leads to formation of conventional composites. Properties of such composites are similar to those of polymer composites reinforced by micro particles.
When extended polymer chains are inserted into interlayer spaces of clay platelets, they increase the interlayer gallery space between clay platelets, however most of the time they do not separate clay platelets completely and result in a well ordered multilayer stacking alternately polymer layers and clay platelets, this leads to intercalated nanocomposites. The other type is the exfoliated nanocomposites, in which the clay platelets are completely and uniformly dispersed in a continuous polymer matrix. Completely exfoliated nanocomposites have shown excellent increase in barrier and mechanical properties of polymers. There are different theoretical models have been suggested to explain these increases in barrier and mechanical properties. Some of them are discussed in following sections.
2.3.1 Permeability Models for Polymer Nanocomposites:

The permeability of small gaseous molecules in a polymer matrix is determined by different factors such as solubility, diffusivity of the small molecules in the matrix and by the morphology of the polymer. The permeability of gas molecules in polymer nanocomposite is very complex. To determine permeability, one must take into account that nano fillers in polymer matrix affect the solubility and diffusivity of penetrate molecules especially in interfacial regions. Nanofillers have high aspect ratio, thus well dispersed nanofillers increase the tortuous path of penetrating molecules (Fig. 2.4) [46].

Clay platelets are rigid and impermeable nano particles and when dispersed in polymer matrix, they do not allow permeating gas molecules to diffuse through them. This means that the permeability of the polymer matrix dispersed with such fillers will be smaller than the permeability of unfilled polymer matrix by a factor equal to path tortuosity in the composite. Neilsen et al. [42] proposed model to calculate path tortuosity by following Equation 1, in which he considered that all fillers are parallel to the surface of polymer matrix.
\[ \tau \approx 1 + \left( \frac{L}{2} W \right) \phi \] \hspace{1cm} \text{Equation 1}

Where, \( \tau \) = tortuosity
\( L \) = length of filler
\( W \) = width of filler
\( \phi \) = volume fraction of filler

From the above equation, it can be concluded that tortuosity is proportional to aspect ratio and volume fraction of filler. Platelet shaped montomollirite fillers have higher aspect ratio than spherical and rod shaped fillers.

The relationship between tortuosity, volume fraction, and permeability is given by Neilsen\[42\], Micheals, Bixler \[43\] and Barrer et al. \[44\]. A simple equation was suggested to obtain permeability of a composite.

\[
\frac{P_c}{P_m} \approx \frac{1 - \phi}{\tau} \hspace{1cm} \text{Equation 2}
\]

Where, \( P_c \) = permeability of composite
\( P_m \) = permeability of matrix
\( \phi \) = volume fraction of filler

Bharadhaj et al. \[45\] had proved that in the case of platelets fillers, orientation of platelets in polymer matrix is a very important factor which affects the overall permeability. He modified the equation 2 to account for non-aligned fillers, by introducing an order parameter \( S \) for the filler orientation.

\[
\frac{P_c}{P_m} = \frac{(1 - \phi)}{1 + \alpha \phi^2 \left( S + \frac{1}{2} \right)} \hspace{1cm} \text{Equation 3}
\]
\[
S = \frac{1}{2} \left(3\cos^2 \theta - 1\right)
\]

\[
= \begin{cases} 
1 & \text{for } \parallel \text{ surface} \\
0 & \text{for random} \\
-\frac{1}{2} & \text{for } \perp \text{ surface}
\end{cases}
\]

Where, \( P_c \) = Permeability of Composite

\( P_m \) = Permeability of Polymer matrix

\[ \alpha = \frac{L}{2w} \]

Bharadwaj et al. [45] while developing the equation 3, took into account sheet length, concentration, orientation and degree of exfoliation on the relative permeability by modifying a simple tortuosity based model. It was concluded that dispersing longer sheets in polymer matrix can increase the tortuosity, reduce the dependence of the relative permeability on the orientation order of the sheets and slow the degradation in barrier property with decreasing state of delamination at low loading. E. Manias et al. [46] performed study that also supports the conclusion of Bharadwaj [45] that randomly orientated fillers of high aspect ratio result in permeability similar to that obtained with perfectly aligned fillers. E. Manias et al. [46] also concluded from their study that high aspect ratio fillers are as effective as smaller aspect ratio fillers at a higher loading of fillers in polymer matrix. This observation is very important because it indicated that instead completely exfoliating a given filler (which has been proved to be very difficult), partially exfoliated or mostly intercalated morphology could achieve the same barrier performance at slightly higher filler loadings.
The Neilson and Bharadwaj permeability models, however, do not take into account the three dimensional nature of clay platelets and the permeant gas molecule’s path was considered as a two dimensional path. EL Cussler et al. [47, 48] proposed another model which took into account three dimensional natures of clay platelets and for random orientation, they proposed following equation:

\[
\frac{P_c}{P_m} = \frac{(1-\phi)}{[1+\mu(\frac{L}{W})\phi^2]} \quad \text{Equation 4}
\]

Where \( \mu \) is geometrical factor given by:

\[
\mu = \frac{\pi^2}{[16\ln^2\left(\frac{L}{W}\right)]} \quad \text{for } \left(\frac{L}{W}\right) \phi \gg 1
\]

Here, the geometrical factor, \( \mu \), depends on clay dispersion and the aspect ratio of the clay platelets. Cussler’s model [47] is useful only when the aspect ratio is very large (\( \alpha \phi \gg 1 \)). When the aspect ratio is small (\( \alpha \phi < 1 \)), it predicts permeability similar to that of other models [49]. By using the above three equations, we can approximately predict the permeability of a polymer composite which depends on aspect ratios, orientation and volume fraction of fillers in polymer matrix. This approximation also depends on dispersion of clay and the structure of polymer nanocomposite.

Bo Xu et al. [50] studied the effects of clay layers on the barrier properties of polymer/nanocomposites containing impermeable and oriented clay layers. In this study, they incorporated the relative permeability theory of semi-crystalline polymers with the detour theory to predict the relative permeability of polymer nanocomposites. While developing this model, they took into account the effects of clay layers, layer length, clay loading, clay dispersion and the chain confinement on barrier properties of polymer nanocomposites. It was reported that increase in lateral dispersion resulted in a decrease
in relative permeability. Also it was observed that intercalation with certain multilayer layers and/or chain confinement due to clay layers could enhance the barrier properties of the polymer nanocomposite.

The structure of polymer nanocomposites is generally obtained from X-ray diffraction (XRD) and transmission electron microscopy (TEM). Either intercalated or exfoliated nanostructure may be identified by monitoring the position, shape and intensity of basal reflections from the polymer materials [1, 51, 52].

2.3.2 Tensile Property Models for Polymer Nanocomposites:

Polymer nanocomposites have shown enhancement in mechanical properties and higher performance compared to conventional polymer composite and neat polymers. Such improvements have been noticed without much increase in the polymer density as well as without recognizable loss of optical clarity. The enhancement in mechanical properties of polymer nanocomposite has been attributed to the high modulus, rigidity and high aspect ratio of clay [37]. The nylon 6-clay nanocomposite prepared by Toyota researchers has exhibited significant improvement in strength and modulus of polymer [9-11]. There are different theories and models are available to predict these increase in mechanical properties. The earliest theory of rigid inclusions in non rigid matrix is based on the Einstein’s equation which was used for the viscosity of the suspension of rigid spherical particles. [53]. Guth and Gold [54] further modified the Einstein’s equation by introducing a quadratic term to take into account the interaction between filler particles and proposed following equation:

\[
E = E_m \left[1 + 2.5 \phi + 14.1 \phi^2 \right] \quad \text{Equation 5}
\]
Where, $E = \text{Young modulus of composite}$

$Em = \text{Polymer matrix young’s modulus}$

$\phi = \text{volume fraction of fillers}$

However, Eq. 5 is only applicable to certain polymer matrices filled with spherical fillers and it is not applicable if the filler volume % is more than 10 in the polymer matrix. Guth et al. [55] developed the following equation [Eq. 6] by taking into consideration that the chains composed of spherical fillers are similar to rod like particles imbedded into polymer matrices and introducing a shape factor alpha ($\alpha$).

$$E = Em [1 + 0.67 \alpha \phi + 1.62(\alpha \phi)^2] \quad \ldots \quad \text{Equation 6}$$

The above equation shows rapid increase in modulus with increase in filler volume % compared to equation 5.

Halpin and Tsai et al. [56] developed equations which are widely used for predicting the stiffness and reinforcement effect of filler in composites. Halpin and Tsai composite theory is based on the micromechanical works of Hermans [57] and Hill [58]. Halpin and Tsai generalized Herman’s equation to a simpler form for a variety of reinforcement geometries. The elastic modulus of composite material reinforced by lamellar shape is expressed as shown in the following equation:

$$\frac{E}{Em} = \frac{1 + \xi \eta \phi}{1 - \eta \phi} \quad \ldots \quad \text{Equation 7}$$

In equation 7, $\xi$ is the shape parameter which depends upon filler geometry, orientation and loading direction and $\eta$ is given by following equation,
\[ \eta = \left( \frac{E_f}{E_m} - 1 \right) / \left( \frac{E_f}{E_m} + \frac{\xi}{2} \right) \]

Where, \( E_f \) represents Young’s modulus of the filler and \( \xi = 2(w/t) \), where “w” and “t” are the width and thickness of perfectly oriented lamellar shaped fillers respectively.
CHAPTER III

PROCESSING TECHNIQUES AND LITERATURE REVIEW OF PET/CLAY NANOCOMPOSITES

There are basically three different processes that can be used to make clay-based polymer nanocomposites. They are in-situ polymerization, melt blending and solution process.

Each processing technique is discussed separately with examples and with respective advantages and disadvantages in following sections.

3.1 In-situ Polymerization:

In this method, layered clays are mixed and swollen within the liquid monomer or a monomer solution. Monomers can be absorbed in an interlayer space of the clay platelets and then polymerization carried out. As a result, when monomers react and polymer chains grow, they increase the interlayer spacing between platelets. This process is suitable for low or non-soluble polymer.

Jin-Hae Chang et al. [59] studied PET nanocomposites made from monomers and organoclay via an in situ interlayer polymerization method. Nanohybrid fibers were examined to compare the influences of the clay content, the different draw ratios (DR), the dispersion, and the intercalation states. It was concluded that the addition of small amounts of modified clay were found to be enough to improve the thermal stability and the tensile mechanical properties of PET hybrid fibers at DR =1. When the DR was increased from 1 to 16, the organoclay in the PET caused significant decreases in the
values of the ultimate tensile strength and the initial modulus due to debonding around the polymer-clay interfaces and void formation.

Guan et al. [60] prepared PET/clay nanocomposites by in-situ polycondensation polymerization to study in depth crystallization behavior of the nanocomposites. It was reported that different surface modification strategies of MMT resulted in odd crystallization behavior. The reason for this behavior was attributed to (1) dispersion morphology of clay in the matrix; (2) surface shielding effect of small organic surfactant molecules; (3) nucleating effects of metallic derivatives released from MMT during in situ polycondensation. From crystallization behavior study and secondary nucleation analysis, it was concluded that nucleating abilities of MMT depends on the dispersion state of clay in polymer matrix, the surface modification and the metallic derivatives released from MMT during in situ synthesis.

Hwang et al. [61] prepared PET nanocomposites by using pristine as well as modified clay (A-10 MMT). They found that modified MMT is more uniformly dispersed than pristine MMT. They also concluded that enhancement of properties is related to the good dispersion of the clay and not the total clay content in the polymer nanocomposite. Modified clay improved compatibility between the PET and clay because of the alkyl modifier. They used Avrami and Ozawa equation to describe the non-isothermal crystallization kinetics, which showed that Na\(^+\)MMT was more effective as a nucleation agent than A10-MMT. Finally they concluded that PET/A-10 MMT nanocomposite showed superior mechanical and thermal properties in comparison to neat PET.

Se-Hoon Kim et al.[62] proposed a novel method for preparation of PET nanocomposites and the clay dispersed trimellitate ester oligomers were prepared by esterification with 1,2,4-Benzene-tricarboxylic anhydride and montmorillonite dispersed in ethylene glycol. By microscopy study, he found that layers of clay were well dispersed and exfoliated and intercalated structures of the clay co-existed in the polymer matrix.
Choi et al. [63] prepared PET nanocomposites by direct polymerization in the presence of clay supported catalyst. Clay supported catalyst was prepared by suspending clay into anhydrous tetrahydrofuran and adding chlorotitanium triisopropoxide to this suspension. This mixture was then stirred for 24 hr and clay supported catalyst was separated by filtration. Wide angle X-ray diffraction (WAXD) results showed intercalation of PET chains into the galleries of silicate layers but exfoliation did not observed. The improvement of oxygen (O₂) permeability by 11.3-15.6 factors for PET/Clay supported catalyst over that of the neat PET was observed.

Ke et al.[64] prepared PET/clay nanocomposites by controlling different parameters such as the pretreatment of the MMT, the content of the MMT, the kinds of reagents used, and the manner by which they added MMT. According to TEM results, Ke et al. [64] did not observed any agglomeration until 3% weight of clay was added, but as the clay weight % increased above 3, agglomeration become unavoidable. They concluded that 3% weight of clay is a critical weight percentage for preparing PET nanocomposites. DSC result proved that MMT affect the nucleation process and increase the rate of crystallization. They also found that exfoliated lamellae’s interaction with the molecular chain result into more regular chain patterns and this affects the PET’s crystallization behavior and morphology.

Some of the research groups had tried to prepare nanocomposites by adding another polymer to PET which will act as a compatibilizer and help to get exfoliation of clay in to the polymer matrices. Chuncheng Li et al. [65] prepared PET/PA6 Copolymer/MMT hybrid nanocomposites. They observed that melting temperature, crystallization temperature and glass transition temperature of the resulting copolymer is located between those of PA6/MMT nanocomposite and PET/MMT nanocomposite. Because of presence of PA6, compatibility between PET and MMT was observed to be increased resulting better dispersion of clay into the copolymer matrix. Sang-Soo Lee et al. [66] had successfully polymerized ethylene terephthalate cyclic oligomers (ETCs) to high
molecular weight polyethylene terephthalate. Na⁺MMT clay modified using N,N,N-trimethyloctadecylammonium bromide. Due to low molecular weight and viscosity, ETCs were successfully intercalated into the clay galleries. Subsequent ring-opening polymerization of ETCs in-between silicate layers yielded a PET matrix of high molecular weight and high dispersion of clay platelets in the PET matrix.

3.2 Solution Process:
In this process, layered clays are dispersed or exfoliated into single platelets using a solvent in which the polymer is soluble. It is well known that such layered clays, owing to the weak forces that stack the layers together can be easily dispersed in a proper solvent. The polymer then absorbs onto the delaminated platelets, and when the solvent is evaporated, the platelets reassemble, sandwiching the polymer to form an ordered multilayer structure. Very few studies have been done using this method because of complications associated with it.

Cheng Fang Ou et al. [67] used a solution interaction to prepare PET/organoclay nanocomposites. The Pristine MMT clay was organically modified with the intercalation agent cetylpyridinium chloride (CPC). They used 3/1(w/w) phenol/chloroform solution to mix PET and clays. In the presence of organo-modified MMT in the polymer matrix, heterogeneous nucleation and an increase in crystallization rate was observed. Nanocomposites, with organoclay loadings from 1-15%, exhibit higher thermal stability than pure PET. The organoclay was highly dispersed in the matrix without a large agglomeration of particles in the 5 weight (wt) % nanocomposites, but an agglomerated structure was observed in the 15 wt % nanocomposites.

Aht-Ong et al. [68] prepared PET/MMT nanocomposites by a solution technique using 50/50 phenol/tetrachloroethane. To increase dispersion and compatibility of MMT in
PET solution, he used ultrasonic power and different types of MMT, pristine MMT and MMT modified with dimethyl dioctadecyl ammoniuam. In the XRD study, it is observed that with pristine MMT, clay diffraction peak appeared at 2Θ = 5.5° (15.9 Å) and with modified MMT, there was no significant clay diffraction peak observed which may be result of almost complete exfoliation of clay platelets into the polymer matrix. It is found that for nanocomposites the maximum tensile strength and Young’s modulus were obtained at low percentage of clay and they decreased with further increase in clay contents. This was attributed to the high interfacial properties and clay agglomeration respectively. Also the % elongation at break decreased with increase in clay content of both clay types, because of natural rigidity of silicate-sheet nanofillers.

3.3 Melt Intercalation/Blending:

In the process of melt blending, a polymer and layered silicate mixture is heated above the Tg or Tm of the polymer. Depending on sheer force of mixing and compatibility between the polymer and clay platelets, polymer chains penetrate into the interlayer spaces between clay platelets and increase the interlayer spacing. This can result in formation of intercalated or exfoliated polymer nanocomposites. This process is environmentally benign process as it does not required solvent. Also in this method nanocomposites can be processed with conventional polymer extrusion and molding technology.

Guozhen et al. [69] synthesized PET-clay nanocomposites with improved tensile strength using a melt bending method. In this work, the hybridization of PET with montmorillonite was investigated by using hydroxypentyltrimethyl ammonium iodide (HPTA) as an ionic anchor monomer adsorbed onto clay surfaces by ion exchange instead of the simple mixing of the organoclay with PET. The HPTA/MMT hybrid films
were copolymerized with bis(hydroxyethyl terephthalate) (BHET) to form a tensile strength-improved PET-clay hybrid as well as to obtain optically transparent materials.

Marius Costache et al. [70] prepared PET/Clay nanocomposites by melt blending using thermally stable surfactants. To organically modify clay, they used hexadecylquinolinium bromide and vinylbenzyl-ammonium chloride-lauryl-acrylate copolymer. Dispersion of clay in polymer matrix was observed to be from very good to poor, depending on the nature of the filler as well as the surfactant. With some exceptions, all modified clays showed remarkable thermal stability, the mass loss at 300°C being less than 2%, which allow them to be melt-blended with high processing temperature PET.

Guoli Wang et al. [71] reported a novel technology, solid state shear milling (S3M), to prepare PET/MMT clay nanocomposites. In this method, they used Na⁺MMT clay without organic modification resulting in reducing the cost of the process. In conventional methods, the clay is organically modified which can not endure the high processing temperatures and thus undergos thermal degradation. This method is based on special pan-mill equipment invented by Sichun University of China, which provides strong shear force and compression force in a solid state and hence excellent pulverization, dispersion and mixing for the polymers and fillers. It is concluded from their research that the PET/ Na⁺MMT nanocomposite can be formed by strong shear forces of pan-milling, increasing interlayer spacing of pristine Na⁺MMT from 1.17 nm to 1.48 nm, which can be further delaminated during subsequent twin screw extrusion. The clay has heterogeneous effects on crystallization of PET.. The nanocomposite obtained from S3M has improved mechanical properties as well as more thermodynamic stability. When the content of clay is 3.5%, the thermal degradation temperature increases by 40°C, also their tensile properties are higher than those of samples prepared by conventional compounding methods because of better dispersion of the clay particles and formation of corresponding exfoliated structure.
Mingfang Lai et al. [72] prepared poly (ethylene terephthalate-co-ethylene naphthalate) (PETN) nanocomposites by using two different organoclays, Cloisite 20A and 30B, by melt intercalation using an extruder. Also organoclays were further treated with epoxy monomer to further improve the polar interaction with PETN matrix. It was found that Cloisite 30B had better interactions with PETN and was more uniformly dispersed within PETN than Cloisite 20A. Epoxy treatment of Cloisite 30B organoclay resulted in improved d-spacing between clay platelets, thermo-mechanical and tensile properties, as well as thermal stability, processing and gas barrier characteristics of the PETN/30B nanocomposites. From these results, they concluded that the epoxy acted as a compatibilizer as well as a chain extender, resulting in improving the chemical interaction between PETN and the organoclay, while discouraging the macromolecular mobility of polymer chains in the vicinity clay particles.

Todorov et al. [73] prepared PET nanocomposites by two independent procedures: mechanical mixing with subsequent direct injection molding (DIM) and mechanical mixing, followed by extrusion blending and injection molding (EIM) by using different nanoparticles. It was found that PET nanocomposite was more prone to degradation than virgin PET. Nanoparticles in the polymer matrix cause chain scission processes leading to reductions of the average molecular weight and that of intrinsic viscosity. Nanocomposite samples prepared by the EIM method showed higher variations of intrinsic viscosity and higher polymer degradation during processing. It was concluded that nanoparticles act as nucleating agents and accelerate the crystallization kinetics. It is also noted that nanoparticles affect crystalline structure. Strain was observed to be related to dispersion: better dispersion result improved strain. Also all nanofillers strongly increased samples haziness.

Barber et al., [74] showed that organic modification of MMT clay coupled with modification of PET containing low levels of sodium sulphate (–SO$_3$-Na) ionomer group results in highly exfoliated PET nanocomposite by a simple melt extrusion process. They
concluded that the ionic interactions, created by the incorporation of random sulfonate groups into the backbone of PET, aid in the dispersion of the organically modified montmorillonite clay. This occurs through electrostatic interactions between the sulfonate groups along the polymer backbone and the edges of the clay platelets which facilitate movement of chain segments attached to the ionic group into the clay gallery. Mechanical properties of PET ionomer (PETI) nanocomposites were observed to be greatly improved over that of PET nanocomposites. Nanocomposites prepared from pristine MMT, did not show good dispersion of clay because of the absence of interactions and mostly showed aggregated structures. From crystallization studies, it is observed that pristine MMT acts as a better nucleating agent than other modified clays, resulting increases in the crystallization rate. It is concluded that better dispersion of clays in polymer matrix does not affect the crystallization process as much as the presence of aggregated clays.

Kracalik et al., [75] studied properties of nanocomposites prepared from pure as well as recycled PET. Modification of MMT was performed by using 1,2-dimethyl-3-octadecyl-1H-imidazol-3-ion and additional treatment was done by using [3-(glycidyloxy)propyl]trimethoxysilane. Nanocomposites prepared by this method showed substantial suppression of matrix degradation during melt mixing, compared to nanocomposite prepared from organoclays modified with quaternary ammonium compounds. Thermal behavior confirmed that nanoparticles act as nucleating agent and increase the rates of polymer crystallization. It was conferred that nanocomposites prepared from neat PET had better mechanical properties than nanocomposite prepared from recycled PET.

Among these different methods, the solution process is the least used method to prepare PET/clay nanocomposites. It is costly compare to other methods as it requires large amount of proper solvent. Research carried out by Kim [1] at the Polymer Institute, University of Toledo, indicated that the in-situ polymerization method is more useful
than melt intercalation as it gives more exfoliated clay platelets structures, results in better properties of PET nanocomposites. However, improvements in the properties of these nanocomposites were not as high as expected because of thermal degradation of organoclay.

3.4 Previous work on PET Nanocomposites at Polymer Institute, University of Toledo:

Kim [1] used modified clays to prepare polymer nanocomposite. For preparation of polymer nanocomposite, he used two methods:

1] In-situ polymerization

2] Melt intercalation

Also to study compatibility between polymer and clays, three different types of modified clays had been used to prepare PET nanocomposites whose properties are tabulated below in Table 3.1:

Table 3.1: Comparison between different organoclays [1]

<table>
<thead>
<tr>
<th>Factors</th>
<th>Cloisite 10A</th>
<th>Cloisite 15A</th>
<th>Cloisite 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal Spacing</td>
<td>19.2 Å</td>
<td>31.5 Å</td>
<td>18.5 Å</td>
</tr>
<tr>
<td>Compatibility*</td>
<td>+</td>
<td>0</td>
<td>++</td>
</tr>
<tr>
<td>Modifier conc.</td>
<td>125 meq/100g</td>
<td>125 meq/100g</td>
<td>90 meq/100g</td>
</tr>
<tr>
<td>Interaction Force</td>
<td>0</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Hydrophobicity</td>
<td>Low</td>
<td>High</td>
<td>Very low</td>
</tr>
</tbody>
</table>

*; + (Positive effect), - (Negative effect)
In the case of in-situ polymerization, two processes were used to evaluate the affinity of
the three clays with monomers or oligomers of PET as well as the effects of the residence
time of the clay in the reactor on nanostructure. The first process had been designated as
the ES clay addition process. This process contains esterification and polycondensation
steps with clay addition at the early stage of the esterification reaction. The second
process had been designated as PC clay addition process and includes clay addition in the
polycondensation step. During in-situ polymerization, different methods were used in
order to increase maximum exfoliation and optimal properties of the PET/clay
nanocomposites. These methods included varying the percentage of clay in the
nanocomposite, using different EG/TPA ratios, adding cyclohexane dimethanol
(CHDM).

From the PET nanocomposite samples prepared, specific two nanocomposites were
chosen to summarize results. The first one is a PET/15A nanocomposite, which was
prepared as a melt mixture of IV 0.74 dL/g PET and Cloisite 15A, and second one is the
PET/30B nanocomposite, which was melt polymerized at 270 °C by the PC clay addition
method with BHET, prepared by EG/TPA=1.2/1 mole ratio.

From morphological analysis of PET/15A clay nanocomposite, no change in interlayer
spacing of 15A clays was observed and the clays remained as tactoids in the polymer
matrix. However, for PET/30B nanocomposite, no major diffraction peak observed in
XRD as well as TEM images also showed increases in interlayer spacing of the clays and
disruption of tactoid structures, but small amount of agglomeration also were observed.
He concluded that the 30B clays were more compatible with PET Polymer compare to
15A and were well dispersed in polymer matrix. The lack of affinity between 15A Clays
and PET hampered the dispersion of clays in the polymer matrix. Both organoclays
observed thermally degraded at PET processing temperature (~ 280 °C) and showed an
agglomeration peak in X-ray diffraction. The exfoliated PET/30B nanocomposite had
11% improvement in tensile modulus and no improvement in tensile strength compared
with those of neat PET. After stretching, tensile modulus improvement disappeared. The exfoliated PET/30B nanocomposite had 29% reduced oxygen permeability at 3wt % clay than that of neat PET, but stretching hampered this improvement also. Tactoid structure of 15A clay did not show any improvement in permeability of nanocomposite. As expected, PET/15A nanocomposites did not have any impact on barrier properties of PET because of tactoid structures of 15A into the polymer matrix. Kim [1] did density calculation, microscopy and DSC experiment on stretched samples and concluded that stretching process caused third component generation in nanocomposite films such as micro voids which affected the polymer properties.

The main problem faced by Kim was the thermal degradation of organoclay. He observed that organoclay gets thermally degraded above 220 °C [1,37] and the PET preparation and processing temperature is above 250 °C. As a result, degradation of clay took place during PET preparation and PET processing. This gave rise to agglomeration of clay in the PET matrix, resulting in hampering properties of nanocomposite.
3.5 Research Objective:

Different methods and ways have been tried to prepare PET/clay nanocomposites. The PET nanocomposites prepared from these methods have shown better thermal, mechanical and barrier properties than that of neat PET. However, improvements in properties were not observed to be significant enough to commercialize the process. For different polymers such as nylon 6, it has been observed that when clays are well dispersed in polymer matrices, resulting polymer shows excellent increase in properties compared to neat base polymer or conventional composite polymer [9-11]. However till now, complete clay dispersion and resulting in high property enhancements have not been achieved in the case of PET polymer, so it was decided to continue research in this area.

It has been observed that organoclays get thermally degraded at PET preparation and processing temperature [1] and hamper the exfoliation and properties of resulting PET nanocomposites. Many researchers have tried to prepare PET nanocomposites by using thermally stable organoclays so degradation could be avoided but expected results were not observed. In my research project, it was decided to use pristine MMT (natural clay or Na⁺MMT) to prepare PET/clay nanocomposites so that thermal degradation and agglomeration problems can be avoided. Kim [1] has proved that in-situ polymerization is better method to prepare PET nanocomposites compared to melt blending. So it was decided to use in-situ polymerization method to prepare PET/Na⁺MMT clay nanocomposite. Some research groups have previously used an in-situ polymerization method to prepare PET nanocomposites. While doing so, however, they directly added clay in to the polymerization reactor. In this research project, it was decided to take new approach and to disperse clay in to the monomers of PET by using appropriate solvents before polymerization reaction is carried out. This step would help intercalation of PET monomers into the interlayer galleries of clay platelets and polymerization step will further separates clay platelets as the PET polymer chains grow. Another main objective
of this research was to study in detail the thermal, mechanical, morphological, and gas barrier properties of PET/Na⁺MMT clay nanocomposites.
CHAPTER IV

EXPERIMENTAL

4.1 Materials:

Ethylene glycol (polymerization grade) was purchased from May’s chemical company and Wellman Inc. Terephthalic acid was kindly donated by Amoco chemical company. Cyclohexane dimethanol, antimony trioxide, cobalt acetate, phosphoric acid, triphenyl phosphate, and tetramethylammonium hydroxide were purchased from Fischer Scientific. Pristine MMT (natural) clay was obtained from Southern Clay Products, Inc., and used as received without further chemical treatment.

Properties of natural clay (Na⁺MMT) [87]:

Table 4.1: Properties of Na⁺MMT

<table>
<thead>
<tr>
<th>Properties</th>
<th>Na⁺MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Modifier</td>
<td>None</td>
</tr>
<tr>
<td>Cation Exchange Capacity (CEC)</td>
<td>92.5 meq/100g clay</td>
</tr>
<tr>
<td>% Moisture</td>
<td>&lt; 2%</td>
</tr>
<tr>
<td>% Weight Loss on Ignition</td>
<td>7%</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>2.86</td>
</tr>
</tbody>
</table>

Typical Dry Particle Sizes: (Microns, by volume):

10% less than: 2 ; 50 % less than: 6 ; 90% less than: 13 ;
Basal spacing: X-ray diffraction result = 1.12 nm

The bench scale polymerization system was provided by RTI Engineering Co., Ltd., South Korea. This melt polymerization system is equipped with an esterification reactor and a polycondensation reactor having 2 gallon capacity each.

4.2 Optical Microscopy:

Optical microscopes have a wide variety of applications; they are very powerful tools for inspecting the microstructure of a range of materials. It is important to use the appropriate mode for the specimen, choosing from reflected-light or transmitted-light modes. A Carl Zeiss Inc microscope equipped with Sony CCD-IRIS/RGB color video camera was used to investigate the presence of impurities and residual stress in the sheets and films at 50 x 1.25 magnification ratios.

4.3 Melt Intrinsic Viscosity:

Intrinsic viscosities (IV) of the samples were measured by the conversion of shear viscosity into intrinsic viscosity. The Melt IV was measured using Rheometric Dynamic Analyzer (RDA III). A parallel plate RDA III was used to perform the dynamic test on the polymer melt sample. The visco-elastic properties of the polymer melt were studied as a function of frequency at a temperature of 280 °C in the presence of nitrogen gas to avoid oxidation.

Test conditions:

- Diameter of die = 25 mm
- Frequency sweep = 10 rad/sec
- Strain = 20%
Gap between parallel plates = 1 mm

Temperature = 280 °C

The environmental chamber was initially heated to 280 °C, the dried polymer sample was placed on the lower plate, and the distance between the plates was set at 1 mm. The oven door was closed and the test progress was observed on the monitor as the frequency increases. The viscosity was observed as a function of frequency (strain rate). In our study, we used the viscosity of materials at a shear rate of 10 sec⁻¹, to replace the zero-shear viscosity. The following relationship between melt IV and the viscosity was used:

\[ IV = m \ln(\eta^*) + b \]  

Equation 8

Here \( \eta^* \) is the complex viscosity at a shear rate of 10 sec⁻¹,

The \( m \) and \( b \) are constants, calculated by calibrating the instrument with pure PET samples of known IVs and in this study,

\[ m = 0.14616 \]
\[ b = -0.18562 \]

4.4 Single Screw Brabender Extrusion:

Extruders are among the most important pieces of equipment in the polymer processing industry. For material which is available only in small quantity, a Brabender is an ideal research tool to evaluate such material. A laboratory scale Brabender single screw extrusion was used to obtain the ribbon sheets with the following parameters: screw diameter \( D=19 \) mm, \( L/D=22/1 \), and compression ratio=3/1. Before extrusion, pellets were
dried in a vacuum oven overnight at 140°C. Extrusion temperature was 280 °C and screw speed was 80 rpm. An extruded sheet was quenched with winder cooling rolls to obtain uniform thickness of the amorphous sheet. All the polymer sheet samples obtained after extrusion were kept at constant temperature and constant relative humidity (25°C and 50 % R.H.)

4.5 Density and Crystallinity Measurement:

The density of a polymer sample can indicate its crystallinity or, in the case of a glassy polymer, its thermo-mechanical history. Density is a measure of the “compactness” of matter within a substance and is defined by the equation:

\[
\text{Density} = \frac{\text{mass}}{\text{volume}}
\]

Equation 9

The standard metric units in use for mass and volume respectively are grams and milliters or cubic centimeters. Thus, density has the unit grams/milliter (g/ml) or grams/cubic centimeters (g/cc).

Densities of the films were measured at 25 °C with a density gradient column filled with aqueous calcium nitrate solutions. This method follows American Society for Testing and Materials (ASTM) D792-91.
Numerical calculation:

\[
\text{Density at } x = a + \frac{(x-y)(b-a)}{(z-y)} \quad \text{.......Equation 10}
\]

Where:

- \(a\) and \(b\) = densities of the two standard floats bracketing the unknown
- \(y\) and \(z\) = height of the two standard, \(a\) and \(b\), respectively,
- \(x\) = height of unknown.

Volume fraction crystallinity (\(f\)) was calculated from the density values using the following relationship.

\[
\text{Crystallinity (f)} = \frac{(d - da) \times 100}{(dc - da)} \quad \text{.............Equation 11}
\]

Where,

- \(d\) = sample density
- \(da\) = the density of amorphous PET (1.333 g/cc)
- \(dc\) = the density of completely crystalline PET (1.455 g/cc) [82, 83]
4.6 Thermal Analysis:

4.6.1 Differential Scanning Calorimeter (DSC):

Differential scanning calorimeter is an invaluable tool in polymer science and engineering. The differential scanning calorimeter or DSC for short determines critical information, such as: the glass transition state, the melt transition state, the crystallization transition state, and heat capacity and percent crystallinity. These characteristics are critical pieces of information used in polymer processing and research. This makes the differential scanning calorimeter a very important instrument in the polymer industry.

The setup of the DSC instrument is fairly simple as shown in the following Fig. 4.1. In the instrument, there are two pans placed in to a chamber. One of the pans contains a polymer sample of a known weight. The other pan is identical to the first one; however, it contains no sample. This is the reference pan. These pans are heated up, simultaneously, with the instrument’s heating element. Precisely, similar conditions for each pan are essential. Also nitrogen gas is used to create nitrogen gas atmosphere around both pans. This eliminates the possibility of any moisture or oxygen contamination with the pans.

![Figure 4.1: Schematic representation of DSC equipment](image)
Both pans in the chamber are heated at a desired rate. Computer software makes sure that both pans get heated at absolutely same heating rates. Since a sample pan contains a polymer sample, it takes more energy to heat it in comparison to the reference pan. The difference in energy is measured by the DSC. The difference in the energy is shown as a graph on computer screen called as a thermograph [84].

The differential scanning calorimeter used in the thermal analysis was a Perkin Elmer DSC-7 (Shelton, CT) calibrated with indium and zinc standards. The samples with weight in the range 5 to 12 mg heated and cooled in N2 environment.

4.6.2 Thermal Gravimetric Analysis (TGA) Measurements:

Thermal gravimetric Analyzer (Fig. 4.2) is a simple thermal property analysis technique that measures the weight loss of material over wide range of temperature. It requires high degree of precision in weight, temperature and temperature change measurements. As materials are heated, they can lose weight by water loss by drying, decomposition by chemical reactions such as oxidation and result in liberating gases. Since the weight loss is a disruptive process for a sample material, knowledge of the magnitude and temperature range of those reactions are necessary in order to design adequate thermal ramps and holds during those critical reaction periods.
Thermal Gravimetric Analysis (TGA) was conducted on a Q500 TGA instrument (Fig. 4.2) under nitrogen atmosphere. The samples with weight between 5-10mg were heated from room temperature to 800°C at a rate of 20°C/min. Each sample was placed into a platinum pan attached to a sensitive microbalance assembly. The sample holder portion of the TGA balance assembly is then placed into a high temperature furnace. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight as heating rate increases. Weight loss profiles are analyzed for the amount or percent of weight loss at any given temperature, the amount or percent of non-combusted residue at some final temperature, and the temperatures of various sample degradation processes.
4.7 Mechanical Property Analysis:

4.7.1 Instron Tester:

Tensile modulus, strength and maximum strain were measured with an Instron 4400R tester according to ASTM D 638 type IV. The specimens for this study were prepared with dog bone die and press. Test conditions are 2 in/min crosshead speed, 50% humidity, and 23°C temperature. Specimen dimensions of sheets were 6.5 inch length, 2 inch gage length, and 0.5 inch width. Thickness of every specimen was measured with micrometer. The film samples were then clamped in the upper and lower grips of the instron tensile tester.

Tensile strength, tensile modulus and percent elongation were measured at a cross head speed of 2 in/min. The instrument was connected to a computer and the tensile strength at break (MPa), modulus at break (MPa) and percent elongation at break were automatically calculated. 10~15 specimens were measured per one sample and averaged. All the samples were conditioned for more than 50 hours under 25 °C and 50 % RH before measuring tensile properties.

**Tensile Strength:** The ability of a material to resist breaking under tensile stress is called as tensile strength. It is one of the most important and widely measured properties of materials used in structural applications. The definition of break or failure can vary according to material type and design methodology. The force per unit area required to break a material in such a manner is the ultimate tensile strength or tensile strength at break.

\[
\text{Tensile Strength} = \frac{\text{Force(Load)(N)}}{\text{Cross Section Area (mm2)}}
\]

………..Equation 12
**Tensile Modulus:** The tensile modulus is the ratio of stress to elastic strain in tension. A high tensile modulus means that the material is rigid - more stress is required to produce a given amount of strain.

\[
\text{Tensile Modulus} = \frac{\Delta \text{Stress}}{\Delta \text{corresponding Strain}}
\]

……..Equation 13

**Tensile Elongation:** The ultimate elongation of an engineering material is the percentage increase in length that occurs before it breaks under tension. Ultimate elongation values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid plastics, especially fiber reinforced ones, often exhibit values under 5%. The combination of high ultimate tensile strength and high elongation leads to materials of high toughness.

\[
\text{Strain} = \frac{\Delta \text{Length}}{\text{Original Length}}
\]

\[
\varepsilon = \frac{\Delta L}{L}
\]

Elongation at break: \( \Delta L = \varepsilon \text{ (at break) } \times L \)

\% Elongation at break = \( \Delta L \times 100 \)

……..Equation 14
4.8 Morphological Analysis:

4.8.1 Basal Space Measurement by Wide Angle X-ray Diffraction:

Wide angle diffraction of monochromatic X-rays is often used to study clay dispersion in polymer nanocomposites. X-ray powder diffraction (XRD) is a rapid, non-destructive analytical technique used for phase identification of a crystalline material and can provide information on unit cell dimensions and clay dispersion. The analyzed material is finely ground, homogenized, and average bulk composition is determined. Either intercalated or exfoliated nanostructure in polymer matrix can be identified by monitoring the position, shape and intensity of basal reflections from the material.

As the wavelength of x-rays is in the range of the size of atoms, because of this, they are useful for investigating the structural arrangement of atoms and molecules in different materials. The x-rays penetrate into the materials and provide information about the morphological structure (Fig. 4.3) [86].

![Figure 4.3: Schematic representation of X-ray diffraction](image-url)
The general relationship between the wavelength of the incident x-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg's law,

\[ n \lambda = 2d \sin \Theta \]  

Equation 15

Where, \( n \) (an integer) is the "order" of reflection,
\( \lambda \) is the wavelength of the incident X-rays,
\( d \) is the interplanar spacing of the crystal and
\( \Theta \) is the angle of incidence.

When clay platelets are completely exfoliated in a polymer matrix, it can be observed from the disappearance of any coherent XRD, whereas the finite layer expansion observed in intercalated nanocomposite is associated with the appearance of new diffraction peak corresponding to larger gallery height.

The basal spacing of nanocomposites and clays were determined by a wide angle x-ray diffraction technique using Rigaku Ultima III Multipurpose X-ray diffraction system; Nickel filter, K-\( \alpha \) (1.541 Å), scan speed (0.4 °/min), in the range of \( 2\theta = 1.5° \sim 9° \) at 45 kV and 40 mA.
4.8.2 Transmission Electron Microscopy (TEM):

To investigate polymer nanocomposite structure thoroughly, it is necessary to perform TEM analysis. It has been observed that XRD does not give clear idea about polymer morphology and it is used to estimate intercalation and exfoliation. The transmission electron microscope (TEM) would help further investigate morphology of polymer nanocomposites. Transmission Electron Microscopy is the microscopy technique which operates on the same principles as the light microscope but uses electrons instead of light to analyze the sample, (Fig. 4.4). In TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density and composition. TEM provides detailed structural information at levels down to atomic dimensions. The most capable TEM can resolve detail at the 0.1 nm level, but such high resolution examination is not usually possible with polymers. By using TEM to analyze polymer nanocomposites, it is possible to obtain information within the range 1 to 100 nm with varying degree of difficulty. This is beyond the range of light microscopy. Another main advantage of the TEM is that it can be easily adjusted to provide electron diffraction patterns of a selected area, facilitating investigation of crystal structure, orientation and enabling particular morphological analysis. The formed image is made visible on a fluorescent screen or it is documented on photographic material. Photos taken with electron microscopes are always black and white. The degree of darkness corresponds to the electron density (differences in atom masses) of the sample.
To do the morphological analysis, we used a Hitachi HD-2300A Scanning Transmission Electron Microscope (situated at the Center for Materials and Sensor Characterization Laboratory, UT) with LKB Nova ultramicrotome. Before using microtome, polymer nanocomposite samples were imbedded in epoxy resin. After curing the epoxy resin, Ultra thin sections of nanocomposite samples were cut by using a LKB nova
ultramicrotome with glass knives. The sample slicing speed was 1mm/s. These samples had thickness in the range of 50 -100 nm. These sections were collected on 300 mesh copper grids and subsequently dried with filter paper, (Fig. 4.5).

Figure 4.5: TEM sample support mesh "copper grid"

During the TEM analysis, the film samples were mounted on an electron gun and inserted into the vacuum chamber which was set at $10^{-7}$ torr pressure. These ultrathin samples were then analyzed by HD-2300A TEM at 200 kV accelerating voltage.

4.9 Oxygen Permeability Test:

One of the main objectives of this research was to improve oxygen barrier properties of PET. The oxygen permeability tests of PET nanocomposite films with different clay wt% loadings were done using the MoCon OxTran 1050 permeability tester according to the ASTM D3985 method (Figure 4.6). These tests were carried out at 23°C and nearly 1 atm. Three samples from each PET nanocomposite were analyzed to determine the effects of MMT clay loadings on the permeation of oxygen through the PET nanocomposite films. The tests were carried out at 50% relative humidity. Prior to performing the test, the films were cut to fit the 12 cm² area of the circular test holder of the permeation cell.
All samples were conditioned for at least twelve hours in the apparatus before commencing the test. During the test, the permeation cell was flushed with oxygen gas on one side and nitrogen carrier gas on the other side. The flow rates of the oxygen and nitrogen gas were 25 cm$^3$/min. This nitrogen gas swept any oxygen towards the coulometric sensor for detection. The oxygen reacts with coulometric detector and generates electric current proportional to the amount of oxygen permeated.

Figure 4.6: Oxygen Permeability Test ASTM D 3985
CHAPTER V

RESULTS AND DISCUSSION

5.1 Na⁺ MMT Clay Selection for PET Nanocomposite:

One major hurdle preventing polymer/clay nanocomposites use in many potential applications is the difficulty to achieve a high degree of exfoliation of clay platelets in polymer matrices. In recent years, many research groups from both academic institutes and industrial sectors have been working on different methods to facilitate clay exfoliation. One frequently used strategy is to modify inorganic clay using organic additives in a hope that the compatibility between hydrophobic polymer and hydrophilic clay is improved and clay exfoliation can be facilitated. However, the structure of the clay tactoids often remains even with the aid of organic modifiers and the modified organoclay is more likely intercalated rather than fully exfoliated. As reported in the literature, most of the nanocomposites usually have a heterogeneous morphology comprising both exfoliated and intercalated structures [59-72]. While transmission electron microscopy (TEM) and wide angle X-ray diffraction (XRD) often show that the clay galleries have been intercalated with polymer chains and the $d$-spacing was enlarged to more than 50 Å, large particle aggregates would be seen when examined under lower magnification (scanning electron microscopy or optical microscopy), indicating that clay particles were neither well-exfoliated nor uniformly dispersed in the polymer matrix. Obviously, the poor clay dispersion observed in conventional PET nanocomposites is mainly due to the preparation process and the intercalation-exfoliation mechanisms
involved. Thus, in most cases, the ordered structure of clay layers is still maintained although the interlayer distance can be enlarged to some extent.

Furthermore, for conventional organoclays, the organic modifiers generally amount to high (25-45) wt% of the modified clay, [37]. While the modified clay does show some advantages in increasing exfoliation and/or dispersion, the use of high content of organic modifier makes organoclay expensive, thermally unstable at higher temperature and polymer matrix-specific. To overcome the drawbacks in the conventional organoclay, Ke Wang et al. [76] reported a new approach in preparing epoxy clay nanocomposites using a “slurry-compounding” technique. This technique leads to a better clay exfoliation with only a very low concentration of organic modifier (<5 wt%). With this approach, the dispersion state of clay in water has been transferred into the epoxy matrix by a solvent exchange step and a surface modification step. The critical step is the replacement of water with organic solvent, which facilitates the surface modification and dispersion of modified clay in epoxy matrix. The most significant feature of the new technique is that absolutely no or very little amount of organic modifier is required to facilitate the high exfoliation and well-dispersion of the clay, which leads to a better clay exfoliation and excellent thermal mechanical property of the resulting nanocomposite. It is clear that the dispersion and exfoliation mechanisms in the new approach are different from that widely reported in epoxy/organoclay systems.

Natural clays are hydrophilic in nature so they get easily dispersed and exfoliated in the water. Polymers are hydrophobic or water susceptible in nature so no-one tried to transfer water exfoliated clays into polymer matrix. But after Ke Wang et al. [76] reported “slurry compounding” method, many research groups had dispersed clay into the water and transfer it to the polymer matrix by various methods.
5.2 Dispersion of Na⁺MMT Clay in the PET Monomers:

5.2.1 Dispersion of Na⁺MMT Clay in Ethylene Glycol:

After reviewing literature, it was decided to use natural clay (Na⁺MMT) for in-situ polymerization. Natural clay is thermally stable at PET preparation and processing temperatures because it does not contain any organic material in it. Jacobson et al. [77] showed that Pristine MMT clay (natural clay) can be easily disperse and exfoliated in water. Luyi Sun et al. [78] exchanged water dispersed clay into acetone by a centrifugation and dispersion method so that it can be transferred to hydrophobic epoxy polymer. Fortunately, ethylene glycol is miscible in water, so it will be easy to transfer exfoliated clays from water to ethylene glycol. Therefore, clays were dispersed into water first by ultra-sonification and then by using magnetic stirring and as shown in following Figure 5.1, it was concluded that clays were swelled/dispersed in water better when magnetiac stirring was used and resulting mixture kept suspended overnight (Fig. 5.1c). In Figure 5.1a, it can be clearly seen that clay tactoids are suspended in water. However, after magnetic stirring, optical microscopy picture are clear and we did not see any black spots (clay tactoids) in optical microscopy pictures.
5.1a: Clay dispersion in water by ultrasonification

Figure 5.1b: Na⁺MMT clay dispersion in water after 6 hours magnetic stirring
As ethylene glycol is also hydrophilic in nature, the clay was dispersed directly into ethylene glycol. However, clay did not completely dispersed into the EG and suspension of clay in the mixture was observed.

Ethylene glycol is miscible in the water so instead of using any other solvent, it was decided to transfer dispersed clay from water to the ethylene glycol. Water-dispersed clay solution was prepared and ethylene glycol was added to it. As ethylene glycol has a boiling point 197 °C which is higher than that of water’s boiling point, it was decided to remove water from dispersion by evaporation, while heating the mixture above 100 °C. It was observed that as long as there was sufficient water present, clay platelets remained well dispersed in the solution, but as the water percentage in the mixture was reduced, agglomeration of clays in the ethylene glycol was observed and the mixture started to become viscous (Fig. 5.1d). This may be because when clays are exfoliated, they require
certain volume to remain exfoliated but as water was removed from the mixture, clay platelets in the mixture did not have enough volume to remain exfoliated and the mixture became viscous, [79]. During polymerization, if TPA was added to this viscous mixture then solid TPA may hamper the exfoliation of the clay.

Figure 5.1d: Viscous mixture obtained after removal of water from water-clay-ethylene glycol mixture
5.2.2 Dispersion of Na⁺MMT Clay in BHET:

Attempt was made to disperse pristine MMT clays directly into melt BHET (bis (hydroxyethyl) terephthalate). It was observed that result was similar to those achieved in the case of ethylene glycol as the clays became suspended in the BHET as shown in Fig. 5.2.

![Image of clay dispersion in BHET](image)

Figure 5.2: Direct clay dispersion in melted BHET (Image obtained by using a Carl Zeiss Inc. optical microscope)

We can clearly see agglomeration and tactoids of clays in the BHET from the picture (Figure 5.2).

D Acierno et al. [80] reported that BHET could be well dispersed in ethanol at room temperature. They dispersed clay into the water and transferred the water dispersed clay into the BHET which was then dispersed in Ethanol. After stirring this mixture for 3 hr at 70 °C and 5 rpm, solvents were evaporated and pristine MMT modified with BHET was
prepared. BHET is the intermediate monomer for the PET and D. Acierno et al. [80] showed it can be used to modify pristine MMT (Na⁺MMT) so it was decided to use this method to disperse clay into BHET. For this experiment, 50 grams of pure BHET was dispersed into 800 ml of ethanol with magnetic stirring for the 2 hours and in this dispersion, water dispersed clay was added and whole solution was stirred for next 2 hours, after that ethanol and water were evaporated by using a hot plate at atmospheric pressure so solid BHET was obtained with 5 wt% clay dispersion in it. Then BHET was powdered and dried in a vacuum dryer for the next 24 hr. After drying, a wide angle X-ray diffraction pattern was obtained for the BHET-clay powder (Fig. 5.3).

Figure 5.3: XRD results for Na⁺MMT, BHET-clay dispersion and pure BHET
From the XRD result (Fig. 5.3), it can be clearly seen that BHET has become intercalated in MMT clay platelets and has increased the basal spacing of the clay. In the XRD, BHET-clay powder gave peak at $2\Theta = 4.45^\circ$ which is equivalent to interlayer spacing $d = 1.96$ nm. Pristine MMT platelets have interlayer spacing $(d) = 1.12$ nm, which gives diffraction peak at $2\Theta = 7.3^\circ$ (Figure 5.3). As a result, it can be concluded that because of intercalation of BHET in clay platelets, interlayer space has been increased from 1.12 nm to 1.96 nm i.e. by 0.84 nm. To make sure this diffraction peak is result of intercalation and not BHET peak, XRD pattern of pure BHET was obtained (Fig. 5.3) and it did not have any diffraction peaks up to $2\Theta = 9^\circ$. So it was concluded that peak at $2\Theta = 4.45^\circ$ was due to intercalation of BHET in clay platelet gallery (Figure 5.4). If polymerization
of this BHET was carried out, which is intercalated in clay platelets, then during polymerization as the polymer chains grow and molecular weight of PET increases, it will definitely make clay platelets to go apart and increase the interlayer spacing between platelets. This should result in better dispersion of MMT clays into the PET polymer matrix.

5.4 Preparation of PET/Na\(^+\)MMT Clay Nanocomposite:

A bench scale polymerization system made by RTI Engineering Co., Ltd., South Korea was used to prepare PET by a melt polymerization process consisting of two steps (esterification and polycondensation) (Figure 5.5). Initially EG and TPA are added to the esterification reactor in 1.5:1 mole ratio. At the start of the reaction, drops of tetramethylammonium hydroxide (TMAH) are added to reactor to act as a diethylene glycol (DEG) suppressor. Esterification reactions are carried out at 220~240 °C and 1.2 kgf/cm\(^2\) of nitrogen (N\(_2\)) pressure. During the esterification reaction, water and BHET are produced. Water is continuously removed during the reaction by distillation and the reaction was stopped when all EG and TPA are reacted to give a colorless BHET solution. The polycondensation reaction is carried out at 275 °C under high vacuum (1~2 torr) by transferring BHET to PC reactor. The amounts of additives for the polycondensation reaction were 250 ppm antimony (Sb), 30 ppm cobalt (Co), and 20 ppm phosphorous (P). These additives were added at the same time with nitrogen flow in the early stage of polycondensation reaction. Before adding these additives, antimony trioxide (Sb\(_2\)O\(_3\)) was mixed with ethylene glycol and heated up to 150 °C for 2 hrs to form antimony glycolate. Cobalt acetate was mixed with hot ethylene glycol to prepare a solution and added to the PC reactor. In this way, neat PET was prepared which was used to compare with the properties of the PET nanocomposites.
As PET melt polymerization has two steps, the clay can be introduced into the reaction system by two different ways:

[1] ES clay addition: by dispersing clay into EG or

[2] PC clay addition: by dispersing clay into BHET.

Figure 5.5: In-situ polymerization reactor system used to prepare PET and PET/Na⁺MMT clay nanocomposites [1]
5.4.1 ES Clay Addition:

In the process of ES clay addition, the proper amounts of clay and water were added to esterification reactor and stirred for 4 hr. Next ethylene glycol and TPA were added in 1.5 mole ratios to the clay dispersion in water and whole mixture was stirred further for 4 hr at 70 °C. Then reactor temperature was raised to esterification reaction temperature (220-240 °C). As the temperature was increased, water was distilled out. When temperature reached in the specific range, esterification was carried out to produce BHET, which was added to the polycondensation reactor and polycondensation reaction was carried out at 275 °C. Using this method, PET nanocomposites were prepared with different clay wt% (0.25-2) in PET matrices.

5.4.2 PC Clay Addition:

In the case of PC clay addition method, BHET was prepared by esterification of EG and TPA in the esterification reactor and taken out and crushed into small pieces. A gallon of ethanol (95%), proper amount of clay and 100 grams of BHET were added to PC reactor and the mixture was stirred for 6 hours at 70 °C to prepare a master batch solution. The remaining amount of crushed BHET was added to the mixture while continuously stirring the whole mixture. Ethanol was evaporated by heating the mixture above boiling point of ethanol (78 °C). BHET and Na⁺MMT clay mixture then dried at 130 °C for 15 hr and the polycondensation reaction was carried at 275 °C. Using this PC clay addition method, PET nanocomposites were prepared with different clay wt% (0.6-5) in nanocomposite.

To reduce the cost of the PC clay addition process, instead of using Ethanol, we tried to disperse BHET directly into the water in which clay was already dispersed. After stirring mixture for 4 hours, water was evaporated and X-ray diffraction was carried out on the BHET- Na⁺MMT clay mixture. It was observed that BHET becomes intercalated in Na⁺MMT platelets without using ethanol. However, because of large amount of water
remaining along with BHET and MMT platelets, polycondensation reaction failed to produce proper PET resin.

5.5 Chemicals and Their Usage during Melt Polymerization:

Various chemicals were used during melt polymerization. These chemicals and their uses during melt polymerization are tabulated in the following table.

<table>
<thead>
<tr>
<th>Name</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>Monomer</td>
</tr>
<tr>
<td>Terephthalic Acid</td>
<td>Monomer</td>
</tr>
<tr>
<td>Antimony trioxide</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Cobalt acetate</td>
<td>Colorant</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>Metal Stabilizer</td>
</tr>
<tr>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>DEG Suppressor</td>
</tr>
<tr>
<td>Na⁺MMT/ Pristine MMT (Cloisite Na⁺)</td>
<td>Nano-sized Fillers</td>
</tr>
</tbody>
</table>
5.6 Intrinsic Viscosity Measurement by RDA III:

Intrinsic viscosities of all polymer nanocomposite dried pellet samples were measured using a Rheometric Dynamic Analyzer III. It was observed that all samples have IV in the range of 0.65 to 0.71. The viscosity of PET nanocomposite sample was controlled by monitoring the torque applied for the stirring. As a reaction progress, the polymer solution in the reactor becomes more and more viscous. As a result, more torque is required to keep constant stirring rate. By monitoring the torque value, we can estimate the reaction progress and so the IV values of corresponding PET nanocomposite. The IV values of PET/Na⁺MMT nanocomposites are as shown in following Table 5.2.

Table 5.2: IV values of melt phase polymerized PET/Na⁺MMT nanocomposites

<table>
<thead>
<tr>
<th>Polymer Composition</th>
<th>Intrinsic Viscosity (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES 0.5% wt clay addition</td>
<td>0.70</td>
</tr>
<tr>
<td>ES 2% wt clay addition</td>
<td>0.65</td>
</tr>
<tr>
<td>PC 0.6% wt clay addition</td>
<td>0.66</td>
</tr>
<tr>
<td>PC 2% wt clay addition</td>
<td>0.71</td>
</tr>
</tbody>
</table>
5.7 Thermal Analysis of PET/ Na⁺MMT Nanocomposites:

5.7.1 Thermal Characterizations by DSC:

A Perkin Elmer DSC-7 (Shelton, CT), differential scanning calorimeter, was used to do thermal analysis of PET nanocomposites. Different DSC measurements carried out to evaluate crystallization behavior of PET nanocomposite. To confirm the results, each DSC measurement was carried out at least three times. Although small variation (5%) observed in results, trends observed were similar to results reported and discussed in this section.

5.7.1.1 DSC Measurement 1:

This DSC measurement was carried out to compare the initial crystallinity of neat PET and PET/ Na⁺MMT nanocomposites films obtained from extrusion. PET and PET/ Na⁺MMT nanocomposite (extruded and converted to film) samples were stress relieved by heating up to 90 °C for 15 minutes and then dried for 24 hours at 60°C. Thermal characterization of the polymer samples (8-12 mg) were carried out using DSC. Figure 5.6 shows thermograms for PET and 0.5% ES clay addition nanocomposite, where the following procedure followed with nanocomposite samples:

Procedure:

[1] Holding a sample at 40 °C for 3 min

[2] Heating from 40°C to 300°C at 10°C/min

[3] Holding sample at 300°C for 5 min
The DSC spectra in Fig. 5.6 show no fundamental differences between neat PET and nanocomposite properties. Glass transition temperature (Tg) and melting temperature (Tm) of polymer samples remained unaffected, (Table 5.3). The crystallization temperature of nanocomposite shifted to lower temperature while heating because of nucleating effect of Na⁺MMT clay in PET matrix. Also initial crystallinity of polymer samples was measured using following formula:

\[ X_c = \frac{(\Delta H_f - \Delta H_c) \times 100}{\Delta H_f^0} \]

Where, \( \Delta H_f \) is the enthalpy of fusion

\( \Delta H_c \) the enthalpy of crystallization

\( \Delta H_f^0 \) the heat of fusion of the completely crystalline materials at the equilibrium melting temperature (135 J/g) [88-91]
Figure 5.6: DSC thermographs for neat PET and ES 0.5 wt% clay addition PET nanocomposite obtained by following procedure for measurement 1 to calculate initial crystallinity
Table 5.3: DSC data for measurement 1 for neat PET and ES 0.5 wt% clay addition PET nanocomposite obtained from Fig. 5.6

<table>
<thead>
<tr>
<th>Polymer Composition</th>
<th>Tg (°C)</th>
<th>-ΔH_c (J/g)</th>
<th>ΔH_f (J/g)</th>
<th>Tm (°C)</th>
<th>% X_c (Initial Xc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>80</td>
<td>21</td>
<td>37</td>
<td>252</td>
<td>12</td>
</tr>
<tr>
<td>0.5% MMT (ES clay addition)</td>
<td>78</td>
<td>17</td>
<td>37</td>
<td>251.5</td>
<td>15</td>
</tr>
</tbody>
</table>

From Table 5.3, it can be seen that, there is no significant change in melting and glass transition temperature. Also for these samples, crystallinity was calculated from above formula and it can be seen that extruded PET and PET/ Na⁺MMT nanocomposites sheets do not have high crystallinity and the degree of crystallinity of neat PET and nanocomposite is nearly in the same range. The mechanical properties of the polymer get affected by the amount of crystalline and amorphous phase that exist in the polymer matrix. [92]. However, from this DSC measurement, we can conclude that if there is any change in mechanical properties of neat PET and PET/ Na⁺MMT nanocomposites, then crystallinity of the polymer will be very minute factor in it. This procedure was followed for other PET nanocomposites (Fig. 5.7) and it is observed that crystallinity of all samples were in the range of 10% to 20%.
Figure 5.7: DSC thermographs for neat PET, ES 2 wt% clay addition, PC 2 wt% and 5 wt% PET nanocomposites obtained to calculate initial crystallinity of the extruded films.
J. Jordan et al. [93] in their polymer nanocomposite review concluded that there has been no major difference in degree of crystallinity found by addition of the MMT or CaCO$_3$ nanoparticles to polymer matrix. However, sizes of crystallites had been observed to be an order smaller than that of neat polymer because of more nucleation sites in the nanocomposite [94-95].

E. Reynaud et al. [96] prepared PA6 polymer nanocomposites reinforced with silica nanoparticles by in situ polymerization. After carrying out thermal and morphological analysis, they concluded that the fillers presence (their concentration and size) do not have any effect on the crystalline phase of silica reinforced PA6 nanocomposites.

Tong wan et al. [97] prepared PET/clay nanocomposite by in situ polymerization process and performed crystallization morphology and isothermal crystallization behavior study. It was observed that the presence of clay does not significantly affect the crystal lattice parameters as well as crystallinity compare to those parameters in neat PET. They also reported that crystallites observed in nanocomposite were irregularly shaped, having no clear boundaries as they interlocked with each other. Ki Hong Kim et al. [98] also observed that crystallinity of neat PET and PET nanocomposites was nearly same. In our research, we also found that crystallinity of neat PET and PET/Na$^+$MMT nanocomposites is in the same range. If the crystallinity of a polymer sample is more than 30% then it can alter the mechanical properties noticeably. It is reasonable, therefore, to assume that the effects of crystallinity of PET/Na$^+$MMT nanocomposite sample on tensile properties was similar to neat PET and can be ignored [99].
5.7.1.2 DSC Measurement 2:

In the next DSC measurement, we dried PET and PET nanocomposites powdered pellets at 130°C in a vacuum oven overnight and then proper weight of sample (8-13 mg) was introduced into the DSC and heated to 300°C and cooled to 40°C by different cooling rates. This DSC measurement was carried out to study the effect of nano particles on crystallization behavior of PET polymer.

Procedure: [1] Holding at 40 °C for 3 min;

[2] Heating from 40°C to 300°C at 10°C/min

[3] Holding at 300°C for 5 min (to remove thermal history)

[4] Cooling from 300°C to 40°C at 300°C/min

[5] Holding at 40°C for 5 min

[6] Reheating from 40°C to 300°C at 10°C/min

[7] Holding at 300°C for 5 min

[8] Cooling from 300°C to 40°C at different cooling rates (5°C/min; 10°C/min; 20°C/min; 40°C/min)

DSC thermograms obtained from the above procedure are shown in Figs. 5.8 (step 6) and 5.9 (step 8). Before obtaining cooling scans at different cooling rates, it was made sure that the thermal history of each sample is removed by heating sample up to 300 °C and keeping sample at 300 °C temperature for next 5 min.
Figure 5.8a: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and various wt% of ES clay addition PET/ Na⁺ MMT nanocomposites (step 6-reheating thermograms)
Figure 5.8b: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and various wt% of PC clay addition PET/Na\textsuperscript{+}MMT nanocomposites (step 6-reheating thermograms)
Figure 5.9a: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and ES 0.5% clay addition PET/ Na⁺MMT nanocomposites (step 8- different cooling rates)
Figure 5.9b: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and ES 2 wt% clay addition PET/ Na⁺MMT nanocomposites (step 8- different cooling rates)
Figure 5.9c: DSC thermographs obtained from following procedure of DSC measurement 2 for PET and PC 2 wt% clay addition PET/ Na⁺MMT nanocomposites (step 8- different cooling rates)
The glass transition temperature (79 °C) and melting temperature (248 °C) of most of the nanocomposites remained nearly the same as that of neat PET (Figure 5.8 a and b). We did not see any major effect of the clay’s presence on the thermal transition temperatures (Tg and Tm) of PET/Na+ MMT nanocomposite. From the thermograms of reheat (Figure 5.8 a and b), it can be clearly seen that most of the PC clay addition nanocomposites were already crystallized during quenching as these thermograms do not show any cold crystallization peak during reheating. The ES clay addition nanocomposites showed cold crystallization peak at low clay loading. As the clay content increased, this peak diminished indicating higher clay content resulted in higher agglomeration of clay, which acted as heterogeneous nucleating agents and caused nanocomposite to crystallized during quenching [100].

From the thermograms (Figure 5.9 a and b) of different cooling rates, it can be concluded that as clay contents increased, crystallization temperatures also increased. This result indicates that as clay content increased, clay agglomeration in polymer increased and this agglomerated clay acted as a nucleating agent, resulting in increases in crystallization rates and higher crystallization temperatures.

It is also observed that crystallization temperatures for PC clay addition nanocomposites were higher than in the case of ES clay addition nanocomposites for same clay wt% and same cooling rate (Figure 5.9 b and c). From this it can be concluded that clay was better dispersed in the polymer materials by the ES clay addition method at low clay contents. It has been observed that if clay remains intercalated and agglomerated in polymer material, than it acts as a nucleating agent and increases the rate of crystallization. If clay is well exfoliated, it does not affect the crystallization behavior of the polymer [104, 105].
5.7.1.3 DSC Measurement 3:

To compare the effect of different clay wt% on crystallization behavior of PET/clay nanocomposites at the same cooling and heating rates, following procedure was followed:

Procedure

[1] Holding at 40°C for 3 min

[2] Heating from 40°C to 300°C at 10°C/min

[3] Holding at 300°C for 5 min (to remove thermal history)

[4] Cooling from 300°C to 40°C at 10°C/min

[5] Holding at 40°C for 5 min

[6] Reheating from 40°C to 300°C at 10°C/min

[7] Holding at 300 °C for 5 min

[8] Cooling from 300°C to 40°C at 10°C/min

The important steps in the above procedures are step 4 and step 6. During the step 4, melt polymer sample was cooled to 40°C and cooling thermogram was obtained during which crystal formation took place. The step 6 was carried out to obtain reheating thermogram of polymer sample in which crystals formed during step 4 were melted and heat of melting was calculated.

Thermo-grams obtained from the DSC for above procedure are as shown below (Fig. 5.10):
Figure 5.10a: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of ES clay addition PET/ Na⁺MMT nanocomposites (step 4- cooling from 300 °C to 40 °C at 10°C/min)
Figure 5.10b: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of ES clay addition PET/ Na⁺MMT nanocomposites (step 6- Reheating from 40°C to 300°C at 10°C/min)
Figure 5.10c: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of PC clay addition PET/ Na\textsuperscript{+}MMT nanocomposites (step 4- cooling from 300 °C to 40 °C at 10°C/min)
Figure 5.10d: DSC thermographs obtained from following procedure of DSC measurement 3 for PET and various wt% of PC clay addition PET/ Na⁺MMT nanocomposites (step 6- Reheating from 40°C to 300°C at 10°C/min)
5.7.1.3.1 Non-isothermal Crystallization Behavior:

From the above thermo-grams (Figure 5.10), melting onset temperature ($T_{m, on}$), melting temperature ($T_m$), crystallization onset temperature ($T_{c, on}$), crystallization temperature, Heat of fusion ($\Delta H_f$) and heat of crystallization ($\Delta H_c$) obtained and tabulated in the Table 5.4. It is clear that there is distinct exothermic crystallization peak in all cooling scans, and the peak is symmetrical in nature. As the crystallization peak is symmetrical in nature, the half crystallization time ($t_{1/2}$) of non isothermal cooling can be obtained from following equation [104]:

$$t_{1/2} = \frac{(T_{c, on} - T_c)}{\chi}$$

Where, $t_{1/2}$ represents the necessary time required for the nanocomposites to reach 50% relative degree of crystallinity, $T_{c, on}$ is the crystallization onset temperature (temperature where the thermograph initially departs from the baseline), $T_c$ is the temperature where the exotherm shows a peak, and $\chi$ is the cooling rate.

It can be easily observed that, for a given cooling rate, $t_{1/2}$ values of PET/MMT nanocomposites are smaller than that of neat PET for all nanocomposites indicates that Na$^+$MMT clay plays a nucleating role during crystallization. It can be seen that $t_{1/2}$ values of ES clay addition nanocomposite are close to that of neat PET, this indicates that clays have not affected crystallization rate very much at low clay loading. All PC clay addition nanocomposites have smaller $t_{1/2}$ values than those prepared through the ES clay addition method for the same clay content.

On the other hand, the values of $\Delta H_c$ for ES and PC addition method nanocomposites are larger than that of neat PET and increase with increase in clay content. This means for a given cooling rate, there is more crystallization in PET/ Na$^+$MMT nanocomposites than neat PET. However increase in $\Delta H_c$ for ES clay addition method nanocomposites is far
smaller than the increase in ΔHc for nanocomposites prepared through PC clay addition method.

From values listed in Table 5.4, we can conclude that the crystallization onset temperature and the Tc values for PET/MMT nanocomposites are higher than those of neat PET because of the increase in crystallization rate.
Table 5.4: Thermal data collected from DSC thermographs of neat PET, ES and PC clay addition nanocomposites (following values were confirmed after three readings for each sample with maximum 5% standard deviation)

<table>
<thead>
<tr>
<th>Composition Of Polymer</th>
<th>Melting</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm, on (°C)</td>
<td>Tm (°C)</td>
</tr>
<tr>
<td>PET</td>
<td>207</td>
<td>248</td>
</tr>
<tr>
<td>PC clay addition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>206</td>
<td>248</td>
</tr>
<tr>
<td>1%</td>
<td>207</td>
<td>248</td>
</tr>
<tr>
<td>2%</td>
<td>206</td>
<td>248</td>
</tr>
<tr>
<td>5%</td>
<td>207</td>
<td>247</td>
</tr>
<tr>
<td>ES clay addition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25%</td>
<td>206</td>
<td>247</td>
</tr>
<tr>
<td>0.5%</td>
<td>204</td>
<td>248</td>
</tr>
<tr>
<td>1%</td>
<td>206</td>
<td>247</td>
</tr>
</tbody>
</table>
If the crystallization rate is defined as the heat of crystallization divided by the time from the onset to the completion of crystallization (ΔHc/time), then the crystallization rates for the nanocomposite are greater than that of neat PET. For PC clay addition method nanocomposites, slight increases in values of ΔHc/time are observed with increase in clay content in the PET nanocomposites. However ΔHc/time values for ES clay addition method fluctuate close to the value of neat PET and show that ES clay addition has not affected crystallization rate at low clay loading as much as the PC clay addition method has.

In programmed cooling, the crystallization temperature reflects the overall crystallization rate, attributed to the combined effects of nucleation and growth. The degree of super cooling (ΔTmc = Tm – Tc) may be measurement of a polymer’s crystallization ability; i.e., smaller the ΔT, the higher the overall crystallization rate. The ΔT values of PC clay addition nanocomposite are smaller by 10°C to 15°C than neat PET and PC clay addition PET/5% Na⁺MMT shows the smallest value. The result again confirms that the overall crystallization rate for the PET/MMT nanocomposite is greater than that of PET in PC clay addition. The ΔT values for ES clay addition nanocomposite are smaller by only 3°C to 4°C confirming similar crystallization rate similar to that of neat PET.

As shown in the Table 5.4, PET/5%MMT (PC clay addition) shows the highest crystallization onset temperature and Tc value, the greatest ΔHc/time, and the smallest ΔT among all nanocomposites prepared as expected because high clay content in PET matrix.

Cheng Fang Ou et al. [67] reported similar crystallization behavior of PET/Montmorillonite nanocomposites prepared from a solution intercalation process. The heat of crystallization, heat of fusion and crystallization rate was observed to be increased with increases in clay content up to 10 wt%. Further increases in clay wt% lead
to decreases in crystallization rate and the reason for this behavior was observed that above 10 wt%, there were no increases in heterogeneous nucleating sites.

Vahik Krikorian et al. [101] obtained complete exfoliation of organically modified clay in the poly (L-lactic acid) (PLLA) by melt intercalation. For fully exfoliated clay, they observed non nucleating behavior of clay. It was claimed that when clay was completely exfoliated in polymer matrix, clay platelets produced hindrance to the molecular chain movement. As interlayer spaces in clay the platelets increased, polymer becomes highly intercalated into this interlayer space. During crystallization, polymer chains need to reorient and arrange themselves in an orderly manner: however; exfoliated platelets confine the movement of polymer chains and reduces the tendency for polymer chains to be crystallized. They also observed nucleating behavior of clay in the case of intercalated PLLA/MMT nanocomposites which is consistent with our results as well as those reported in literature [41, 102].

Guohu Guan et al. [103] investigated crystallization behavior of PET/clay nanocomposites prepared by in situ polymerization. The DSC result clearly showed that Na⁺MMT clay effectively accelerated nucleation in PET; whereas modified clays were not as efficient as Na⁺MMT because of their compatibility with the PET matrix. Most of the nanocomposite showed intercalated morphology and clay tactoids in the polymer matrix increased the rate of crystallization. The sizes of tactoids observed in nanocomposites prepared from modified clays were larger than those in Na⁺MMT nanocomposite. This observation contributed to the higher nucleation density of Na⁺MMT nanocomposites which result in higher crystallization rate. Guohu et al. [103] also studied the effects of metal derivatives released from clay, on the nucleation rates of nanocomposite. The release of metal derivatives from the clay during nanocomposite preparation was affected by the surfactant molecules used to modify clay. The research indicated that metal derivatives released from Na⁺MMT significantly enhanced the crystallization ability of PET and thus acted as nucleating agents. Carmen Calcagno et al.
[104,105] obtained nearly complete exfoliation of clay into polypropylene/PET/clay nanocomposite with maleic anhydride modified polypropylene as compatibilizer. The presence of clay in PP/PET matrix resulted in decreases in crystallization rate of the PET phase. This result was more evident with the nanocomposite prepared with a compatibilizer. From morphological analysis, more of the clay was observed to be located in PET phase than in the PP phase. The retardation of crystallization rate was related to higher clay content in PET which makes it difficult for the polymer chains to reorient and crystallize.

These observations are similar to the trends observed in my research; however, there are some articles, as discussed below, which have claimed that although the clay is exfoliated in polymer matrix, it acts as a nucleating agent which contradict the above observations.

V. Causin et al. [107] studied crystallization behavior of isotactic polypropylene/clay nanocomposites. It was concluded that the greatest nucleating activity was observed when MMT clay was exfoliated, while it reduced when it was intercalated. The spherulite dimensions were observed to be in the decreasing order from the base polymer, to the intercalated nanocomposite to the exfoliated nanocomposites. That means exfoliated MMT platelets acted as a nucleating agents and more spherulites were observed in exfoliated nanocomposite because of more nucleating sites.
5.7.2 Thermal Stability Analysis by TGA:

To get the information about thermal stability and exact weight percentage of Na⁺MMT clay into the PET matrix, I carried out thermal gravimetric analysis of PET/ Na⁺MMT nanocomposites. The thermal degradation onset temperature, temperature at 50 wt% degradation and weight % of clay into the PET matrix are obtained from the Figure 5.11 and tabulated in Table 5.5. The thermal degradation onset temperature is the temperature at which first major change in weight of PET nanocomposite sample was observed. The temperature at 50 wt% degradation obtained from the Figure 5.11 and it’s the temperature at which 50 wt% degradation of the PET nanocomposite sample took place.
Figure 5.11a: TGA graphs for PET and ES 0.5% and 2% wt clay addition PET/ Na⁺MMT nanocomposites obtained by heating polymer samples from room temperature to 800 °C with constant heating rate (20°C/min)

Figure 5.11b: TGA graphs for PET and PC 0.6% and 2% wt clay addition PET/ Na⁺MMT nanocomposites obtained by heating from room temperature to 800 °C with constant heating rate (20°C/min)
Table 5.5: TGA data obtained from Figures 5.11 for neat PET, ES and PC clay addition nanocomposites (w.r.t : with respect to)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Clay weight %</th>
<th>Volume Fraction of clay in PET (φ)</th>
<th>Degradation Onset Temperature (T-onset(°C))</th>
<th>Temperature at 50% weight Degradation (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w.r.t. BHET</td>
<td>w.r.t. PET</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neat PET</td>
<td>0</td>
<td>0</td>
<td>391</td>
<td>478</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.5</td>
<td>1.4</td>
<td>0.0072</td>
<td>392.5</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>2</td>
<td>3.5</td>
<td>0.018</td>
<td>392</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.6</td>
<td>1.6</td>
<td>0.0082</td>
<td>391</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>2</td>
<td>3.8</td>
<td>0.029</td>
<td>392</td>
</tr>
</tbody>
</table>

From above Table 5.5, it can be seen that the weight % of clay in the PET matrix was higher with respect to PET than BHET. The wt% of clay with respect to BHET decided by the amount of clay added into the reactor according to the BHET weight present in the reactor while carrying out melt polymerization reaction. The wt% of clay with respect to PET was obtained by TGA. In this thesis, while comparing properties of neat PET and PET/ Na⁺MMT nanocomposites, we have mentioned clay weight % with respect to BHET. However, to calculate theoretical values of mechanical properties and permeability of PET, weight % with respect to PET is used to calculate volume fraction of clay into the PET matrix.
In Table 5.5, volume fraction is calculated by following equation,

\[ \phi = \frac{mc}{\rho c} \left( \frac{mp}{\rho p} \right) \]

………………..Equation 16

Where, \( \phi \) is the volume fraction of the clay, \( mc \) and \( mp \) are the mass fractions of the clay and polymer, respectively. \( \rho c \) is the density of the Na\(^+\)MMT which is 2.6 g/cm\(^3\) (as quoted by the suppliers) and \( \rho p \) is the density of amorphous PET which is 1.333 g/cm\(^3\).

It was observed that there is not much difference between thermal degradation onset temperature of neat PET and PET/ Na\(^+\)MMT nanocomposites prepared from both methods. As well, there was not much difference in temperature observed at 50 wt% degradation for neat PET and PET/ Na\(^+\)MMT nanocomposites. From these results, it can be concluded that the neat PET and the PET/ Na\(^+\)MMT nanocomposites prepared with ES and PC clay addition methods have nearly same thermal stability. Many studies have concluded that the dispersion of nanoparticles into the polymer matrix can improve the thermal stability of polymer [107, 108, 118]. The presence of Na\(^+\)MMT enhances the formation of char and hinders diffusion of volatile decomposition products. However, in case of ES and PC clay addition nanocomposites, this trend was not observed.
5.8 Density and Crystallinity Measurement:

The Na⁺MMT clay has much higher density compared to PET polymer leading to a higher density of nanocomposites. As a result, it is natural to have PET/nanocomposites higher density than the neat PET [109].

The density and crystallinity values of PET/ Na⁺MMT nanocomposites are calculated by using Eq. 10 and 11 and are tabulated in Table 5.6 and shown in Fig. 5.12.

Table 5.6: Density and Volume fraction crystallinity values of PET and PET/ Na⁺MMT nanocomposites obtained by using equation 10 &11

<table>
<thead>
<tr>
<th>Polymer Composition</th>
<th>Density ( (\text{g/cm}^3) )</th>
<th>Volume Fraction Crystallinity ( (X_c) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.337</td>
<td>3.3</td>
</tr>
<tr>
<td>ES 0.5 wt% clay addition</td>
<td>1.343</td>
<td>8.2</td>
</tr>
<tr>
<td>ES 2 wt% clay addition</td>
<td>1.351</td>
<td>14.75</td>
</tr>
<tr>
<td>PC 0.6 wt% clay addition</td>
<td>1.344</td>
<td>9.01</td>
</tr>
<tr>
<td>PC 2 wt% clay addition</td>
<td>1.353</td>
<td>16.4</td>
</tr>
</tbody>
</table>
Figure 5.12: Change in the density with respect to wt% of clay in ES and PC clay addition nanocomposites
From the Fig. 5.12, we can clearly see that as the clay wt% increases in the PET nanocomposite, density of the nanocomposite increases. This result is obvious because Na⁺MMT clay has a very high density compared to that of neat PET. As a result, as the wt% of clay in PET nanocomposite increases, its density also increases [110]. An increased density was used to calculate the volume fraction crystallinity of PET nanocomposite. Therefore, values of volume fraction crystallinity in Table 5.6 are at the higher end and do not represent actual volume fraction crystallinity of PET/ Na⁺MMT nanocomposite films. This can be confirmed from the fact that extruded PET nanocomposites films had quite good clarity as shown in following Fig. 5.13.

Figure 5.13: Picture of neat PET and PET/ Na⁺MMT nanocomposites films
5.9 Mechanical Properties of Neat PET and PET/ Na\(^+\)MMT Nanocomposites:

5.9.1 Comparison between Experimental Mechanical Properties of Neat PET and PET/Na\(^+\)MMT Nanocomposites:

The tensile modulus, tensile strength and maximum strain at elongation were measured with an Instron 4400R tester according to ASTM D 638 type IV. The tensile properties of PET nanocomposites were obtained from stress strain curves obtained from an Instron tester and they are summarized in Table 5.7.

Table 5.7a: Mechanical Properties of PET and PET/ Na\(^+\)MMT nanocomposites (STDEV= standard deviation)

<table>
<thead>
<tr>
<th>Composition Of Polymer (Clay wt %)</th>
<th>Tensile Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength at Yield (MPa)</td>
</tr>
<tr>
<td>PET</td>
<td>49(2.7)</td>
</tr>
<tr>
<td>ES Clay Addition</td>
<td></td>
</tr>
<tr>
<td>0.25%</td>
<td>70 (4.1)</td>
</tr>
<tr>
<td>0.5%</td>
<td>90 (5.2)</td>
</tr>
<tr>
<td>1%</td>
<td>71 (3.7)</td>
</tr>
<tr>
<td>2%</td>
<td>51 (7.2)</td>
</tr>
</tbody>
</table>
Table 5.7b: Mechanical Properties of PET and PET/ Na⁺MMT nanocomposites (STDEV= Standard deviation)

<table>
<thead>
<tr>
<th>Composition Of Polymer (Clay wt %)</th>
<th>Tensile Properties</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength at Yield (MPa) (STDEV)</td>
<td>% Increase</td>
<td>Tensile Modulus (MPa) (STDEV)</td>
<td>% Increase</td>
<td>% Elongation At break (STDEV)</td>
<td>% Increase</td>
</tr>
<tr>
<td>PET</td>
<td>49(2.7)</td>
<td>0</td>
<td>960(55)</td>
<td>0</td>
<td>350 (50)</td>
<td>0</td>
</tr>
<tr>
<td><strong>PC Clay Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>70 (2.1)</td>
<td>43</td>
<td>1160 (80)</td>
<td>21</td>
<td>540 (46)</td>
<td>54</td>
</tr>
<tr>
<td>1%</td>
<td>65 (1.6)</td>
<td>32</td>
<td>1080 (40)</td>
<td>12.5</td>
<td>Brittle</td>
<td>-</td>
</tr>
<tr>
<td>2%</td>
<td>68 (2.9)</td>
<td>38</td>
<td>1200 (52)</td>
<td>25</td>
<td>Brittle</td>
<td>-</td>
</tr>
<tr>
<td>5%</td>
<td>38 (2.4)</td>
<td>-22</td>
<td>1005 (60)</td>
<td>5</td>
<td>Brittle</td>
<td>-</td>
</tr>
</tbody>
</table>
From the Table 5.7, it can be seen that PET nanocomposites prepared using both methods have better mechanical properties compared to that of neat PET up to a certain degree of clay content due to reinforcement effect. Nanocomposite prepared from ES clay addition with low clay loading method showed excellent increase in mechanical properties compared to neat PET and nanocomposite prepared from PC clay addition method.

If the tensile strengths are compared (Fig. 5.14), then the PET/ Na⁺MMT nanocomposite having 0.5 wt% clay with the ES addition method shows the maximum increase in the tensile strength (84%) compared to neat PET. In the case of PC clay addition method, maximum increase in the tensile strengths observed for 0.6 wt % clay addition (43%). For ES clay addition nanocomposite, it is observed that as the clay wt% increases, the tensile strength of nanocomposite goes on increasing up to 0.5 wt% of clay. Further increase in clay wt% resulted in a decrease in tensile strength. The substantial increase in the tensile strength of PET nanocomposite can be attributed to good dispersion of clay in to the polymer matrix providing more surface area of Na⁺MMT clay to interact with PET chains. This result into the large interfacial area and stress applied on polymer gets transferred to the rigid clay platelets resulting in increase in its tensile strength.
Figure 5.14a: Comparison of tensile strengths of neat PET and ES clay addition nanocomposites
Figure 5.14b: Comparison of tensile strength of neat PET and PC clay addition nanocomposites
In the case of PC clay addition, the maximum increase in tensile modulus (25%) is observed for 2 wt% clay additions, however, PET nanocomposite prepared with ES 0.5 wt% clay addition showed excellent increase in tensile modulus (92%). The effect of Na⁺MMT content on the mechanical properties of PET nanocomposite can be seen from following Fig. 5.15. The improvement in mechanical properties of PET/ Na⁺MMT nanocomposites is a result of good dispersion of clay particles i.e. intercalation and exfoliation of nano particles in polymer matrix and availability of high surface area of clay platelets for interfacial adhesion and ionic band formation [111]. Clays are very rigid and they have very high modulus [112] compare to the polymer matrix. Therefore when force is applied on PET nanocomposites, most of the force transferred to the clay particles. This gives PET/clay nanocomposites higher modulus compared to neat PET. The mobilities of the polymer chains are also reduced close to the clay platelets surfaces. As a result, increased modulus can be attributed to these reduced mobilities of polymer chains [113, 114].
Figure 5.15a: Comparison of tensile modulus of neat PET and ES clay addition nanocomposites

Figure 5.15b: Comparison of tensile modulus of neat PET and PC clay addition nanocomposites
Both nanocomposites; however, showed relatively similar mechanical properties at higher clay loading. As the clay loading increases, agglomeration of clay in PET matrix increases. The nanocomposites containing more than 1.5 wt% of Na⁺MMT showed extreme brittleness and it was difficult to measure their mechanical properties. This may be because, we did not use any organic modifier to increase the compatibility between PET and Na⁺MMT and at a higher clay loading, and clay got easily agglomerated. It has been reported that tensile properties of polymer nanocomposite prepared from organically modified clay shows better properties than nanocomposite prepared from natural clay (Na⁺MMT) at higher clay loading [61, 68, 98, 115, 116].

Jiri Kotek et al. [117] concluded that the presence of clay in polyamide nanocomposite enhances the tensile strength as well as tensile modulus. It was also concluded that at certain clay loading level, there is no difference between exfoliated and intercalated systems. This is ascribed to the competing effect between clay reinforcement of an exfoliated system and the polymer crystalline structure present in an intercalated system. Yimin Wang et al. [118] studied mechanical properties of PET/MMT nanocomposites and observed that high aspect ratios of clay platelets and strong interaction between clay and PET chains leads to enhancement of tensile properties. Because of high aspect ratio and large surface active centers, it was difficult to separate PET chains from the PET matrix and impact was transfer to more rigid clay platelets, leading to dissipation of the impact energy into the surrounding matrix. At higher clay loading, clay platelet’s dispersion was not observed to be ideal and tensile properties were observed to decrease. This result is in agreement with our research observations.

The % elongation at break showed the same trend as that of the tensile strength and tensile modulus. For low clay content PET/ Na⁺MMT nanocomposites (wt%<1), % elongation at break was observed to be increased up to 50 to 80% in comparison to neat PET (Table 5.7). At high clay loading, % elongation at break decreased drastically, because of increases in stiffness as a result of agglomeration and micro voids formation.
The % elongation at break seems to be very sensitive to the dispersion of clay, size of nano-particles agglomeration and content of clay in polymer nanocomposite; as small increases in clay contents resulted in brittle behavior of the PET/ Na⁺MMT nanocomposites.

From the mechanical property analysis, we can conclude that the most important factor contributing to the enhancement of mechanical properties of PET/ Na⁺MMT nanocomposites is not the quantity of the clay, but the degree of dispersion and exfoliation of the clay platelets in to the polymer matrix [61, 115].

5.9.2 Theoretical Calculation of Tensile Modulus of PET/Clay Nanocomposites:

The enhancement in mechanical properties of PET/ Na⁺MMT nanocomposites can be attributed to the good dispersion of clay platelets into the polymer matrix, high rigidity and aspect ratios of the clay platelets and more interface points in between clay platelets and polymer chains. The tensile modulus of PET/clay nanocomposites are theoretically calculated by using modified Halpin-Tsai equation 7 (Page 20) which take into account various parameters which affect the tensile modulus such as filler’s volume fraction, particle size and shape, polymer as well as fillers modulus. The values obtained from this equation are tabulated in Table 5.8.
Table 5.8: Comparison between experimental and theoretical tensile modulus of PET nanocomposite, (Clay Modulus used for theoretical calculation: 175 GPa, [112, 119])

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Volume Fraction of Clay</th>
<th>Experimental Modulus (E) (MPa)</th>
<th>Theoretical Modulus (E) (MPa)</th>
<th>E/Em (Using Experimental Modulus)</th>
<th>E/Em (Using Theoretical Modulus)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0</td>
<td>960</td>
<td>960</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.0072</td>
<td>1840</td>
<td>1580</td>
<td>1.91</td>
<td>1.64</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.018</td>
<td>1120</td>
<td>2500</td>
<td>1.17</td>
<td>2.62</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.0082</td>
<td>1160</td>
<td>1670</td>
<td>1.20</td>
<td>1.73</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.019</td>
<td>1200</td>
<td>2600</td>
<td>1.25</td>
<td>2.71</td>
</tr>
</tbody>
</table>
In Table 5.8, we compare the experimental and theoretical modulus of the PET/Na⁺MMT nanocomposites. As shown in Table 5.8, the experimental and theoretical values of the ES clay addition nanocomposite are in good agreement at low clay loading. However, as clay loading increases, the effects of agglomeration on the modulus of the nanocomposites is quite obvious and a dramatic drop in modulus is observed. There are many factors such as dispersion of clay, its aspect ratio and compatibility between clay and polymer which affect the final modulus or mechanical properties of polymer nanocomposite, [120, 123]. From the result, it can be concluded that there must be certain clay volume or weight fraction in each polymer matrix, at which nanocomposite obtains its optimal properties. Above this volume fraction, deterioration in properties of nanocomposite has been observed. Similar trends have been reported in literature for polymer nanocomposites [116, 121]. Xiang Li et al. [122] et al. proposed three phase model based on polymer matrix, interfacial region and fillers to calculate the tensile modulus of polymer nanocomposite. They concluded that for the fixed volume fraction of the dispersed phase, smaller particles provide an increase in modulus for the composite compare to larger fillers. It was concluded that for the well dispersed small sized fillers, there is more interfacial area available between fillers and polymer which greatly affects the composite’s modulus. Based on percolation concept, they also concluded that there is a percolation threshold in the matrix for the fillers, which is about 0.2. This percolation threshold corresponds to a volume fraction of Na⁺MMT at about 0.013 in a polymer nanocomposite.
5.10 Morphological Analyses:

5.10.1 Basal Space Measurement by Wide Angle X-ray Diffraction:

The structure of polymer nanocomposite samples was studied using XRD results. Figure 5.16 shows the XRD result for ES 0.5 wt% clay addition nanocomposite and Na⁺MMT clay and it can be seen that peak for Na⁺MMT (2θ = 7.4°, d = 1.12nm) has been shifted to lower angle in polymer nanocomposite (2θ = 5.7°). This shift in peak to lower angle clearly indicates intercalation of polymer nanocomposite chains in interlayer space of platelets and interlayer space increased to 1.5 nm from 1.12 nm of pristine clay.

Figure 5.16: XRD pattern of Na⁺MMT and ES 0.5 wt% clay addition nanocomposite
Figure 5.17 shows the WAXRD pattern for PC clay addition nanocomposite. As expected from WAXRD pattern of BHET-clay dispersion (Figure 5.3), the polycondensation reaction further delaminates the clay platelets as reaction progress to produce PET from BHET and the intensity of the peak appeared in BHET clay powder WAX pattern reduced dramatically at $\theta = 4.4^\circ$ ($d = 1.96$ nm). This shift of peak of Na$^+$MMT to $2\theta = 4.4^\circ$ and reduction in intensity clearly shows increase in the interlayer spacing of Na$^+$MMT platelets as a result of intercalation of MMT by PET polymer chains.

![XRD pattern of Na$^+$MMT, Clay-BHET powder, PC 0.6 wt% clay addition nanocomposite](image)

Figure 5.17: XRD pattern of Na$^+$MMT, Clay-BHET powder, PC 0.6 wt% clay addition nanocomposite
Intercalation of polymer chains usually increases the interlayer spacing of clay leading to a shift of the diffraction peak towards lower angle values. The more the diffraction peak shifts to lower angles, the better the intercalation. When clay gets completely exfoliated, the diffraction peak disappears from the wide angle X-ray (WAXR) pattern and as clay gets exfoliated, it improves properties of the nanocomposite tremendously.

If we compare the WAXR diffraction (WAXRD) pattern of ES clay addition nanocomposite and PC clay addition nanocomposite then according to XRD morphology analysis, the PC clay addition nanocomposite (2θ = 4.4°, d= 1.96) showed much higher intercalation of PET chains in clay platelets compare to ES clay addition nanocomposite (2θ =5.7°, d = 1.54). According to X-ray diffraction results, PC clay addition nanocomposites should have better thermal and mechanical properties; however this was not observed. According to mechanical and thermal properties, ES clay addition nanocomposite had much better dispersion of clay in polymer material than PC clay addition nanocomposites.

5.10.1.2 WAXRD Paradox:

To find the exact reason of diffraction peak at 2θ =5.7° in ES clay addition nanocomposite, ethylene glycol was added to water in which clay is well dispersed. After stirring the mixture for 4 hr, water was evaporated by heating mixture above 100 °C. After the water evaporated, a viscous gel like mixture was obtained. The WAXRD pattern for this ethylene glycol-clay mixture is shown in Figure 5.18. The WAXRD pattern of EG-clay clearly shows a diffraction peak at 2θ =5.5. Various research articles also have reported that EG-clay mixture gives intercalated XRD pattern having diffraction peak at 2θ =5.6° [52, 124].
Figure 5.18: WAXRD pattern of Na\textsuperscript{+}MMT and EG- Na\textsuperscript{+}MMT clay dispersion
From these results, it was concluded that diffraction peak appearing in WAXRD pattern of ES clay addition nanocomposite was the result of clay agglomeration in the EG. To prepare PET, EG and TPA had been used in the mole ratio of 1.5 and as a result, there was an excess amount of EG that remains in the reactor after esterification in which clay remained agglomerated. For the small amount of wt% of clay in the nanocomposite, this agglomerated clay was small and most of the clay was exfoliated in the polymer material. As a result, when clay content was low, excellent property improvements were observed; however, as the clay wt% increased in the nanocomposite, intercalated/agglomerated clay in polymer increased. This agglomeration of the clay affected the properties of PET nanocomposites and they showed properties similar to those of the intercalated nanocomposite (PC clay addition).

These predictions were in parallel with Kim’s [1] results for nanocomposites with modified clays which showed intercalation of clay in the PET matrix, resulting in only 10-20% improvement in mechanical properties. The ES clay addition nanocomposite with 0.5% clay had shown 92% increment in mechanical properties which means most of the clay was well dispersed in the PET polymer matrix.

The XRD technique had been used extensively to do morphological analysis. It had been observed that XRD analysis does not able to give clear picture of clay dispersion in polymer matrix [50, 52].
5.10.2 Morphological Analysis of PET Nanocomposite by Transmission Electron Microscopy:

In order to verify the result obtained from morphological analysis of PET nanocomposites by the XRD, transmission electron microscopy (TEM) has been used. This technique provides a quantitative understanding of the internal structure of a nanocomposite through direct observation. Figure 5.19 shows the TEM images of PET nanocomposites, which are chosen by the overall aspect observed in several different regions and thus in general they are representative of the nanostructure of the nanocomposites prepared. The dark lines in the Figure 5.19 represent each MMT clay sheets having 1 nm thickness and around 100 nm aspect ratios. The grey area, space between the dark lines and surrounding them, represent the volume occupied by the polymer matrix. These TEM images are for low clay loading. From Figure 5.19a, we can see lot of grey areas in the TEM image. Similar amount of gray areas were noticed in other images also for low clay content at lower magnification. It can be concluded that higher/optimum clay loading requires, if clay needs to be good dispersed in PET matrix thoroughly.
Figure 5.19a: TEM image of low clay loading (0.5 wt%) ES PET nanocomposite (low magnification)
Figure 5.19b: TEM image of ES 0.5% Clay addition PET nanocomposite
Figure 5.19c: TEM image of PC 0.6% Clay addition PET nanocomposite
Figure 5.19b is the TEM image of the 0.5wt % ES clay addition nanocomposite and it can be seen that the layer structure of Na\(^+\)MMT clay is more distorted/disturbed in ES clay addition nanocomposite than 0.6 wt% PC clay addition nanocomposites which is shown in the Figure 5.19c. Single and double black lines can be seen for ES clay addition nanocomposite in Figure 5.19b which represents the clay platelets separated from the layered structure and dispersed in PET matrix. This verifies that good dispersion of clay platelets in PET matrix which has shown excellent enhancement in thermal and mechanical properties of PET/ Na\(^+\)MMT nanocomposites. Also for both types of nanocomposites, some clusters or agglomerated clay particles were detected. For the PC clay addition nanocomposite, TEM images showed that some of the MMT clay layers were randomly distributed with face to face stacked style with increased interlayer space between them in which PET chains are intercalated, which is consistent with the results obtained from WXRD.

From the XRD and TEM images (Fig. 5.16-5.19), it can be concluded that ES and PC clay addition methods gave partially intercalated and exfoliated structure of Na\(^+\)MMT clay in the PET matrix. None of the nanocomposite showed complete exfoliation of clay platelets.
5.11 Barrier Properties of Neat PET and PET/ Na⁺MMT Nanocomposites:

5.11.1 Oxygen Permeability of PET/ Na⁺MMT Nanocomposites:

One of the main objectives of this project was to improve barrier properties of PET polymer by dispersing nano clay into the PET matrix. Oxygen permeability of neat PET and PET/ Na⁺MMT nanocomposites was measured using a MoCon OxTran 1050 permeability tester according to the ASTM D3985 method. The permeability’s of the PET and PET/ Na⁺MMT nanocomposites are tabulated in following Table 5.9 and graphically compared in Figure 5.20.

Table 5.9: Experimental O₂ Permeability values of neat PET and PET/ Na⁺MMT nanocomposites

<table>
<thead>
<tr>
<th>PET Nanocomposite</th>
<th>Clay wt %</th>
<th>O₂ Permeability (cc − mil/ (100 in² * atm * day))</th>
<th>STDEV</th>
<th>Average % decrease in O₂ Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PET</td>
<td>0</td>
<td>8.4</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.5%</td>
<td>5.4</td>
<td>0.26</td>
<td>36</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>2%</td>
<td>5.8</td>
<td>0.40</td>
<td>29</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.6%</td>
<td>5.7</td>
<td>0.30</td>
<td>31</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>2%</td>
<td>6.3</td>
<td>0.50</td>
<td>25</td>
</tr>
</tbody>
</table>
Figure 5.20: Comparison of O$_2$ Permeability of neat PET and PET/ Na$^+$MMT nanocomposites (PNC: polymer nanocomposite)
The permeability of PET and PET nanocomposite is compared in Table 5.9 and Fig. 5.20. The ES 0.5 wt% Clay addition nanocomposite shows a permeability which is around 35-40% lower than that of the pure PET, which is indicative of good dispersion of MMT clay in polymer matrix. Although the decrease in permeability is not very high, for the very low clay loading (0.5 wt %), it is a significant decrease. This change in O\(_2\) permeability has been explained by tortuous path model of permeant molecules in the section 2.1. It was observed that as clay loading increased further, increase in O\(_2\) permeability was observed. This trend in barrier properties with increase in clay loading is similar to that of mechanical properties; it results from agglomeration of Na\(^+\)MMT clay in PET polymer matrix for both, ES and PC, clay addition method. These results show that if clay platelets are well dispersed in the polymer matrix, a decrease in O\(_2\) permeability is observed. Obtaining good dispersion at high clay loading however is still a challenge which needs to be overcome.

Masoud Frounchi et al. [125] prepared PET nanocomposites with melt extrusion by adding two different MMT based organically modified clays (nanolin and cloisite). They observed that permeability is directly related to degree of exfoliation of clay platelets in the PET matrix. The PET nanocomposite containing 1 wt% of nanolin clay showed the lowest permeability and as the clay wt% increased, the permeability increased because of agglomeration of clay. Won Choi et al. [63] has showed impressive improvement in O\(_2\) barrier properties of PET/clay nanocomposite prepared with clay supported catalyst under certain conditions. Similar result was obtained by J. Grunlan et al. [126] who showed poly(vinyl alcohol)(PVOH)/clay nanocomposite had superior barrier properties in comparison to neat PVOH at high clay loading and certain relative humidity (RH) conditions.
Theoretical Calculation of Permeability of PET/Na⁺MMT Nanocomposites:

Rigid clay platelets act as a barrier for a diffusing gas/liquid molecules in polymer nanocomposites. However, there are different factors that affect the permeability such as degree of exfoliation or intercalation, aspect ratio (L/W), orientation angle θ, dispersion spacing ξ between platelets, volume fraction of clay in polymer matrix. Neilson et al. [42] first proposed simple equation to predict permeability for the composite material. However, they did not take into account the orientation of clay platelets. As a result, the Neilson permeability equation was modified by Bharadwaj et al. [45] by introducing order parameter (S).

\[
\frac{P_c}{P_m} = \frac{(1 - \phi)}{1 + \alpha \phi \frac{2}{3}(S + \frac{1}{2})}
\]

\[
S = \frac{1}{2} (3\cos^2 \theta - 1)
\]

\[
= 1 \quad \text{for } || \text{ surface}
\]

\[
= 0 \quad \text{for random}
\]

\[
= -\frac{1}{2} \quad \text{for } \perp \text{ surface}
\]

While calculating theoretical permeability values of PET/Na⁺MMT nanocomposites, random and perfectly aligned orientation of clay platelets in PET matrix were considered (Table 5.10 and Figure 5.21). For the random orientation, Bharadwaj’s order parameter ‘S’ turns to zero and Bharadwaj’s modified equation reduces to Neilson’s basic equation of permeability [45]. Cusseler’s equation was not used to calculate theoretical values because Cusseler’s equation is useful when clay platelets have aspect ratios higher than 300 and on an average, Na⁺MMT clay platelets have aspect ratio less than 100, [49].
Table 5.10: Comparison of experimental and theoretical Pc/Pm values of neat PET and PET/ Na⁺MMT nanocomposites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Volume fraction of clay in matrix (φ)</th>
<th>$\frac{P_c}{P_m}$ (Experimental)</th>
<th>$\frac{P_c}{P_m}$ (Theoretical- ‘S’ = 0)</th>
<th>$\frac{P_c}{P_m}$ (Theoretical- ‘S’ = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PET</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.0072</td>
<td>0.64</td>
<td>0.89</td>
<td>0.75</td>
</tr>
<tr>
<td>ES Clay addition</td>
<td>0.018</td>
<td>0.69</td>
<td>0.77</td>
<td>0.54</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.0082</td>
<td>0.68</td>
<td>0.88</td>
<td>0.72</td>
</tr>
<tr>
<td>PC Clay addition</td>
<td>0.019</td>
<td>0.75</td>
<td>0.76</td>
<td>0.52</td>
</tr>
</tbody>
</table>
Figure 5.21a: Graph of P_c/P_m Vs φ of PET/ Na⁺MMT nanocomposites for “S” = 0 (random orientation)

Figure 5.21b: Graph of P_c/P_m Vs φ of PET/ Na⁺MMT nanocomposites for “S” = 1 (parallel orientation)
From the Table 5.10 and Figure 5.21, it can be clearly seen that at low Na\textsuperscript{+}MMT clay loading, experimental and theoretical values are in nearly in the same range which supports our claim that at low clay loading, clay platelets are well dispersed in the polymer matrix. As a result, tortuous path of permeating molecules increases and results in decrease in O\textsubscript{2} permeability. At low clay loading, O\textsubscript{2} permeability values of ES clay addition nanocomposites are lower than that of the theoretical values. This may be because, as discussed previously, permeability values depend on complex parameters as well as Neilson’s and Bharadwaj’s permeability models do not take into account the three dimensional nature of clay platelets and interfacial area between clay platelets and polymer chains which play an important role in gas permeability of polymer. Because of rigid and non permeable clay platelets, most of the interfacial area also acts as a non permeable region for the gas molecules. As a result, for nanocomposite having high interfacial area between clay platelets and polymer matrix, permeability decreases further. At high clay loading, however, theoretical permeability values are lower for ‘S’ = 1 compare to ‘S’= 0 than experimental values. This suggests that to get the maximum decrease in permeability of polymer matrix, it is very important that clay platelets are orientated parallel to the surface of polymer. Chensheng Lu et al. [127] suggested that the reason for a sudden drop in permeability and mechanical properties of nanocomposites at higher clay content may be the lack of exfoliation and decrease in aspect ratio [128]. They claimed that there must be a critical volume for the clay content in the polymer matrix. They developed a simple renormalization model to predict critical volume fraction of clay in polymer. According to their study, values obtained from the renormalization model are in good agreement with available data but more work need to be done to obtain optimal parameters of the clay fillers.
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions:

PET nanocomposites with different weight % of natural montmorillonite clay (Na⁺MMT) were prepared from esterification clay addition (ES clay addition) and polycondensation clay addition (PC clay addition) methods. In our research, we studied the effect of Na⁺MMT clay on thermal, mechanical and barrier properties of PET packaging polymer. Among these two methods, the ES clay addition method with low clay content showed excellent increases in properties of PET/Na⁺MMT nanocomposite compare to neat PET and PET nanocomposites prepared using the PC clay addition method.

DSC results analysis indicated that PET/Na⁺MMT nanocomposites prepared using the ES clay addition method resulted into better clay dispersion and exfoliation in the PET matrix at low clay loading than that of the PC clay addition method. Reheating thermograms of ES clay addition method showed cold crystallization peak. The cold crystallization peak was not observed in the case of PC clay addition nanocomposites. Also, while cooling from 300 °C to 40 °C at same cooling rates, we observed that PC clay addition nanocomposites crystallized at higher temperature compared to nearly same wt% of ES clay addition method. The crystallization rate was observed to be increased more for PC clay addition nanocomposites because of agglomeration of Na⁺MMT clay in the PET matrix. The agglomerated clay particles acted as nucleating agents and increased
the crystallization rate. Thus, thermal analysis from DSC confirmed that ES clay addition method resulted into better dispersion of clay into the PET matrix.

From the density measurement it was observed that density of PET/Na⁺MMT nanocomposites was bit higher compare to neat PET without substantial increase in crystallinity of PET films. This result was confirmed by DSC measurement (measurement 1) also. It was expected that PET/ Na⁺MMT nanocomposites will have higher density because Na⁺MMT clay has high density compared to neat PET.

The ES 0.5 wt % clay addition PET nanocomposite showed excellent increase in mechanical properties compared to that of neat PET and PC clay addition nanocomposites. The tensile strength, tensile modulus and % elongation at break observed to increase 84%, 92% and 51% respectively for ES 0.5% clay addition nanocomposite compare to neat PET. At low clay loading, ES addition nanocomposite showed improvement in tensile modulus better than expected from theoretical calculations. At higher clay loading, however, there was a sudden drop in mechanical properties of the PET/ Na⁺MMT nanocomposites, because of clay agglomeration in PET matrices.

XRD and TEM results also confirmed the highly intercalated nature of clay platelets in PET. From morphological analysis, we concluded that at low clay loading, the nanocomposites prepared from ES clay addition method result into better clay dispersion in the PET matrices compare to that of nanocomposites prepared from PC clay addition method. However, tactoids and agglomeration of clay observed in polymer matrix at higher clay loading for both methods.

The barrier properties of PET/Na⁺MMT nanocomposites were observed to increase compared to that of neat PET. The ES 0.5 wt% clay addition nanocomposite showed maximum decrease in O₂ permeability (36%). The decrease in O₂ permeability can be explained by the increase in tortuous path of permeant molecules because of dispersion of
impermeable clay platelets in PET matrix. ES clay addition nanocomposite, at low clay content in PET matrices, showed excellent increase in barrier properties compared to predication from theoretical models. At high clay content, however, expected increase in barrier properties was not observed because of agglomeration of clay in PET matrices.

In a summery, an in-situ polymerization method was used to prepare PET/Na⁺MMT nanocomposites. To avoid thermal degradation, natural clay (Na⁺MMT) was used to prepare PET nanocomposites. Different amount of the Na⁺MMT clay was added into the esterification (ES) as well as polycondensation (PC) reaction during melt polymerization. The PET/Na⁺MMT clay based nanocomposites showed improved mechanical and barrier properties compared to that of neat PET. From the DSC results, it was observed that PET/Na⁺MMT nanocomposites prepared by ES clay addition method resulted into better dispersion of the clay platelets into the PET matrix compared to that of PC clay addition nanocomposites. This result was also confirmed by morphological analysis and TEM images showed enhanced separation of clay platelets into the PET matrix by ES clay addition method. As expected from thermal and morphological analysis, PET/Na⁺MMT nanocomposites prepared from ES clay addition method showed excellent increase in mechanical and barrier properties of PET polymer at low clay content. However, at higher clay loading, PET/Na⁺MMT nanocomposites prepared from both methods had high percentage of clay agglomeration which resulted into diminishing properties. As a result, more research needs to be done to achieve proper dispersion of clay into the PET matrix at higher clay loading.
6.2 Recommendations:

Although different methods and techniques have been used, getting good dispersion of clay platelets at higher loading is still a challenge that needs to be overcome to enhance properties of PET/clay nanocomposites and to make PET/clay nanocomposites preparation commercially feasible.

- To get good dispersion at higher clay loading, compatibility between PET and clay platelets is very important. To increase compatibility between PET and clay, it is recommended to use small amount of copolymer, ionomer or thermally stable modified clay to prepare PET/clay nanocomposites.
- To enhance barrier properties of PET, it is suggested to use high aspect ratio (>300) fillers. As a result there will be increase in tortuous path of diffusing molecules and this will result in lower permeability.
- There are very few articles which have studied in depth the melt intercalation method for preparation of PET nanocomposites with natural clay. The melt intercalation method could also be studied to prepare PET/Na\textsuperscript{+}MMT nanocomposites.
CHAPTER 7

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