A Dissertation

Entitled

PET and MXD6 Montmorillonite Nanocomposites

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Doctor of Philosophy Degree in Engineering

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August 2012
Poly (ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester widely used in the packaging industry. One of the main markets for PET is plastic bottles for carbonated drinks (CSD), water, juice and oxygen sensitive products. In order for PET to be utilized in packaging applications requiring even lower gas permeability, coating of PET bottles and melt blending with higher barrier polyamides have been studied. For example, a blend component with PET is poly (m-xylylene adipamide), MXD6, which itself shows excellent barrier properties and good transparency. In recent decades, the polymer/montmorillonite (MMT) nanocomposite route indicates other possibilities to enhance properties of conventional PET, and reveals better mechanical and barrier properties than traditional polymers.

In this research, a modified melt blending method was developed to prepare PET/Na-MMT, MXD6/Na-MMT, and PET/MXD6-Na-MMT nanocomposites with Na-MMT loading from 0.5% to 5% (wt), and with the purpose of preparing exfoliated nanostructure in the absence of organic modifiers. The hydrophilic nature of Na-MMT allows it to be exfoliated in water to form clay dispersion. The melt blending of PET with
a Na-MMT slurry, and MXD6 with a Na-MMT slurry of different clay weight percentages were performed in a twin screw extruder. The thermal degradation and hydrolytic degradation in the presence of water resulted in the reduction of molecular weight (M.W.) of the nanocomposites. All the nanocomposites processed by solid state polymerization reached specific M.W. values (0.8 dL/g) which were similar to each other.

In order to study the effects of pristine nanoclay on the thermal properties of PET and MXD6, all nanocomposite samples were subjected to thermal analysis by differential scanning calorimetry (DSC) and the results are discussed. The introduction of Na-MMT hinders the mobility of polymer chains, which results in slight increases of the glass transition temperatures. Additionally, the presence of Na-MMT in the PET or MXD6 matrix acts as a nucleating agent, which accelerates the rate of crystallization. Among the nanocomposites with different concentrations of Na-MMT, there are no significant differences in the crystallization behaviors. This indicates that the exfoliation morphological structure achieved for the polymer nanocomposite shows the similar thermal behavior.

Wide angle X-ray diffraction (WXRD) and transmission electron microscopy (TEM) are used as indicators of the extents of the dispersion state of clay platelets within the polymer matrices. The micrographs of PET/Na-MMT nanocomposites (0.5 wt%, 1 wt%, 2 wt%, 3 wt%) as well as MXD6/Na-MMT nanocomposites (2 wt% and 3 wt%), reveal a well-exfoliated structure. The 5 wt% MXD6/Na-MMT nanocomposites and 5 wt% PET/Na-MMT nanocomposites show partial intercalation and agglomeration. The absence of diffraction peak indicates the possibilities of formation of exfoliation
morphism while TEM reveals the agglomerates at high clay concentration. The results give strong evidence that the WXRD needs to be combined with TEM in the study of morphology of polymer nanocomposites.

Tensile tests show that the maximum improvement of Young’s modulus is around 24% at 2 wt% clay addition in PET and 21% for the 2 wt% MXD6 nanocomposite. The polymer becomes brittle due to the presence of Na-MMT. Dynamic mechanical analysis (DMA) showed that the storage modulus doubled at 5 wt% clay addition in the case of PET/Na-MMT nanocomposites, and is 1.5 times larger than recorded for neat MXD6. Moreover, it is observed that PET nanocomposites had lower permeability values than the pure PET. When introducing 2 wt% Na-MMT into a PET matrix, the value of permeability dropped to 4.2 cc*mil/(100*in²*day*atm), which shows a 52% enhancement of the oxygen barrier. For MXD6/Na-MMT nanocomposites, optimum oxygen barrier was given by 3 wt% clay loading with this nanocomposite, showing 70% barrier enhancement. It was, therefore, concluded that nanocomposites prepared by using modified melt blending method showed better oxygen barrier properties compared to neat PET and MXD6.

It also has been found that orientation can strongly influence the morphology of layered silicate nanocomposites and thus have an influence on their mechanical, and barrier properties. During uniaxial orientation, in the presence of Na-MMT in PET, strain hardening occurs sooner than in pure PET. In order to describe the stress-strain behavior of PET nanocomposites during uniaxial stretching, a computational model was successfully developed to enable the prediction the effect of clay loading and varies extension ratios on the mechanical properties. For biaxially stretched blow molded PET
bottles, strain-induced crystallization causes enhanced oxygen barrier properties for PET. The presence of microvoids in the case of blow molded nanocomposite bottles, however, results in less improvement between PET and PET nanocomposite bottles.

When exfoliated MXD6 nanocomposite is transferred into the PET matrix, it is found that the majority of clay platelet stays inside the MXD6 domain. It is found 37% and 87% improvements were achieved for Young’s modulus and oxygen barrier properties of PET/MXD6-MMT. The obtained 5 wt% MXD6 nanocomposite blended with PET, shows a high degree of exfoliation, indicating that the morphology structure plays a significant role in property enhancement.
This work is dedicated to my grandma.

With eternal love and respect to my parents, for sacrificing many comforts in their life for me. I am very grateful that they have trusted me and given me the freedom to live my life on my own terms. The life principles they believe in have been an endless source of inspirations for me.
Acknowledgements

I would like to express sincere gratitude to following individuals and institutions for their valuable contribution in the completion of this thesis:

Dr. Saleh A. Jabarin, my Ph.D advisor, for his guidance and encouragement which contributed to the coherence and value-added scientific research.

Ms. Lofgren, Mr. Mumford, and Dr. Cameron, for providing training and courses through my research life, which allows me to become acquainted with all the testing instruments.

I am also grateful to all of my committee members – Dr. Coleman, Dr. Escobar, Dr. Lapitsky, and Dr. Gan, for all the invaluable source of advice and support to finish my research thesis.

Special thanks to Polymer Institute, TEM center in Medical School at UT, and CMSC in UT for the facilities and equipment provide for this research.

Also don’t miss an opportunity to express thanks to all my colleagues and friends in Toledo who helped me in various ways for all their love and encouragement during my stay in Toledo and make my study life enjoyable at the University of Toledo.
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Chapter 1

Introduction

1.1. Background of Dissertation

PET (ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester widely used in the manufacture of fibers, films, and beverage containers, due to its high transparency, high dimensional stability, and good thermal and mechanical properties [1-3]. Since it was firstly developed to be used as synthetic fibers by British Calico Printers in 1941 [4], it has become a very important polymer for the production of fibers (Terylene, Dacron) and to an extent films (Melinex, Mylar). Later, with the development of solid state polymerization (SSP) the molecular weight could be elevated to such an extent that the production of injection molded parts and extruded products became possible. Soon after this development DuPont turned their attention to the development of injection stretch blow molded (ISBM) containers and were finally able to issue a patent on biaxial stretched PET bottles in 1973 [5-6]. This new process utilized the basic properties of PET which allowed amorphous preforms to be injection molded due to the high $T_g$ (80°C) and slow crystallization rate. The amorphous preforms can then be heated about $T_g$ (but below $T_m$, usually at about 100°C) and blown under high pressure to the desired shape. This development led to the widespread usage of PET as a packaging material for liquids (i.e. PET bottles), and in particular carbonated beverages. The usage
of PET has increased rapidly over the past decades to the point where 12.5 million tons of PET was used in packaging application in 2006 (bottle and film applications) [7]. Of this 12.5 million tons, 9.5 million tons were used in bottles (only 200,000 tons was used for beer bottles).

PET global demand over the last 15 years marked a substantial growth, as it is shown in Fig 1-1. The outlook for 2020 is a growth of about 5.5 times, following the demand trend for films, bottles and fibers [8]. It has been found that PET enjoys considerable growth as a packaging material as a replacement for glass, metal, and other plastic materials. In many applications, PET is a commodity polymer competing directly with polyethylene, polypropylene and polystyrene in the markets of food and beverage packaging. PET is used to make containers for soft drinks, juices, alcoholic drinks, water, edible oils, household cleaners and other food and non-food applications.

In the barrier and packaging industry, one of the main markets for PET is plastic bottles for carbonated soft drinks (CSD) due to its inherent properties including good resistance to gas permeation (particularly oxygen and carbon dioxide). Therefore, large amounts of PET resin are used for the production of stretch blow molded bottles. With increasing demand for high performance PET materials for sensitive beverages applications, such as beer, wine, and juices, the focus of recent research has been to produce products at minimal changes in equipment, processes and cost of inputs, with enhanced barrier properties for food packaging and beverages applications.
In attempts to achieve these objectives, several strategies have been proposed, in the last 20 years, to increase the barrier properties of PET to gases (mainly oxygen and carbon dioxide). For example, some companies such as Sidel, PPG and Dupont have developed bottle coating systems for the reduction of both $O_2$ and $CO_2$ permeation. Alternatively, a multi-layer approach whereby a thin layer of a higher barrier polymer, such as ethylene-vinyl alcohol (EVOH) copolymer or poly m-xylene adipamide (MXD6) is inserted between an inner and outer layer of PET. If this is based on MXD6, the routine multilayer container has barrier properties an order of magnitude higher than that of the PET [10-11]. In comparison to EVOH, aromatic polyamides retain higher barrier properties under conditions of high humidity [11], making them more suitable for beverage packaging applications [12]. Another approach proposed is based on PET blending with high barrier constituents, which could be dispersed as domains oriented
perpendicular to the direction of gas flow thus increasing tortuosity of the diffusion pathway [13]. The main problem related to this approach is the non-perfect compatibility between PET and polyamides, resulting in yellow color and haziness, in oriented blend films and in bottle walls [14]. Mitsubishi, and Nanocor are among the companies developing such technologies.

There has been tremendous research and development interest in polymer nanocomposites (PNC). Polymer nanocomposites are polymers (thermoplastics, thermosets, or elastomers) that have been reinforced with small quantities (less than 5% by weight) of very high aspect ratio (l/t > 300) fillers in the matrix. Since the past two decades, incorporation of inorganic particles such as mica, talc, CaCO₃ and glass beads to enhance toughness, and stiffness has increased. Superior mechanical properties have been achieved with poly (vinyl chloride) (PVC)/CaCO₃ [15], high density polyethylene (HDPE)/CaCO₃, nylon-6/CaCO₃ [16-18]. Among different types of fillers, those based on clay and natural silicates are very widely used because of their abundance and easy availability. Polymer silicate nanocomposites are in new class of multifunctional materials and are filled with the nanoalloys with thickness of a few nanometers and hundreds to thousands of nanometers in length. These composites are formed by intercalation of polymers within the platelets of the fillers. Uniformly dispersed nanoclays of very high aspect ratios have proved to provide a wide variety of added advantages by the combination of mechanical, thermal, electrical, optical and several other physical properties to the material [19-23].

Nanoclay is derived from montmorillonite (MMT) which is widely used for the preparation of polymer nanocomposites. MMT is a mineral deposit that has layered
structure of dimension around 1 nm thick and a specific surface area of 700-800 m$^2$/g [24-25]. Because of the cations (Na$^+$, K$^+$, Ca$^{2+}$) in the interlayer, the natural layered silicates are hydrophilic and thus are mostly compatible with a hydrophilic polymer, such as poly (vinyl alcohol) (PVA) [26], resulting in poor clay dispersion in most hydrophobic polymers. The cations in the galleries between the clay platelets, however, can be replaced with organic cations such as alkyl ammonium ions to obtain organophilic layered silicates that would be more likely to have hydrophobic compatibility. The organic cations reduce the surface energy within the galleries and will increase the interlayer distances, therefore, modified MMT can more easily interact with the polymer matrix, forming exfoliation morphology and enhance the strength of the interface between the clay and the polymer [27].

There are continuing efforts to take advantage of recent advances in nanotechnology. Persico et al. [28] studied the possible use of melt compounded nylon 6 nanocomposite with different percentage of clay/jajoba oil for cosmetotextile applications. They studied the desorption of oil from nanoclay composite fibers with different morphologies. Study of the structure and properties of a polypropylene/montmorillonite hybrid composite and melt spun fibers showed that good intercalation of clay in a PP matrix improves the spinnability [29]. It has been claimed that good intercalation of clay in PP matrix slightly reduced the viscoelasticity due to disruption of chain entanglement by high aspect ratios of clay platelets, and also eliminated the surface melt fracture [30], and postponed the critical shear rate for onset of melt fracture. At the same draw ratio, fibers with clay had higher crystallinity, lower orientation, and improved moisture absorption and dye affinity [29].
PET/Na-MMT nanocomposites and MXD6/Na-MMT with enhanced barrier properties and mechanical properties [31-33] have been described previously in the literature. Several workers have attempted to synthesis exfoliated silicate in PET as well as MXD6 matrices using melt blending and in situ polymerization methods. Some authors have reported 25% oxygen permeability reductions for PET/MMT (1 wt%) by using in situ polymerization. A 50% water vapor permeability reduction for PET/MMT nanocomposite produced by melt blending was also reported [34]. Due to high temperatures needed for processing PET, the PET nanocomposites have become major technological challenge due to potential degradation of clay’s organic modification during processing [35].

Since it has been recognized that both PET-aromatic polyamides blends and PET clay nanocomposites have given good results in terms of barrier properties, additional MMT gives better dispersion in MXD6 than PET. Therefore, there is a potential to combine these two approaches, to develop a technology to prepare a monolayer PET polyamide (MXD6) nanocomposite with low oxygen permeability, and paying attention to the relationship between barrier properties and the processing route adopted.
1.2. Objectives

The use of inorganic nanoparticles in polymers is a widely investigated area of research. The commercialization of polymeric nanocomposites has begun in the past few decades. Products that are based on nanocomposites have already entered the market and are mainly in automotive (polymers for fuel lines and flame retardants) and packaging (gaseous barriers for food packaging). Many new products are presently being developed for electronics (capacitors, solid electrodes for batteries, nanoscale switches and sensors). Other commercialization of nanocomposites are slowly following because they are hindered by the lack of understanding of processing and effects of the nanoparticles in the polymeric matrix.

Although nanocomposites show promising properties for various applications, it is difficult to fabricate nanocomposites exhibiting a controlled dispersion of nanoparticles [36-38]. For example, each individual clay platelet offers a large surface area and high aspect ratio, both of which can be critical in improving mechanical properties, thermal stability and barrier properties. Separating and distributing these layers throughout polymer matrices represents a challenging task. For a larger number of polymers, an effective method to uniformly disperse the individual layers remains unavailable. Even for certain polymers in which controlled dispersion was successful, the understanding of interaction between polymer matrices and nanoparticles, and the structure-property relationships remain unclear. When the particle dimension approaches a length scale comparable to that of a single polymer molecule, the effect of interfacial interactions becomes dominant and the physical and chemical properties of polymers may be fundamentally different from those of bulk polymers [39-41].
In this work, the main objective of the investigation is to develop a novel processing method for preparing exfoliated PET/Na-MMT, MXD6/Na-MMT, and PET/MXD6- Na-MMT nanocomposites. It is believed that by using suitable modified processing, one can achieve good dispersion of nanoclays in polymeric products, and that achieving good dispersion or intercalation will result in improved properties of PET. This research is conducted to examine if pristine MMT dispersion/intercalation is successfully accomplished by using the developed novel processing method and if so, whether they result in morphological, mechanical and barrier properties improvement for both unoriented and oriented PET nanocomposites.

Specific objectives are:

- Development of effective and reliable ways to create uniform dispersion and exfoliation of nanoclay at nanoscales
- Introduction of novel processing/preparation methods (clay slurry + polymer melt extrusion) for nanocomposite materials
- Selection of adapted characterization methods for nanostructured polymers
- Evaluation of the thermal and crystallization behaviors, mechanical property as well as barrier property of PET/Na-MMT nanocomposites and MXD6/Na-MMT nanocomposites
- Optimization of the synthesis of nanocomposites with different wt% concentrations of Na-MMT
- Optimization of compatibility of PET nanocomposites and MXD6.
- Addition to the knowledge platform for nanocomposites, manufacturing, processing and application, and to make this available to commercial production
1.3. **Organization of Dissertation**

In order to achieve the aims and objectives of this project several distinct phases of work were required. Chapter 1 briefly describes the motivation, prime objectives and the scope of the work.

Chapter 2 provides an overall introduction of polymer nanocomposites and the different factors that have effects on the properties. These are the necessary background information relevant to the content of the thesis. A comprehensive review of the improvement of different properties, such as thermal, barrier and mechanical properties are discussed. This allows familiarization with the techniques and processes required for clay/polymer nanocomposite research.

Chapter 3 discusses the materials for preparation of PET/MXD6-Na-MMT nanocomposites. The characterization technologies used in the research are also introduced. These characterization technologies illustrate the basic nanocomposite production process and its related properties analysis (thermal, morphological, mechanical, oxygen barrier).

Chapter 4 describes the experimental method for the preparation of PET/MXD6-MMT nanocomposites. The processing technology is discussed in four steps: preparation of clay slurry, processing of PET/Na-MMT nanocomposites, processing of PET/MXD6-MMT nanocomposites, and the solid state polymerization of all the nanocomposites. The essential backgrounds of the experimental methods and reaction parameters are included.

Chapter 5 reports on the experiments results on dispersion, crystallinity, oxygen permeability, and mechanical properties of the PET/Na-MMT and MXD6/Na-MMT nanocomposites.
Chapter 6 follows the analysis of the exfoliation transfer of MXD6 nanocomposite with PET. The potential for the MXD6 studied to act as carrier for exfoliated clay in PET was studied and the best materials for this approach and novel processing technology were developed. Aspects of clay dispersion and properties are investigated with particular attention to the effects of clay/polymer compatibility.

Chapter 7 concentrates on the stress-strain relationship of uniaxial stretched PET nanocomposites films as well as the effect of extension ratio on strain hardening point are also studied. A suitable stress-strain model was developed for PET nanocomposite. The changes of properties (morphology, mechanical and barrier) of PET nanocomposites during the process of stretching are evaluated. Additionally, the success of preparation of PET nanocomposite bottles shows the presence of microvoids for PET bottle with nanoclay, and this phenomenon is demonstrated in this chapter.

Chapter 8 shows the overall conclusions of the work carried out in this study and proposes recommendations for further work on this project.
Chapter 2

Polymer Nanocomposite

2.1. Fundamental Knowledge On Polymer Nanocomposite Studied

Polymers can be broadly defined as large macromolecules formed from a repeating smaller unit. Polymer materials can be both naturally occurring (proteins), and synthetic (polyethylene). For the purposes of these studies and for use as packaging materials for beverages, thermoplastic polymers (polymers that can be heated to form a liquid or melt and then cooled to a solid state) are generally used. The two main types of thermoplastic are glassy amorphous materials (polystyrene) and semi-crystalline materials (HDPE), which tend to have a less regular structure and also exhibit less intermolecular attractions than semi-crystalline polymers.

2.1.1. Poly (ethylene terephthalate) (PET)

In this study, two different polymers are studied based on their thermal transitions, mechanical properties, and barrier properties [42-44]. Of these the most widely used thermoplastic barrier polymer is poly (ethylene terephthalate) (PET), which belongs to the generic family of polyesters and finds its major commercial applications as fibers, bottles, and films. PET is one of the most versatile engineering plastics because its low
cost, chemical resistance, good thermal resistance, excellent electrical insulation and optical properties and high strength and stiffness with good processability. Among a variety of applications, PET is used in the manufacture of automotive and electronic parts, textiles, soft drink containers, and high performance films.

PET is synthesized by step-growth polymerization, which requires two reaction steps [6, 43]. Initially, the monomer, bis-hydroxyethyl terephthalate (BHET) of PET monomer, is produced by the trans-esterification reaction of dimethyl terephthalate (DMT) and ethylene glycol (EG) at a temperature of between 150°C and 220°C and a pressure of 100kPa or by the direct esterification reaction of terephthalic acid (TPA) and EG at a temperature of 240-260°C and a pressure of 300-500KPa. The next step is a pre-polymerization reaction of BHET at a temperature of 250-280°C that produces PET with a degree of polymerization (DP, the number of repeat unit in an average polymer chain) of 30. A higher molecular weight PET with DP of 100 is made by a further reaction at a temperature of 280-290°C and a pressure of 50-100 Pa. This product is used for the manufacture of fibers and sheets that have a number-average molecular weight (Mn) of 15 to 20 kg/mole corresponding to an intrinsic viscosity (IV) of between 0.55 and 0.67 dL/g. For products such as containers, the polymer is produced with DP of 130-150 by the additional process of solid state polymerization (SSP) at 210°C under vacuum environment for 12hrs. The container-grade PET has an average molecular weight ranging from 24 to 36 kg/mol that corresponds to an IV of between 0.75 and 1.00 dL/g. Today, more than 70% of global PET manufacture is based on TPA. Fiber grade and bottle grade PET account for most of the global production of PET.
The selection of the appropriate grade of PET for a specific end-use requires considerable care. In this context, one of the first considerations is the molecular weight of the polymer, which is generally reported as intrinsic viscosity, IV. PET grades of different IV are used depending of the application, namely [6]:

- **fiber**: uses homopolyesters made in a wide range of molecular weights to meet different end-use requirements. The IV range is usually from 0.40 to 0.98 dL/g.

- **film and sheet**: the first uses homopolyesters with IV in the range 0.55 to 0.65 dL/g that contains slip additives added during polymerization, whereas the second use (sheet for thermoforming) was IV in the range of 0.70-1.00 dL/g.

- **bottle**: uses resins having IV in the range of 0.70-0.85 dL/g, and low acetaldehyde content. Although of less concern in fibers and films, acetaldehyde content is importance in bottle applications because of an off-taste caused in the contents of the bottled beverage.

Nowadays, most of the PET bottle grades are copolymers slightly modified through addition of 1-2% isophthalic acid or cyclohexanedicarboxylic acid dimethyl ester during polymerization, in order to disrupt the polymer chain. These modifiers reduce the melting point and decrease the rate of crystallization, effectively broadening the processing window of the resin.

PET is a slow crystallizing material, being a prime example of a polymer whose crystallinity can be controlled via processing. The crystallization behavior of PET has been broadly studied, and can be generally achieved by one of the following pathways [6, 44]:
**Quiescent crystallization**: the amorphous PET is exposed to temperatures above the glass transition temperature ($T_g$). The thermal energy imparts mobility into the polymer chains, allowing for reorganization into a crystalline structure. When crystallization takes place PET becomes white and opaque, due to the growth of spherulitic structures large enough to interfere with visible light [45].

**Strain-induced crystallization**, SIC: If amorphous PET is oriented under the proper conditions, the material forms a strain-induced crystallization morphology which has three dimensional packing order triclinic unit cell [46-54]. The domain sizes of the crystals remain small enough for optical transparency to be maintained. This method is commercially important for processing of films and bottles.

**Combination of strain induced the thermal crystallization:** PET samples with strain-induced crystallization morphology can be exposed to additional thermal energy, by annealing above its crystallization temperature ($T_{cc}$), in order to further crystallization [55]. The crystallization time in this case is between a few minutes to a few hundred milliseconds [44, 56-57], depending on the annealing temperature and on the morphology of the sample. The annealing process promotes the growth of the crystals and residual stress relaxation that improves the uniformity and the thermal resistance of the products.

In the packaging industry, one of the main markets for PET is plastic bottles for carbonated soft drinks (CSD), water, and juice. Large quantities of PET resin are used for the production of stretch blow molded bottles. The resin is PET-copolymer that contains 2.3-3 wt% of added comonomers, such as isophthalic acid (IPA) or cyclohexanedomethanol (CHDM) to disrupt the polymer chains. These resins have a
lower melting point $T_m$, slower crystallization and improved clarity particularly in heavy wall applications compared to the homopolymer. Materials with a higher IV offer greater mechanical strength and lower crystallinity relatives to materials with a lower IV. Generally, the PET-bottle grade has an IV between 0.70-0.85dL/g, a glass transition temperature ($T_g$) of 69-115°C, a melting temperature $T_m$ of approximately 250-260°C, and a density between 1.3-1.4 g/cm$^3$.

The properties of PET are not only dependent on high crystallinity as in Polyamide (PA) and polyoxymethylene (POM) [58], its excellent mechanical properties are also attributed to molecular orientation in the matrix, achieved by stretching during processing. The mechanical properties of the polymer are greatly enhanced in the orientation direction. The oriented PET molecules can, however, relax and change to random state during cooling process. This relaxation results in the loss of the improvement obtained from the orientation. In order to keep the orientation, the oriented molecules are frozen during the stretching process. Unoriented PET has average tensile strength of 50-55MPa compared with up to 165MPa when PET has an orientated structure. The key properties of PET are attributed to molecular orientation, resulting in PET having the following [59]:

- Excellent gloss and clarity
- Very tough and impact resistant
- Low permeability to CO$_2$
- Good processability
- Good dimensional ability
- High heat resistance
A processing approach for getting the orientation effects is:

PET film with extremely low crystalline content is produced by melting PET pellets, shaping and then cooling rapidly in cold water. The amorphous film is warmed up to 25°C above glass transition temperature ($T_g$) and the stretched in the machine direction. The PET molecular chains orient in the stretch direction.

The film is then stretched in the cross direction. Biaxial orientation structure of polymer molecules takes place in the PET film. The alignment of stretched molecules results in the formation of tiny crystallites (50-75Å) during the heat-stretching process [60]. This phenomenon is called strain-induced crystallization. The film is then cooled down to set the shape. The product is oriented and solidified to keep the orientation locked in place.

PET resins have a slow crystallization rate when this method of treatment is used so a low crystallinity is obtained during processing, resulting in transparent products. Most beverage bottles, such as CSD and water bottles produced by biaxial orientation blow molding, have 25% crystallinity and heat resistance around 85°C. The bottle from this method can be filled with a hot liquid product with a temperature 82-85°C. But in hot fill applications with a temperature of about 91-93°C, for instance juices, sport drinks, and high acid drinks, the properties of the blow molded PET bottles have to be enhanced by annealing at temperature between $T_g$ and $T_m$ in a hot mold with a wall temperature of 125-145°C [60]. This process is called as heat setting technique which significantly increases the crystallinity to 39-42% and thus raises the heat resistance to nearly 95°C, and enhances the gas barrier properties.
Because of the very slow crystallization rate, PET injection molded parts, for examples automotive, electronic, and furniture parts, have poor mechanical properties. To promote crystallization in injection molded parts, the mold temperature is increased to 140°C and resin is modified using nucleating agents. Generally, commercial PET resins used in engineering applications are filled with 20-50% of fiber to increase strength, and stiffness [61].

2.1.2. Poly-m-xylylene Adipamide (MXD6) [62-64]

Poly-m-xylylene adipamide (MXD6), is a semi-crystalline aromatic polyamide used as a plastics material and was first disclosed by Lum et al in 1956 [62, 64]. Despite the development of laboratory samples, commercialization did not occur until the early 1970’s when Mitsubishi Gas Chemical Company began production of para-xylene diamine free meta-xylene diamine. It is formed by the condensation of m-xylene diamine with adipic acid. A generalized synthesis would involve low stream pressure (~400-700 KPa) addition of meta-xylene diamine to molten adipic acid (mp 153°C) until the ratio of functional groups approaches one. This procedure is enough to produce resins a reasonable molecular weight although higher molecular weight materials can be produced through post polycondensation SSP.

Initially these materials were emphasized as replacements for adiphatic polyamides where increased rigidity and good surface finish are desirable properties in injection molded parts. Other applications involve the use of fillers which allows the substitution of metals due to the high mechanical strength, modulus and heat resistance [65]. In more recent times greater attention has been paid to the gas barrier properties of MXD6. In
1974 Mantsunami et al. produced the first patent on high gas barrier flexible MXD6 film [66], followed by Okudaira et al. [67] who were able to publish a patent on multi-layer, stretch blow molded bottles in 1983. Further work on MXD6 has shown that in the presence of small quantities of cobalt compounds MXD6 acts as an oxygen scavenging compound [68] and that blending of polyamides with PET can also produce packaging materials with improved gas barrier properties [69].

Due to the wide processing window for MXD6, manufacture of such multi-layer and blend materials results in doubled shelf life with a 5 wt% barrier layer. In addition to MXD6 multi-layered structures Mitsubishi has collaborated with Nanocor on the development of a nanocomposite grade of MXD6 called Imperm. This material offers an additional one hundred percent increase in the gas barrier properties of multilayer bottles compared to standard PET [70]. Blending of MXD6 with PET has also achieved some commercial success in improving the barrier properties but the results are much more modest. Polyshield™ produced by Invista offers CO₂ permeation reduction of 15% in conjunction with oxygen ingress of less than 1 ppm per year due to combined passive barrier and scavenging [71]. Overall the use of MXD6 as a barrier material for PET packaging offers many possibilities, but so far some limitations have prevented its widespread usage. These limitations include difficulty in recycling, reduced transparency and yellowing. For multilayer packages in particular, there are the added issues surrounding increased manufacturing complexity and possible delamination of the layers.
2.1.3. Montmorillonite Layered Silicate

There are two main types of clay structure 1:1 kaolinite type and 2:1 layered silicate [72]. Both contain stacks of layers held together by hydrogen bonds (as in 1:1) or by interlayer cations (as in 2:1). Kaolinite 1:1 consists of metal-hydroxide and silicon-oxygen network of sheets fused together by hydrogen bonding. The 2:1 layer silicates include mica, smectite, vermiculite, and chlorite. The smectite group is further divided into montmorillonite (MMT), nontronite, saponite and hectorite species [21-22, 73-77].

Among these layered silicates, MMT is the most commonly used nano-filler for processing the nanocomposites. The crystal structure of montmorillonite consists of layers made up of two silica tetrahedral fused to an edge shared octahedral sheet of either aluminum or magnesium hydroxide [78]. Van der Waals force balances these layers, referred to as interlayer of gallery regions. Because of the cations on the interlayers, the layered silicates are greatly hydrophilic and thus naturally incompatible with most polymers. The cations in the galleries, however, can be easily replaced with other cations to make the clay more compatible with polymers. The surfactants are cationic and migrate into the galleries where they are substituted in place of hydrated cations. The most common surfactants used are alkylammonium and alkyphosphoniu salts. The role of alkylammonium cations in the organo silicates is to lower the surface energy within the galleries and improve the interlayer distance [79]. The sodium ions in natural clay are exchanged with an amino acid such as 12-aminododecanoic. A schematic of the reaction is shown in Equation 1.

\[
Na^+ - Cl + HO_2C - R - NH_3^+ Cl^- \rightarrow HO_2C - R - NH_3 - Clay + NaCl
\] (2.1)
The modified clay is more compatible and facilitates the interaction of polymer chains between the clay galleries. At a given temperature, layer spacing depends on the organic chain length [64] and cation exchange capacity (CEC) of layered silicate [80].

The smectite clays have a basic lattice similar to that of talc and mica. The exchangeable cations in the interlayer, however, make the smectite clays different from talc and mica that do not have the exchangeable cations. The exchangeable cation is able to be replaced with other cations with long alkyl tails that results in an increase in the gallery spacing. This phenomenon is not found in talc and mica. The ion exchange property of MMT is an important property for the production of polymer nanocomposites. The smectite group of clay minerals such as MMT, hectorite, and saponite has been mainly used in the production of nanocomposites. MMT is chemically categorized as Magnesium Aluminum Silicate, Al$^{3+}$ substituted by Mg$^{2+}$ while hectorite is chemically classified as Magnesium silicate, Mg$^{2+}$ replaced by Li$^{+}$ [81]. This difference in chemical composition produces a difference in the lattice structure. As a result, MMT is likely to have a sheet-like structure while hectorite is likely to have strip like structure. The properties of the final nanocomposites depend on the type of clay, clay modifier, types of polymers, and the intercalation methods. These factors affect the degree of exfoliation of layered silicates in the polymer matrix. The effective exfoliation and dispersion of the layered silicate is important to accomplish the maximum performance of the nanocomposites.
2.1.4. Blends of PET with MXD6

Several approaches have been used to attempt to enhance the barrier properties of PET resins. So far, a few studies have been carried out on blending high barrier polyamide with PET to improve PET container performance [63, 82-93]. Poly (m-xylene adipamide) (MXD6) is one of the crystalline polyamides, which is produced through polycondensation of xylene diamine (MXDA) with adipic acid. The oxygen permeability of PET can be dramatically reduced by blending it with this high barrier aromatic polyamide [94]. Moreover, the barrier properties of the final blend depend not only on the composition or intrinsic barrier properties of the components but also on the final morphology of the blend. It is found that the orientation could transfer the spherical morphology into high aspect ratio platelets creating a tortuous pathway for the diffusion of oxygen, water molecules and thus decreases the gas permeability [95-96].

Even though the barrier performance of PET is dramatically improved by incorporation of the MXD6, reduced clarity of stretch blow molded bottles was observed and limited the application of PET/MXD6 monolayer bottles [97]. Lower haze values obtained in quenched isotropic blends of PET/MXD6 resulted from the close match of their refractive indexes. After the orientation, the haze value increases because the orientation process changes the refractive index values of PET and MXD6 so they no longer matched [84].

In order to solve the compatibilization issue of PET/MXD6 blends. Many studies attempted to change the composition, through copolymerization of the PET or MXD6 to obtain a match in which either the refractive index of the oriented polyamide constituent is increased, or the refractive index of the oriented polyester decreased [98]. Some studies
selected PET-ionomer as a compatibilizer to minimize of the differences in refractive indexes of the two phases [84]. This approach is expected to achieve enhanced barrier properties for PET bottles as well as the good clarity by blending MXD6 with PET.

Besides the copolymerization of PET with isophthalate to match the refractive index with MXD6 after orientation, PET-ionomer is another route used to compatibilize the PET/MXD6 blends. Sodium 5-sulfoisophthalate (SIPE) brings the highly polar constituent whose ionic groups are presumed to interact with the polar constituent, whereas the non-ionic backbone of the ionomer is compatible with the less polar constituent. The use of sulfonated ionomers as compatibilizers for PET and aliphatic polyamides has been demonstrated, with both ion-dipole interactions and transesterification reactions [99-101]. It is found that the reduced domain size of polyamide effectively reduced the haze for PET/MXD6 blends.
2.2. Polymer Nanocomposite Processing [26, 102-103]

Nanocomposites, in the most general sense, are formed by the incorporation of a nanoscale particle (referred to as the filler) into a macroscopic sample (known as the matrix). Through the incorporation of filler on the nanoscale rather than the microscale it has been shown that the properties of a polymer matrix can be greatly enhanced at lower filler concentration than observed with microscale fillers. Many matrices have been investigated with numerous fillers such as clays, graphite, carbon nanotubes, metal oxides, nitrides and polyhedral oligomeric silsequioxanes. Over the past two decades considerable research effort in both academia and industry has been directed towards the development of nanocomposites and in particular, the development of clay/polymer nanocomposites [72, 104]. This interest in polymer/clay nanocomposites was investigated by the pioneering work conducted by the Toyota group [105-106]. The Toyota group’s method was to prepare intercalated clay with a suitable organic modification followed by mixing the organoclay with a monomer (i.e. carpolactam) and possibly catalyst/activator. The mixture was then heated to the prescribed polymerization temperature. The resultant nanocomposite exhibited improvements in mechanical strength without the embrittlement associated with microcomposites and additional improvement in high temperature properties. Following this work many researchers investigated the technology using numerous polymers until finally; in 1995 Allied Signal patented a new method for the manufacture of nanocomposites. In this method the inventive step was to use a silane in conjunction with alkyammonium to induce sufficient affinity between the organoclay and matrix polymer (PA6) to exfoliate the clay in the melt compounding (e.g. twin screw extruder). The final method used for nanocomposite synthesis is from solution and has
been attempted with many polymers, but so far has not achieved the commercial success of in-situ polymerization and melt processing methods due to the quantities of solvent required.

2.2.1 Formation of Nanocomposite from Solution [26, 103, 107-109]

The solution process involves mixing a polymer solution with clay. This method is based on a solvent system in which the polymer is soluble and the swollen polymer adsorbs onto the delaminated sheets before the solvent is evaporated at higher temperature (Figure 2-1). First, the clay is dispersed in the appropriate polarity media e.g. water for hydrophilic clay or organic solvent for organoclay. The second step is to dissolve the polymer in the same, or alternative compatible solvent. Care should be taken that the clay can be readily dispersed in the solvent used for the polymer. The clay dispersion and polymer solution are then mixed and the polymer displaces solvent molecules within the swollen clay layers. The solvent is removed and an intercalated/exfoliated composite is produced.

Depending on the interaction of the solvent and the layered silicate, the crystalline clay may be delaminated in a solvent due to the weak van der Waals force stacking the layer together. Polymer chains then can be adsorbed onto the delaminated individual layer. However, upon solvent removal, the layers can reassemble to reform the stack with polymer chains sandwiched in between, forming a well ordered intercalated nanocomposite.

Historically many water soluble polymers such as polyethylene oxides (PEO) [110], poly (vinyl alcohol) [26, 111-112], and polyvinylpyrrolidone (PVP) have been used in
intercalate clay galleries by this method. Organic solvents have also been used to produce nanocomposites by the solution method. For example, Jeon et al. [114] produced HDPE nanocomposites by dissolving HDPE in xylene/benzonitrile mixture with dispersed organoclay. Further examples include the synthesis of syndiotactic PS nanocomposite [115], polyimide nanocomposite [116], poly (dimethylsiloxane) nanocomposite [117].

Ou et al. [107-108] produced PET/MMT (1, 5, 10 and 15 wt%) nanocomposite via solution assisted blending. MMT was modified with an intercalation agent, such as cetyltrimethylammonium chloride (CTAC) [107] and cetylpyridinium chloride (CPC) [108]. After that it was dispersed in the PET solution. They observed the same trends with both surfactants. TEM and WAXS results detected a mixed structure of intercalated/exfoliated morphology, for nanofiller contents between 1 to 10 wt% and tactoid morphology of PET/OMMT from 10 to 15 wt%. Differential scanning calorimetry (DSC) analysis showed that OMMT behaves as a nucleating agent and enhances the crystallization rate of PET, with maximum enhancement for OMMT content of 10 wt%. Thermogravimetric Analysis (TGA) investigations have shown that thermal stability of nanocomposites are enhanced for all concentrations of MMT [108].

Although lots of nanocomposites have been produced using solution processes, it is evident that only a few nanocomposites can be formed using this method. Another disadvantage of this method is the large amount of solvent needed, resulting in a higher cost. Also the types of polymers than can be used to fabricate nanocomposites ultimately depend on the availability of a proper solvent, limiting the applicability of this method.
2.2.2. Formation of Nanocomposite from Melt Blending [119-123]

Instead of using solvent as the medium, organically modified layered silicates can be mixed directly with molten polymer either statically or under shear. This method utilizes conventional extrusion technology such as a twin screw extruder, to blend clay into a polymer during melt processing. The main factors stimulating interest in the technique are flexibility in formulation, economic favorability and that the technique requires only commonly used compounding and fabrication equipment. In this technology, the mixing and resultant shear generation break down agglomerated silicate particles into stacks of clay platelets which, are in turn broken down further into smaller tactoids. Diffusion of polymer chains coupled with shear generated in the extruder is thought to peel apart the remaining platelets in the clay platelet stacks to improve dispersion further. If the clay is compatible with the polymer, the expanded polymer chains could diffuse into its galleries easily and form intercalation and exfoliated nanocomposites. Pristine Na-MMT clay is incompatible with PET and other polyester, therefore, this method is widely used for blending modified clay with polymer.
Several factors have been found to be significant in optimizing the melt mixing process to produce the highest level of dispersion possible. Studies conducted by Paul et al. [124] have illustrated the importance of clay treatment in conjunction with differences in extruder type and screw configuration on the dispersion of polyamide (PA) nanocomposite. In addition, this study also elucidated the importance of extruder residence time indicating longer residence times to be beneficial in producing the best dispersed nanocomposite. In addition to these factors it has been determined that melt viscosity [79] and the location of organoclay addition [125] can also play an important role in determining the extent of exfoliation, and the final nanocomposite properties.

In the work of Sahu et al. [126] the properties of nanocomposite films were examined and some improvements were observed, although biaxial stretching, and fatigue of sample during stretching resulted in reduced properties compared to the PET control. Sanchez-Garcia and co-workers [119, 127] have also investigated the permeability behavior of PET nanocomposites produced from the melt. Nanocomposites were produced from NanoBioMatters Nanoter 2000 organoclay (5 wt%), which contains an undisclosed surface modification. The resultant nanocomposites were investigated to determine morphology, crystallization properties and barrier properties to oxygen, water, and limonene. In his study, the barrier properties were improved to all the permeants tested (50% reduction in oxygen permeation) further confirming good dispersion of the clay and development of a tortuous pathway.

Wang at el. [128] produced intercalated PET/OMMT (1, 3, and 5 wt%) nanocomposite via extrusion in a twin-screw extruder. Best delamination was observed for the MMT content of 1 wt%. Addition of MMT led to a $T_m$ increase, decrease of a $T_{cc}$
and reduced half peak width of the crystallization peak during cooling. This was achieved owing to the nucleating effect of OMMT. A PET/OMMT nanocomposite has the optimum comprehensive mechanical property when OMMT content is 1 wt%. While for 3 wt% and 5 wt% nanocomposites properties such as tensile strength, impact strength, flexural strength, and elongation at break are less than that of the neat PET. Thermal stability was improved for 1 wt% content of MMT, as measured by TGA.

Tsai et al. [33] synthesized PET/OMMT (0.7, 1.2, 2.5 wt%) nanocomposites with exfoliated morphology. IV was increased with MMT load. Nanocomposites showed a significant improvement of anti-UV properties and CO₂ gas barrier properties with MMT load increases were measured. A PET/OMMT nanocomposite with 2.5 wt% was characterized by the reduction of clarity, while the other formulations were transparent.

The thermal stability of commercial organoclays and other ammonium modified clays has been explored in the literature and it is clear that degradation of the surfactant occurs at temperatures well below the processing temperature of PET. In order to address this fundamental deficiency in commercial organoclays, considerable research time has been invested. In the work conducted by Davis et al. [129], PET nanocomposites were produced by twin screw extrusion, while varying conditions of screw speed and varying residence time. The nanocomposite was processed at 290°C with 5 wt% clay added. The ammonium modified clay nanocomposite was quickly found to be extremely discolored due to degradation of the clay surfactant.

In another study conducted by Costache et al. [130] novel thermally stable surfactants based on quinolinium and a vinylbenzyl-ammonium copolymer were used in the melt synthesis of PET nanocomposites. Despite the increased thermal stability the
nanocomposites produced had intercalated morphology and full exfoliation was not achieved.

In summary, melt intercalation offers a 'simple' way of preparing nanocomposites. However, very careful attention has to be paid to finely tune the layered silicate surface chemistry to increase the compatibility with the polymer matrix. Processing conditions have profound effects on the structure evolution of polymer nanocomposites prepared by melt intercalation and these effects are still unclear and full understanding continues to be a challenge.

2.2.3. Formation of Nanocomposite through in situ Polymerization [131-141]

In this technique, the clay (modified clay) is dissolved and swollen in liquid monomer. This system helps the monomer to start migrating into the interlayer spacing of the clay. The reaction then occurs in the galleries of the layered silicate. When the monomer penetrates into clay particle layers and forms long polymer chains, the interlayer spacing is expanded and promotes the clay exfoliation leading to a well-dispersed system.

In addition to epoxy clay nanocomposites, a wide variety of other thermoset, e.g., polyimide, polyurethane, poly (dimethylsiloxane) (PDMS) nanocomposites were prepared. Exfoliated PDMS nanocomposites were prepared when hydroxyl terminated oligomer resulted in little intercalation. This again demonstrates the importance of the favorable interaction between the constituents of the system. Unsaturated polyester (UP) nanocomposites were also reported in the literature. Instead of using onium cations to
modify the clay surface, a methacryl - containing silane coupling agent was used and exfoliated unsaturated polyester nanocomposite was synthesized.

The synthesis of PET nanocomposites has some distinct advantages over the solvent assisted process as large quantities of solvent are not required and there is potential for PET resin manufacturers to produce nanocomposite materials with very little modification of existing plant facilities. As would be expected with these advantages there is a larger body of literature pertaining to PET nanocomposites synthesized by this route.

In addition to clay based nanocomposites, it is of note that researchers have produced PET nanocomposites with alternative nanofillers such as silica, calcium carbonate, barium sulphate and alumina. These studies examine factors such as dispersion of the filler, influence on crystallization behavior and wear rate.

For PET/clay nanocomposites Zhang et al. [32] modified MMT with hydroxypentyl trimethy ammonium iodide (HPTA) and hydroxyethyl isonicotinamide (HENA) and polymerized with BHET to produce composites with polymer anchored to the clay.

In the work of Ke et al [142], clay was modified with a quaternary ammonium, with carboxylic acid functionality and dispersed in ethylene glycol. Polymerization was carried out by ester interchange of dimethyl terephthalate and ethylene glycol/clay slurry to produce nanocomposites with 1, 2, 3 and 4 wt% clay. XRD and TEM were used to investigate the nanocomposite morphology and it was found that the clay had dispersed evenly in the matrix to produce a mixture structure of exfoliated platelets and small tactoids. Other tests on the nanocomposites showed that the clay acted as a nucleating
agent for cold crystallization and that a 50% reduction in oxygen transmission of films could be achieved with 3 wt% of clay.

In the work conducted by Ke and Stroeve [143] polymerization of PET monomers was conducted in the presence of the modified clay and also clays modified with ethanolamine, cetyl trimethylammonium salt, laurilamine and hexanediamien. Resulting morphological investigation revealed an intercalated nanocomposite had formed with an interlayer spacing of approximately 3.4 nm and some large agglomerations of clay. As per previous examples the clay acted as a nucleating agent and improvements in tensile strength and HDT were also observed.

Chang et al. [144] produced PET/OMMT (1, 2, and 3 wt%) nanocomposites. All concentrations of OMMT led to slight increases of IV. Some of the OMMT particles were well exfoliated in the PET matrix, and some of them had tactoid. Improved thermal stability and tensile properties compared to the pure PET were observed for all nanocomposites. The values of the ultimate tensile strength and the initial modulus of the PET/OMMT fibers decreased markedly with increasing stretching ratio from 1 to 16.

Previous papers have also focused on ammonium based surfactants for clay, which may degrade at PET polymerization temperatures. It is believed that poor thermal stability of surfactant and subsequent degradation may lead to reduce clay dispersion and hence lower quality nanocomposites.

2.3. Structures of Polymer Nanocomposite [145-147]

The advantage of clay compared to other mineral fillers for plastics, such as talc and mica, comes from its ability to be delaminated and dispersed into individual layers of the
order of about 1 nm thickness. Based on the extent of dispersion of platelets in the polymer matrix, polymer nanoclay based composites are classified into three widely known morphologies: intercalated, exfoliated, and tactoid [34]. In Fig 2-2, the lighter background is polymer while the black lines are the cross-section of clay platelets. The characteristic of tactoid nanocomposites is that the modified layered silicate structure are retained after introduction into the polymer. The term intercalation describes the case where a small amount of polymer chains penetrate into galleries of silicate and expand by 2-6 nm. Exfoliation occurs when polymer chains further separate the clay platelets, e.g., by 8-10 nm or more. Exfoliated structure refers to dispersion and homogeneous spreading of platelets in the polymer matrix beyond 10 nm.

The morphology of intercalated polypropylene/clay nanocomposites was studied using wide angle x-ray scattering, small angle x-ray scattering, transmission electron microscopy, polarized optical microscopy and light scattering. In an intercalated structure, the inter-layer spacing is usually 1-4nm and in an exfoliated system, the particle separation is about 20-50 nm.

Figure 2-2 TEM images of three types of microstructure of nanocomposites: tactoid, intercalated, exfoliated (from left to right) [34]
2.4. Examination of the Factor Leading to Property Improvement

2.4.1. The effect of mineral filler type [148-149]

Kazuhisa et al. [21] worked on a polyimide mica hybrid. It is generally believed that the improvements of the barrier and other mechanical properties are mainly caused by the high aspect ratios (10-1000) or larger surface areas of exfoliated clay particles. The typical silicates consist of stacked sheets that in his research are about 460 Å (hectrite), 1650 Å (saponite), 2180 Å (montmorillonite), and 12300 Å (synthetic mica) in length. It was found that the longer the length of clay mineral, the more effectively properties were improved. (Fig 2-3) [21]

The theoretical critical volume fraction $\Phi_C$ versus aspect ratio $L/W$ (S=0) of the silicate platelets was studied in the work of Chunsheng et al. [150] In Fig 2-4, two solid symbols indicate the test date of $O_2$ gas permeability in $C_{18}$-montmorillonite ($L/W=150$ and $\Phi_C =1.25$ [151]) and polyester-clay ($L/W=200$, $\Phi_C =1.4\%$ [22]) nanocomposites. These experimental data are consistent with the predications and indicate that aspect ratio $L/W$ of clay plays a key role in controlling the barrier properties.
Figure 2-3 Clay length dependence on relative permeability coefficients of water vapor
Jin-Hae et al. [152] reported effects of aspect ratio on the properties of PET hybrid fibers. In his study, two kinds of thermally stable organoclays (MMT, mica) were used to prepare PET nanocomposites. It was observed that a decline in the tensile properties occurred with increasing aspect ratio, in the case of PET-MMT nanocomposites. In contrast to the results for PET-MMT hybrid fibers, the ultimate strengths and initial moduli of organo-Mica hybrid fibers were found to be independent of increases in aspect ratio.

T. D. Fornes et al. [79-80] evaluated the effect of two sodium montmorillonite sources (Yamagata, Japan, and Wyoming, USA) on the morphology and mechanical properties of nylon 6 nanocomposites. TEM images revealed a slightly larger average particle length and slight higher degree of platelet exfoliation for the Yamagata based...
nanocomposite than for those from Wyoming. Similar results were obtained indicating that higher stiffness and strengths are attainable with increased particle aspect ratio.

Gatos [153] showed the influence of the aspect ratio on oxygen permeation properties of hydrogenated nitrile rubber (HNBR) nanocomposite. This work showed that increasing aspect ratio (MMT<fluorohectorite) leads to lower permeability.

2.4.2. The effect of particle surface treatment [154-166]

The compatibility between the pristine clay and polymer matrix can be enhanced by modifying the polymer with a polar function [165-166]. The strong interaction between the two phases could further improve the clay dispersion.

Milan et al. [167] modified three organoclays of Closite 10A, 25A and 30B with silane, [3-(glycidyloxy)-propyl] trimethoxysilane. The recycled PET was prepared by blending with organoclays and results showed that Closite 25A with further silane modification increased the homogeneity of clay in the PET matrix. The Closite 10A and 30B gave a low level of exfoliation. Davis et al. [168] investigated two systems prepared via twin-screw extrusion, utilizing different organic modifiers in PET/MMT. Matayabas et al. [169] prepared PET copolymer nanocomposites by melt blending with a commercial organoclay, called Claytone APA (modified montmorillonite), with 1, 4-cyclohexanedimethanol modified PET. Sanchez-Solis et al. [119] reported that the introduction of alkylamines (n-decylamine, N-dodecylamine, n-tetradecylamine, and n-octadecylamine) as modifier in the nanocomposite matrix significantly increases the homogeneous dispersion of clay into the PET matrix.
Clays are hydrophilic in nature, resulting from the hydration of the interlayer alkali metal or alkali earth metal cations. This leads to the incompatibility of the clay with most of the polymers as well as most hydrocarbons. The interlayer cations, however, are readily exchangeable with organic cations, e.g., alkyl ammonium or phosphonium cations, which lowers the surface energy of the silicate surface and improves the wetting with polymer matrix [170-171]. This is characterized by the cation exchange capacity and is directly related to the surface charge of the silicate layers. The organically modified layered silicates have been widely used in the petroleum and paint industries as a thickening or gelating agent to adjust the rheological properties. In addition to improving the wetting characteristic of clay with polymer, organic cations also expand the galleries and weaken the Van der Waals force. Other than organic cations, silane coupling agents can also be used to modify the clay surfaces, relying on the reactions between the silanol groups and the hydroxyl groups on the clay surfaces. In the paper of Kamal et al. [172], ammonium and phosphonium modified clays are directly compared and although the overall dispersion was improved in the phosphonium organoclay, both nanocomposites exhibited a predominantly intercalated structure with some exfoliated platelets.

In contrast to those authors dealing directly with the issue of organoclay degradation [173-175] and its effect on PET nanocomposite properties, other authors have chosen to tackle the issue of PET/clay compatibility. In one such work Thellen et al. [176] investigated the effect of using maleic anhydride (MA) coupling agent on the properties of PET nanocomposites. The authors investigated both hydrophobic (Closite 20A) and hydrophilic (Closite 30B) clays with and without the MA and found that intercalation of the organoclays occurred and that the hydrophilic clay had slightly better dispersion.
based on TEM data. The authors observed that the dispersion was not improved by the addition of the MA and this did not influence the crystallization behavior of the nanocomposites produced either. In another study Yuan et al. [177] produced a hexadecyltrimethyl ammonium clay and also similar clay modified with both hexadecyltrimethylammonium and poly (ethylene glycol). The resulting nanocomposite indicated better dispersion in the PEG/ammonium modified clay although the morphology was intercalated rather than exfoliated based on the XRD data and TEM. The results indicated that the PEG has indeed improved the affinity of the PET for the clay compared to the ammonium based organoclay but the compatibility was not such that complete exfoliation occurred. In a paper by Lai and Kim [178], a PET/PEN copolymer (8 mol% PEN) and epoxy modified organoclay were investigated. The authors further modified Closite organoclays C20A and C30B with diglycidyl ether of bisphenol A and then produced PET nanocomposites by twin screw extrusion. The XRD and TEM analysis indicates that intercalated nanocomposites had been produced for both C20A and C30B although the peak intensity from XRD for C30B was much diminished indicating improved dispersion compared to the C20A, which was confirmed by TEM.

2.4.3. The effect of compatibilizer [119]

In addition to improving the compatibility of PET and clay, a second approach taken by some researchers to enhance the miscibility between PET and clay was to modify the polymer [174, 179-180]. In the work of Barber et al. [181] PET ionomer was used to increase the polarity of the polymer and hence improve compatibility with the clay
surfaces. The ionomer was synthesised by replacing a small quantity of terephthalic acid with sulfoisophthalic acid to yield a copolymer with ionic content.

The authors were able to demonstrate that the compatibility of PET with clay could be considerably improved by the incorporation of small quantities of the ionomer moiety and that the dispersion improved further as the ionomer content increased. The explanation of these phenomena was that the ionomer was able to interact strongly with the clay platelet edges, and this assisted the dispersion during shearing in melt processing to improve the dispersion. The author has shown that improvements can be obtained with various organoclays and even unmodified sodium clay.

More recently a novel approach to the use of PET ionomer has been suggested by Ammala et al [182]. In this study AQ55 polyester ionomer from Eastman Chemical Company was dispersed in water with the required quantity of clay (Cloisite 10A montmorillonite, somasiff MEE and somasif ME100 modified and unmodified synthetic fluorine mica). The authors observed improved dispersion for ionomer treated clays compared to the nanocomposites containing untreated clays. From XRD data, peaks were observed in all cases, but for the ionomer treated clay nanocomposites the intensity of these peaks was reduced indicating more delaminated clay particles, which was confirmed by TEM.

Zhang et al. [33] reported for preparation of PET/OMMT (5 and 10 wt%) nanocomposites with surfactant (compatibilizer) hydroxypentyl trimethylammonium ioide, HPTA, and ionically charged terminal monomer intercalated into the MMT. The PET/OMMT nanocomposites had an exfoliated morphology, enhanced tensile strength (58 wt%) and better optical transparency than that of the neat PET.
Hao et al. [183] studied the effect of amount of compatibilizer used for preparation of PET/OMMT (2 wt%) nanocomposite with commercial OMMT. Delamination of MMT, as measured by TEM and XRD, was mainly in the form of tactoids. Compatibilizer results in the reduction of IV, that is proportional to it concentration, as compared to neat PET. DSC results revealed a nucleation effect, denoted by the decrease of $T_{cc}$, and reduction of $T_m$. Thermal stability evaluated by thermal gravimetric analysis (TGA), showed a higher degradation temperature for nanocomposite than for PET. Dynamic mechanical analysis (DMA), experiments observed a decrease in $T_g$ and increase of storage modulus.

Choi et al. [184] obtained PET/MMT (1, 2, and 5 wt%) nanocomposites via MMT-supported catalysts. Nanocomposites were characterized by a higher IV and TGA measurements registered much better thermal stability of PET/MMT nanocomposites, compared to neat PET. Mixed intercalated/exfoliated morphology was achieved, as detected by XRD and TEM. The oxygen permeability was gradually decreased with increase of MMT content.

In addition to PET, polypropylene-grafted-maleic anhydride (PP-g-MA) is one of the most widely investigated compatibilizers in synthesis of blends of nylon 6-PP and melt extruded PP nanocomposites. If PP-g-MA is used as a compatibilizer in the case of nylon 6-PP blends, PP-g-MA reduces the interfacial tension between nylon 6 chains. The co-polymerization occurs in the melt state between amine end groups of nylon-6 chains and anhydride groups of maleated polypropylene (m-PP). These reactions occur at higher temperature of melt (200°C). Thermal analysis shows that the polypropylene (m-PP) acts as a nucleating agent and facilitates the crystallization kinetics of the nanocomposites.
2.5. **Properties of Polymer Nanocomposites [185-187]**

Layered silicate has provided tremendous property improvement of the polymer matrices. This includes modulus and strength, crystallization and thermal behavior, barrier properties, fire retardance, and chemical resistance. All the improvements can be achieved at relatively low particle concentrations (< 10 wt%) without sacrificing the light weight of the polymer matrices.

Increased modulus and strength has been demonstrated in numerous polymer systems with the dispersion of layered silicates in the matrix [188-191], and with the particle concentration as low as 1 wt%. The enhancement is dependent on the degree of exfoliation of the silicates [192].

Nanocomposites also provide superior barrier properties [193-194]. For example, in an epoxy nanocomposites containing 4 wt% of the clay, the water vapor transmission rate drops to an order of magnitude lower than that of the neat matrix. Due to the presence of the platelet particles, molecules have to take tortuous diffusion pathway, leading to a reduced diffusion rate. Improved chemical resistance is also observed and related to the increased diffusion path length. Some work tried to model the effective diffusion coefficient of composite systems containing high aspect ratios of disk-like particles and examined the effects of particle disorder and interconnection. Other work considered the effects of sheet length, concentration, orientation, and degree of delamination of silicates on the relative permeability of polymer clay nanocomposites by modifying a simple tortuosity-based model [21, 79-80, 152]. It was shown that dispersion of high aspect ratio particles in a polymer matrix is particularly beneficial in several respects by increasing the tortuosity and reducing the dependence of the relative permeability on the orientation.
order of the sheets. The degree of exfoliation was the most important factor that controls the barrier properties.

Improvement of thermal stability has been observed for numerous systems. The silicate surface may deactivate the center that is active in the polymer chain decomposition, restrict the thermal motion of polymer in the confined space and prevent chain scission, or delay the emission of volatile decomposed products as a result of reduced permeability. Extensive studies have been carried out in preparing nanocomposites for fire retardant applications [195]. Significant reduction in heat release rate was observed. Upon burning, the clay layers collapse and form char, effectively reducing the amount of ignitable small molecules into the vapor phase, reducing the heat release rate. The char also holds the material structure integrity, preventing fire from spreading.

In nanocomposites, clay is more than just high aspect ratio filler. The nanoscale confined geometry and interaction between the clay surface and polymer may effectively alter the structure and dynamics of polymer matrix and thus the properties [196]. For example, disappearance of distinct phase transitions was observed and was attributed to the change of mode of motion of the polymeric chains in the nano-sized confinement. In the nylon 6 nanocomposite system, it was found that the presence of clay could significantly affect the ratio of different crystal phases, promoting forming and stabilizing meta-stable γ phase, while equilibrium α phase dominates without clay. The modulus of α phase nylon 6 decreases much more rapidly than γ phase nylon 6, indicating that γ phase nylon 6 has a higher heat distortion temperature. Thus the increased formation of γ phase will provide higher distortion temperature, regardless of the contribution of clay layers.
For the polypropylene nanocomposites, the effect of clay on the spherullite size and impact strength was also reported [197]. It was found that PP/PP-MA330k/clay, an intercalated three-component system containing some dispersed clay as well as the clay tactoids, showed a much smaller size of spherulites and a slight increase in impact strength with increasing clay content.

2.5.1. Effect of Processing conditions on clay dispersion [124, 168, 198]

The processing conditions have significant influence on the dispersion of clay additive in the matrix. This is because the extruder provides high shear stresses and shear rates that are useful for accelerating the clay dispersion [198]. Hatzikiriakos et. al. [199], studied the effect of nanoclay additives on the processability of polyolefins. According to their claim, addition of nanoclay eliminates the surface melt fracture and elevates the critical shear rate for onset of melt fracture. Higher melt viscosity is known to impose higher shear stresses to platelets during melt mixing in an extruder. According to Newtonian Law;

\[
\text{Shear stress } \sigma = \eta \gamma
\]  

Where, \(\eta\)-melt viscosity, \(\gamma\)-shear rate,

The higher shear stress in the extruder breaks the organoclay particles into stacks of platelets or tactoids, which can be subsequently sheared apart into smaller platelets.

Lertwimolnum studied the polyproylene (PP)/organoclay nanocomposites at varies extrusion conditions. The results indicated that no evolution of intercalated structures occurred using a twin screw extruder [200]. Tanoue et al. [201] reported the effects of
screw rotation speed (rpm) on the mechanical, rheological and clay dispersion states of polystyrene (PS) nanocomposites. For Young’s modulus, the maximum value was obtained at a screw rotation speed of 70 rpm. Therefore, it is necessary to determine the optimized screw speed for melt blending method. Recycled PET/clay nanocomposites were prepared at two different screw rotation speeds: 250 and 150 rpm [198]. TEM images revealed that the better exfoliated clay platelets were found in samples prepared at 150 rpm.

2.5.2. Effect of nano-silica on crystallization

The crystallization kinetics of PET/clay nanocomposites has been investigated and it was found that the introduction of silicate acts as a heterogeneous nucleating agent by accelerating the crystallization rate [202-204]. The crystallization process contains primary crystallization (nuclei formation) and secondary crystallization (the growth of crystals). The primary crystallization kinetics of PET under isothermal conditions is described by the Avrami equation [205-206]. Calcogno et al. [125], studied the effect of organically modified MMT on the morphology and crystallization properties of PET nanocomposites and showed improved dispersion of the modified MMT into the PET matrix. The work done by Liu et al. [207] indicated that they successfully prepared PET/silica nanocomposites with mono-dispersed nanoparticles. They found that the nanoparticles can act as an effective nucleating agent during crystallization and the rate of crystallization becomes faster as the silica content increases.

Yuan et al. [208] have studied the effects of temperature and glass bead content on the brittle to ductile transition temperature (BDT) and thermo-mechanical properties of
glass bead reinforced polypropylene. Strong interactions between the glass beads and polymer molecules was observed resulting in a shift of the glass transition temperature from 27.1°C to 35°C. Thermal stability/HDT of PP was effectively increased with the incorporation of glass beads. Yield strength of clay reinforced PP was higher than that of neat PP due to the interaction between the clay particle and polymer matrix.

The influence of nanoclay additive on crystallinity and crystal structure of melt compounded nylon nanocomposite has been carefully investigated by Fornes et al. [27]. They found that the clay additives acted as nucleating agents, and increased crystallinity and enhanced γ-crystal structure.

Baekjin et al. [209] investigated the crystallization kinetics of maleated polypropylene/clay hybrids. They found that crystallization rates of modified silicate hybrids were slower compared to natural nanoclay hybrids. Unmodified silicate platelets formed agglomerates and hence acted as nucleating agents, whereas the exfoliated modified silicate platelets acted as barriers to crystallization.

The crystallization behavior of polypropylene reinforced with conventional composites and nanocomposites has been extensively studied. The surface of the filler particles is known to act as nucleation sites and influence and crystallization mechanism, the amount of crystallinity, and crystal growth. Unit cell structure did not change from monoclinic, but the the dimensions changed. They found that the change in dimensions with the crystallization temperature ($T_c$) and clay content might be due to defects entering in to the lattice.
2.5.3. Effect of nano-silica on mechanical properties

Tensile strengths of nanoclay based composites from PP, nylon-6, PMMA and PS have been compared. Among the different matrices, nylon-6 nanoclay composite had the highest tensile stress at break, compared to the rest. This high strength is due to the polar nature of nylon 6 and a possible ionic bond between clay and nylon-6 chains.

Bauer et al. [210] shows that the strengthening of a polyester resin by montmorillonite nanofillers treated by grafting silane functions led to a sharp increase in mechanical properties and in particular the energy propagation of rupture. Mechanical property is doubled compared to the virgin resin, with a proportion of nanofillers 1.5% by volume. The mixing time between treated montmorillonite and hydroxypropyl acrylate (reactive solvent can be used instead of styrene crosslinked unsaturated polyester resins) may affect the mechanical properties of nanocomposite, depending on the treatment of montmorillonite.

In the work of Shubel et al. [211], the study has investigated the potential use of nanoscale silicates for reducing the volumetric shrinkage in unsaturated polyester resin. Volumetric shrinkage is a major drawback of polyester resins, because it causes dimensional changes and distortion of the composite parts. It is found that the shrinkage of a resin is lowered from 7.5% to 5.8% with only the addition of 1 wt% Cloisite 10A. The breaking strength of a nanocomposite with 4% nanofillers is increased by 108% and 53% of tensile strength and Young's modulus. In contrast, an anti-shrinkage conventionally used such as polyvinyl alcohol (PVA) should be used in higher proportions (about 30%). This causes a decrease in breaking strength of a nanocomposite with 4% nanofillers is increased by 108% and Young's modulus of 53%.
The PET/organoclay nanocomposite with N-methyl diethanol amine-based organoclays revealed an increased tensile strength with 0.5% clay addition and a higher barrier property at 1 wt% well-dispersed organoclays [198]. Chang [42] found the tensile mechanical properties of the C_{12}PPh-MMT/PET nanocomposite increased with increasing amount of organoclay in the polyester matrices. Lichfield [212] showed that both Young’s modulus and tenacity reach to maximum value at 1 wt% loading of clay for PET/organoclay nanocomposites.

Influence of clay loading on properties of polypropylene-clay nanocomposites has been studied by Liu et al. [213], where they observed increases in tensile strength, tensile modulus, and storage modulus, with 0 to 5 wt% clay additives.

2.5.4. Effect of nano-silica on barrier properties

Nanocomposites also provide superior barrier properties. For example, in an epoxy nanocomposites containing 4 wt% of clay, the water vapor transmission rate drops to an order of magnitude lower than that of the neat matrix. Due to the presence of the platelet particles, molecules have to take tortuous diffusion pathway, leading to a reduced diffusion rate.

Zoppi et al. [214] introduced an inorganic filler in the copolymer of polyamide and poly (ethylene oxide) blocks, i.e. poly (ethylene oxide-b-amide-6) (PEBAX). The authors found a clear effect of the inorganic phase on the gas permeability. Messersmith and Giannelis [215] measured permeability of water through composite films of poly (ε-caprolactone) (PCL) containing modest amounts of organically modified mica-type silicate (OMTS). The permeability of nanocomposites containing as low as 4.8% silicate
by volume was reduced by nearly an order of magnitude compared to pure poly (ε-caprolactone).

Okamoto et al. [72] reported O$_2$ gas permeability of PBS nanocomposites with three different types of OMLS (C$_{18}$-MMT, qC$_{19}$-MMT, qC$_{16}$-SAP). The permeabilities were according to the aspect ratio of dispersed clay particles in the various nanocomposites. The higher the aspect ratio in the nanocomposite, the lower was the permeability. i.e. Aspect ratio of PBS/C$_{18}$-MMT>PBS/qC$_{19}$-MMT>PBS/qC$_{16}$-SAP,

Auras et al. [216] investigated the barrier properties of PLA films and found them comparable to synthetic polymers such as polystyrene (PS) and polyethylene terephthalate (PET). The authors found that the CO$_2$ permeability coefficients for PLA resins were lower than that for crystal PS at 25°C and 0%RH. However, they have higher than O$_2$ permeability coefficient for PET.

Strawhecker et al. [217] measured the water vapor transmission rates (WVTR) of pure poly vinyl alcohol (PVA) and its low concentration nanocomposites. These researchers found that the permeabilities decreased to about 40% of the pure WVTR values for lower silicate loadings up to 6 wt%.

Pannirselvam [218] reported that polypropylene (PP) nanocomposites were prepared by polyether treated montmorillonite and PP. The oxygen permeability was reduced by 30% of the corresponding values for pure PP. Ammala et al. [182], showed the work done on three kinds of organo-modifed MXD6/MMT nanocomposites (Cloisite 30B, 10A and 93A), and the Cloisite 10A additive gave a 66% reduction of oxygen transmission rates (OTR). In the study of Kim [133], PET/organoclay nanocomposites was prepared by in situ polymerization, the oxygen barrier property of nanocomposistes loaded with 1
wt% showed a 50% reduction when compared to pure PET. Zhang et al. [219-220], developed a new synthetic strategy for the homogenous dispersion of layered silicate into PET by in situ polymerization, but reported that high processing temperature (280 °C) causes the thermal decomposition of the organic modifiers.

2.6. Model Predications for Polymer Nanocomposite Properties

2.6.1. Tensile Property Models

It is well known that composite materials have advantages over traditional materials. Nanocomposites, where nano-sized reinforcements (fillers) are dispersed in the base materials (matrix), offer a novel class of composites with superior properties and added functionalities [221-223]. Although the applicability of continuum mechanics (including micro mechanics) to nanocomposites have been subjected to debate [221, 223], many recent works directly applying continuum mechanics to nanostructures and nanomaterials have reported meaningful results and elucidated many issues [224-233]. Thus, mechanics-based formulas for predicting the mechanical properties will be reviewed. The popular micromechanical models for prediction of modulus of elasticity are summarized and discussed in the following:
2.6.1.1. Voigt upper bound and Reuss lower bound (V-R model)

Assumed aligned fibers, and fibers and matrix are subjected to the same uniform strain in the fiber direction, Voigt [234] illustrated the effective modulus in the fiber direction as:

\[ E_L = \phi E_f + (1-\phi)E_m \]  \hspace{1cm} (2.3)

Reuss [235] applied the same uniform stress on the fiber and matrix in the transverse direction (normal to the fiber direction), and revealed the effective modulus in the transverse direction as:

\[ \frac{1}{E_T} = \frac{\phi}{E_f} + \frac{1-\phi}{E_m} \]  \hspace{1cm} (2.4)

Where \( \Phi \) is the volume fraction of fiber in the two phase composite system, and subscripts “f” and “m” respectively refer to the fiber and matrix, whereas the subscripts “L” and “T” refer to the longitudinal and transverse directions, respectively. Equation 2.3 is the parallel coupling formula, and it is also called the “rule of mixtures”, whereas is the series coupling formula, and it is also called the “inverse rule of mixtures”.

Equations (2.3) and (2.4) can be extended to any two-phase composites regardless of the shape of the filler, and represents the upper and lower bounds of the modulus of the composite, respectively. Note that in these formulas, only three parameters are involved, i.e. modulus of the fiber and the matrix, and the fiber volume fraction.
2.6.1.2. Hashin and Shtrikman upper and lower bounds (H-S model)

Hashin and Shtrikman [236-237] assumed macroscopic isotropy and quasi-homogeneity of the composite where the shape of the filler is not a limiting factor, and estimated the upper and lower bounds of the composite based on principles of elasticity. Depending on whether the stiffness of the matrix is more or less than that of the filler, the upper and lower bounds of the bulk moduli, $K_{upper}$ and $K_{lower}$, and shear moduli, $G_{upper}$ and $G_{lower}$ of the composite are given as:

$K_{upper} = K_f + (1 - \phi)[\frac{1}{K_m - K_f} + \frac{3\phi}{3K_f + 4G_f}]^{-1}$  \hspace{1cm} (2.5)

$K_{lower} = K_m + \phi[\frac{1}{K_f - K_m} + \frac{3(1 - \phi)}{3K_m + 4G_m}]^{-1}$  \hspace{1cm} (2.6)

$G_{upper} = G_f + (1 - \phi)[\frac{1}{G_m - G_f} + \frac{6\phi(K_f + 2G_f)}{5G_f(3K_f + 4G_f)}]^{-1}$  \hspace{1cm} (2.7)

$G_{lower} = G_m + \phi[\frac{1}{G_f - G_m} + \frac{6(1 - \phi)(K_m + 2G_m)}{5G_m(3K_m + 4G_m)}]^{-1}$  \hspace{1cm} (2.8)

The subscripts “f” and “m” refer to the filler and matrix, respectively. The upper and lower bounds of the elastic modulus can then be calculated using the following relationship:

$E = \frac{9K}{1 + 3K/G}$  \hspace{1cm} (2.9)
Similar to the Voigt and Reuss models, the H-S model only involves three parameters.

2.6.1.3. Halpin-Tsai model (H-T model)

For aligned fiber-reinforced composite materials, Halpin and Tsai [238-241] developed the equations for predication of elastic constants based on the work of Hermans [242] and Hill [243]. The H-T model is a semi-empirical model, and the longitudinal and transverse moduli are given by:

\[
E_L = \frac{1+2(l/d)\phi \eta_L}{1-\phi \eta_L} E_m
\]
\[
E_T = \frac{1+2\phi \eta_T}{1-\phi \eta_T} E_m
\]

Where l and d are the length and diameter of the fiber, and \( \eta_L \) and \( \eta_T \) take the following expressions:

\[
\eta_L = \frac{E_f - E_m}{E_f + 2(l/d)E_m}
\]
\[
\eta_T = \frac{E_f - E_m}{E_f + 2E_m}
\]

2.6.1.4. Hui-Shia model (H-S model)

Mori and Tanaka [244] developed analytical expressions for elastic constants based on the equivalent inclusion model of Eshelby [245]. Taya and Mura [246] and Taya and Chou [247] used the Mori-Tanaka approach to predict the longitudinal modulus of fiber-reinforced composites, Weng [248] and Tandon and Weng [249] further developed equations for the complete set of elastic constants of composite materials with aligned spheroidal isotropic inclusions. Based upon the results of Tandon and Weng [249], Hui
and Shia [250] and Shia et al. [251] derived simplified formulas for predicting the overall moduli of composites with aligned reinforcements with emphasis on fiber-like and flake-like reinforcements, and found that their theoretical predictions agree well with experimental results. The H-S model presents the Young’s modulus as follows:

\[
E_L = E_m \left[1 - \frac{\phi}{\xi}\right]^{-1}
\]

\[
E_T = E_m \left[1 - \frac{\phi}{4} \left(\frac{3}{\xi + \Lambda}\right)\right]
\]

(2.14-2.15)

Where

\[
\xi = \phi + \frac{E_m}{E_f - E_m} + 3(1 - \phi) \left[\frac{(1 - g)\alpha^2 - g/2}{\alpha^2 - 1}\right]
\]

\[
\Lambda = (1 - \phi) \left[\frac{3(\alpha^2 + 0.25)g - 2\alpha^2}{\alpha^2 - 1}\right]
\]

(2.16-2.17)

\[
g = \frac{\alpha}{(\alpha^2 - 1)^{3/2}} \left\{ \begin{array}{l}
\sqrt{\alpha^2 - 1} - \cosh^{-1}\alpha \quad \alpha \geq 1 \\
\cosh^{-1}\alpha - \sqrt{\alpha^2 - 1} \quad \alpha \leq 1
\end{array} \right.
\]

(2.18-1.19)

and \(\alpha\) is the aspect ratio of the filler, defined as the ratio of the filler’s longitudinal length to its transverse length.
2.6.1.5. Wang-Pyrz model (W-P model)

For a composite material composed of an isotropic matrix and randomly oriented transversely isotropic spheroids, Qiu and Weng [252] and Chen et al. [253] gave the formulas for the overall bulk and shear moduli using the Mori-Tanaka method. These formulas are expressed in terms of the Eshelby tensor [245]. Wang and Pyrz [254] further gave the closed and concise formulas for the overall bulk modulus and shear modulus as follows:

\[
K = K_m + K_m \frac{\phi \phi}{1 - \phi(1 - \alpha)}
\]  
(2.20)

\[
\mu = \mu_m + \mu_m \frac{\phi \phi}{1 - \phi(1 - \beta)}
\]  
(2.21)

Note that W-P model is based on the Mori-Tanaka approach, and deals with the composite materials reinforced with randomly oriented and transversely isotropic spheroids. By varying the aspect ratio, the oblate spheroids can be approximated to platelets, and the prolate spheroids can be approximate to fibers.

2.6.1.6. Cox model (Shear lag model)

The shear lag model was the first micro-mechanics model for fiber-reinforced composites. Cox [255] analyzed a single fiber of length \(l\) and radius \(r_f\), which is encased in a concentric cylindrical shell of matrix having radius \(R\). He derived the longitudinal modulus as

\[
E_L = \eta_L \phi E_L + (1 - \phi) E_m
\]  
(2.22)

Where \(\eta_L\) is a length-dependent efficiency factor,
\[ \eta_l = 1 - \frac{\tanh(\beta l / 2)}{\beta l / 2} \]  
\[ \beta^2 = \frac{4\mu_m}{r_j^2 E_j \ln(K_R / \phi)} \]  

(K_R) is a constant that depends on the fiber packing arrangements. For some typical fiber packing arrangements, the values of K_R are given in Table 2.1 [256].

<table>
<thead>
<tr>
<th>Fiber Packing</th>
<th>K_R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cox</td>
<td>$2\pi/\sqrt{3} = 3.628$</td>
</tr>
<tr>
<td>Composite Cylinders</td>
<td>1.000</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\pi/2\sqrt{3} = 0.907$</td>
</tr>
<tr>
<td>Square</td>
<td>$\pi/4 = 0.785$</td>
</tr>
</tbody>
</table>

It is well known that the orientation of the dispersed phase has a dramatic effect on the composite modulus. It is apparent from their geometry that flake-like platelets can provide equal reinforcement in two directions, if appropriately oriented, while fibers provide primary reinforcement in one direction. If the longitudinal modulus $E_L$ and the transverse modulus $E_T$ are known, then the effective modulus of the composite with randomly oriented fibers and platelets in all three orthogonal directions are given by: [257]

\[ E_{3D}^{\text{fiber}} = 0.184E_L + 0.816E_T \]
\[ E_{3D}^{\text{platelet}} = 0.49E_L + 0.51E_T \]  

(2.25-2.26)
2.6.2. Permeability Models

Because of the barrier role of silicate platelets, a diffusing gas/liquid molecule must detour the sheets forming a very tortuous path. Therefore, the influence factors on the permeability of polymer-layered silicate nanocomposite (PLS) are mainly dependent on the degree of exfoliation or intercalation and the state of dispersion of silicate platelets in the polymeric matrix, such as aspect ratio L/W (L and W are length and thickness of silicate platelets, respectively), orientation θ, dispersion spacing ξ between two sheets, volume fraction Φ, etc. In terms of dimensional analysis, the permeability \( k_c \) of gas/liquid molecules in a PLS nanocomposite is given by:

\[
k_c = \frac{ud}{\Delta p} f\left(\frac{L}{W}, \frac{L}{\xi}, \phi, \theta\right) = k_p f\left(\frac{L}{W}, \frac{L}{\xi}, \phi, \theta\right)
\]  

(2.27)

Where \( k_p \) is the permeability coefficient of a polymeric matrix, and \( f \) is a function of four dimensionless parameters: L/W, \( L/\xi \), \( \Phi \) and \( \theta \). Here, the aspect ratio L/W measures the degree of exfoliation or intercalation, and the ratio \( L/\xi \) represents the extent of dispersion of the silicate platelets. On the basis of the tortuosity argument, Nielsen [258] developed a simple model to describe the permeability of filled-polymers. In an ideal case where clay particles are fully exfoliated and uniformly dispersed along a preferred orientation (\( \theta=0^\circ \)) in a polymeric matrix, the tortuous factor \( \tau \) becomes:

\[
\tau = \frac{d''}{d} = 1 + \frac{L}{2W \phi}
\]  

(2.28)

Thus, the relative permeability \( k \), with and without the addition of clay fillers in a polymeric matrix, can be expressed as:
where $1 - \Phi \approx 1$, since the volume fraction $\Phi < 1$ in most PLS nanocomposites.

Clearly, the relative permeability $k$ decreases as the aspect ratio $L/W$ (or extent of exfoliation) increases. It is noted that, however, the exfoliated silicate platelets in PLS nanocomposites are randomly dispersed in the polymeric matrix. To consider the influence of platelet orientations on permeability, Bharadwaj [259] extended the Nielsen model by introducing an order parameter $S$ that is defined by:

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

(2.30)

Where $-1/2 \leq S \leq 1$. For example, $S=1$ ($\theta=0^\circ$) indicates the case of perfect alignment, and in the case of $S = -1/2$ ($\theta=90^\circ$), silicate platelets are almost no barrier to the diffusion of gas/liquid molecules in PLS nanocomposites. $S=0$ ($\theta=54.74^\circ$) corresponds to a random distribution of exfoliation silicate platelets in a polymer-matrix [260]. Hence, the relative permeability of a PLS nanocomposite can be rewritten as [259]:

$$k = \left[ 1 + \frac{2S + 1}{6} \frac{L}{W} \phi \right]^{-1}$$

(2.31)

It is easy to see that, the influence of orientation on permeability is equivalent to the decrease of effective aspect ratios of platelets. Also, we should point out that the potential permeability along a third direction was omitted in a two-dimensional model. Further, Cussler et al. [261] developed another expression for the relative permeability in a three-dimensional and disordered situation, which is given by:

$$k = \left[ 1 + \mu \left( \frac{L}{W} \phi \right)^2 \right]^{-1}$$

(2.32)
where $\mu$ is a geometric factor that depends on details of exfoliated platelets and their spatial distribution, and in the case of $(L/W)\Phi \geq 1$, $\mu = \frac{\pi^2}{16\ln^2(L/W)}$ [262].

2.7. Deformation mechanism of PNCs during uniaxial stretching

The preparation of polymer nanocomposites with MMT have been studied among the reinforcements due its availability and comparatively easy surface modification. As discussed previously, three types of MMT morphologies can appear in the PNCs, such as: i) tactoid, ii) intercalated and iii) exfoliated, depending on the fact that a variety and complex deformation mechanisms that take place during the uniaxial stretching of the composite.

Kim et al. [263-264] proposed a model for the micromechanical deformation of PNCs with MMT tactoids and morphology structure upon uniaxial stretching PA/MMT samples that were prepared by injection molding. They recognized as a main deformation mechanism, microviod formation inside tactoids or intercalated MMT particles, where large voids from around large non-homogeneities. This void was based on in situ voltage electron microscopy investigations. The formation of voids takes place during the plastic deformation, since the individual MMT layers stacked in the polymer matrix are weakly bonded to each other. The nanoparticles are load-bearing because their surfaces in the microvoids are connected and hinder further growth of the microvoids, thus preventing catastrophic failure. As a consequence, the stiffness/strength/toughness balance has been synergistically improved. Finally, based on the present experimental results, a molecular network in polymer nanocomposites is proposed, that leads to the desired superfunctional characteristics.
Renner et al. [265] investigated the deformation mechanisms in PA/OMMT nanocomposites, with tactoid morphology, via in situ acoustic emission and volume strain measurements. Attention was paid to nanocomposite morphologies consisting of mixed MMT’s morphology like tactoids, intercalated and exfoliated. They concluded that elastic deformation and shear yielding dominated during the elongation of the specimens. The free volume also increases due to void occurrence, mainly generated by the fracture of the tactoids and rarely owning to polymer/OMMT separation as based on the acoustic events. The authors, claimed that the type and amount of the surfactant used for modification played an important role in the determination of deformation processes and properties, since it influenced both polymer/MMT interactions and the internal adhesion of MMT particles.

Kim et al. [264] via TEM investigations revealed that microvoids in the range of micrometers are elongated in the stretching direction and homogeneously distributed in specimen with exfoliated morphology. The authors suggested that an exfoliated morphology is much more effective in transfer of the external applied stress from the polymer matrix to the MMT, as compared to a tactoid and intercalated one, due to the increased number of polymer/MMT interactions which results in the uniform formation of microvoids. And a significant improvement in the Young’s modulus is achieved. Furthermore, the uniformly well-develop formation of microvoids throughout deformed specimens and their subsequent growth should enhance matrix shear yielding, which is directly associated with energy dissipation; that is, it is reflected in the enhancement of the toughness of the system of exfoliated morphology.
2.8. PET/MMT nanocomposite with recycled PET [167, 266-267]

Pegoretti at el. [164] studied extrusion blending and subsequent injection molding of rPET/MMT nanocomposites with 1, 3, and 5 wt% of MMT and OMMT. Better intercalation was observed in the case of MMT than OMMT, according to the TEM and WAXS results. Incorporation of OMMT contributes to enhanced modulus as compared to PET/MMT. Increasing contents for both clays resulted in enhance modulus, which showed that strain at break dramatically dropped. The yield strength was not affected. The tensile compliance of the nanocomposites was only slightly lower than that of neat rPET, the reinforcing effect of OMMT being somewhat stronger. Both MMTs had beneficial effects on the dimensional stability of the nanocomposites, in contrast to the neat rPET, the creep rate did not rise at long creep periods.

rPET/OMMT (1, 3, and 5 wt%) nanocomposites were compounded via co-rotating twin-screw extruder and subsequently injection molded [268]. A large decrease of rPET matrix IV after extrusion-injection processing was detected. The combined WAXS and TEM results showed tactoid morphology with various tactoid sizes. Thermal analysis did not show significant changes in the thermal properties from those of rPET. The OMMT in this work did not act as an effective nucleating strength (yield stress). This improvement was attributed to nanoscale effects and strong interactions between the rPET matrix and the MMT interface.

Kracalik at el. [167] compounded 5 wt% of various commercially available OMMT, with rPET in a co-rotating twin screw micro-extruder under a nitrogen environment. Morphological investigations by WAXS and TEM revealed partial exfoliation of more hydrophobic OMMTs and intercalated for less one. The dynamic flow properties of the
prepared composites were related to structural changes associated both with the reinforcing effect (formation of physical network with OMMT loading) and degrading aspect (chain scission of rPET and OMMT decomposition tendency). Moderate matrix degradation caused by some OMMTs did not affect optical properties, mainly the transparency.

In more recent work of Kracalik et al. [167] was using co-rotating twin screw extruder under nitrogen environment to prepare PET/OMMT (5 wt%) nanocomposites with virgin PET and rPET, and two types of surface modification of MMT, namely 1,2-dimethyl-3-octadecyl-1-himidazol-3-ium chloride (OMMT-IM) and additional treatment with [3-(glycidyloxy)propyl] trimethoxysilane (OMMT-IME). According to TEM and WAXS results indicated intercalated morphologies for both OMMT’s where a slightly higher level of intercalation in the case of PET/OMMT-IME. Rheological investigations revealed a typical shear thinning behavior with OMMT addition and a higher melt viscosity of nanocomposites in the whole measured range of shear rates compared with unfilled matrixes. In comparison with the neat polymers, the melt strengths of all nanocomposites were significantly enhanced by the formation of 3D physical networks. DSC analysis of nanocomposites prepared from rPET revealed a decrease in degree of crystallinity and T_m, a faster formation of crystalline nuclei, an increase in T_g and in T_cc compared with a neat matrix.
2.9. Commercial Applications of Polymer Nanocomposites [269]

The first commercial nanocomposite product was a PA6 nanocomposite that was developed by Toyota Motor Company for timing belt covers [270-271]. The use of these materials has also been extended to the Toyota [272]. A further PA6 based automotive engine application has been developed by Unitika for engine covers for Mitsubishi GDI engines [272-273].

Polyolefins have also seen some significant commercialization, particularly in automotive applications. Basel and General Motors jointly developed a thermoplastic polyolefin for use in door panels of the Chevrolet Impala and have followed this with the development of a step assist component used in GMC Safari and Chevrolet Astra vans [274-275]. More recent developments by Honda Acura in conjunction with Noble polymers have seen the commercialization of another thermoplastic polyolefin for the manufacture of seat backs [276].

In addition to automotive applications PA6 has also been developed by Honeywell as a barrier material for multilayer bottles [272]. Nanoscale innovation could potentially introduce many new improvements to food packaging in the form of barrier and mechanical properties. The nanolayer of aluminum that is contained in the interior of many snack food packages is one common example of the role that nanotechnology already plays in food packaging. PA-MXD6 has been developed into a commercial nanocomposite through the collaboration of Mitsubishi Gas Chemical Company and Nanocor. The resulting material is an excellent CO₂ barrier in multilayer bottles and has been used by the Miller Brewing Co. in the USA.
Since polymer nanocomposites have been recognized as the next great frontier of materials for packaging, these materials were developed to improve barrier performance to gases such as oxygen and carbon dioxide. They also enhance the barrier to ultraviolet rays, as well as adding strength, stiffness, dimensional stability, and heat resistance. New packaging created with this technology demonstrates an increased shelf life. It will also make them attractive for use in food, beverage and pharmaceutical packaging applications. In 2001, nearly 453 tons of nanocomposites were used in the packaging industry and by 2011, the market in the United States is expected to be around 453515 tons for rigid and flexible packaging [277]. Fig 2-5 shows the worldwide market of PNCs, representing the very fast increase in demand of PNCs, in particular with thermoplastic polymer matrix from 2003 to 2008.

Nowadays, several industrial solutions are available for improving the gas barrier performance of bottles based on the PNC technology. PA/MMT PNCs are used as barrier layers for multilayer PET containers, and reported to be two to three times better than the traditional ethylene vinyl alcohol, EVOH. When used in a 0.47 L beer bottle, Imperm® nanocomposite guarantees almost seven months of shelf life. Honeywell produces three versions of their nylon/MMT nanocomposite Aegies®: i) OXCE, ii) HFX and iii) CDSE [278]. Ageis™ OX contains an oxygen scavenging component intended for use in beer bottles that provides a shelf life of 6-12 months which is comparable to the glass bottles. In 2003, Aegies® was used in a three layer 1.6 structure for a South Korean Brewery [279]. Beer was expected to be the biggest consumer of PNC by 2006 with 148.5 tons. Carbonated soft drinks bottles are projected to surpass that by 2011, with the use of 2474.7 tons of PNC [280].
The PET/PNC multilayer bottle is a relatively expensive solution and requires complex processing. PET based PNCs can be used for production of monolayer containers with similar or superior, barrier and mechanical properties compared to the multilayered one.

Figure 2-5 Worldwide market for polymer PNCs (2004). [281]
2.10. Previous Work on PET Nanocomposites at the Polymer Institute

Two previous graduate students at the Polymer Institute of UT have worked on PET nanocomposites. Their work studied the preparation methods of PET nanocomposites including melt blending and in-situ polymerization. In their work, both organo-modified clay and natural clay (Na-MMT) were introduced into a PET matrix in order to improve the material’s mechanical and barrier properties.

Melt blending [35]

The first work on PET nanocomposites was done by Kim [35]. In his research, three different types of organo-modified clays (Cloisite 10A, Cloisite 15A, Cloisite 30B) had been used to prepare PET nanocomposites using both melt blending and in-situ polymerization. Among these nanocomposites, the one with 30B modified clay showed an improvement in interlayer spacing based on the results from X-ray diffraction (XRD) and transmission electron microscopy (TEM), and gave an 11% improvement in tensile modulus and 29% reduction oxygen permeability compared to that of neat PET. Tactoid structures of 15A modified clay were observed, which resulted in no improvement in barrier properties.

The challenge for his work was the thermal degradation of organoclays during PET processing. The decomposition from the modifier at high processing temperature could not only give a problem to cause the agglomeration of clay in the PET matrix, but also affect the properties of PET nanocomposites.
In-situ polymerization [131]

With the purpose of avoiding thermal degradation caused by decomposition of an organic modifier, natural clay (Na-MMT) was selected in another study done by Labde [131]. In this work, an in-situ polymerization method was used to prepare PET/Na-MMT nanocomposites. Na-MMT with different weight loading was added into either the esterification (ES) or the polycondensation (PC) reactions.

The PET matrix is hydrophobic, while Na-MMT is hydrophilic. Based on this incompatible characteristic of two compounds, Labde tried to add the clay-EG and clay-BHET mixture into the reaction, with the purpose of expanding the d-spacing of the clays. In his work, morphological analysis based on XRD and TEM indicated the intercalated structure of PET/Na-MMT nanocomposites. The best property improvement observed was that the oxygen permeability was reduced by 36% with 0.5 wt% clay addition, during the esterification reaction process.
Chapter 3

Materials and Characterizations

3.1. Materials

Sodium montmorillonite (Nanofil®116) was supplied by Southern Clay Products with a cation exchange capacity (CEC) of 92.6 meq/100gm. Commercially available PET (grade HP806) as pellets (Intrinsic Viscosity = 0.841) from Wellman company was used as the polymer matrix. MXD6 (Grade 6011) with a density of 1.2 g/ml was obtained from Mitsubishi Gas Chemical Company. All the materials were used without any additional treatment. Physical and chemical properties of natural clay (Na-MMT) provided by the manufacturer, are listed in Table 3.1 [282].

<table>
<thead>
<tr>
<th>Physical &amp; Chemical Properties</th>
<th>Na-MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical state &amp; Form</td>
<td>Solid &amp; Power</td>
</tr>
<tr>
<td>Color &amp; Odor</td>
<td>Off-white &amp; odorless</td>
</tr>
<tr>
<td>PH</td>
<td>9-11 2% aqueous solution</td>
</tr>
<tr>
<td>Melting point</td>
<td>&gt;1832°F (&gt;1000°C)</td>
</tr>
<tr>
<td>Density g/cc</td>
<td>2.6</td>
</tr>
<tr>
<td>Basal spacing</td>
<td>1.12 nm</td>
</tr>
</tbody>
</table>

Table 3.1 Physical & Chemical properties of Na-MMT
3.2. Experimental Techniques

3.2.1. Wide Angle X-ray Diffraction (WXRD)

X-ray diffraction is an analytical technique that reveals detailed information about the chemical composition and crystallographic structure of natural and synthetic materials [283]. This technique has been applied to provide information in several areas:

- Measure the average spacing between layers or rows of atoms
- Determine the orientation of a single crystal
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

XRD analysis applications:

- Nano-materials: Phase composition, crystallite size and shape, lattice distortions and faulting, composition variations, orientation, in-situ structure development
- Catalysts
- New materials development
- Polymers and composites: crystalline form, crystallinity, crystalline perfection
- Pharmaceuticals and organics: polymorphs, crystallinity, orientation

For XRD technique, the quality of the collected data cannot be superior to the quality of sample and to the quality of its preparation and deposition. A majority of the materials examined by XRD need to be ground to obtain a fine powder. To make a plastic material into powder, we can
• Perform the grinding or milling within a liquid nitrogen environment
• Repeated grinding process 3-4 times, 30 s for one time
• Sieving the powder between 25-60 µm

The sample deposition, shown in Fig 3-1, the dusted samples are filled into the hollow space of the plastic/aluminum/glass sample holder. Flatten the powder to the same horizontal level of sample holder. Remove the excess powder from the sample holder by razor blade. Repeat the process 3-4 times until the testing powder is filled and fit with the horizontal level of sample holders.

Figure 3-1 Schematic representation of XRD sample preparation and deposition of XRD.
Fig 3-2 shows a schematic diagram of a diffractometer system for the XRD technique. The X-ray tube, specimen and receiving slit are the three major components for XRD. The incident angle θ is defined as the angle between the incident beam and the sample, and 2θ is defined as the angle between the incident and diffracted beams. In most powder diffractometers systems a series of parallel plates (soller slits) are arranged parallel to the plane of the diffractometer circle and several scatter and receiving slits (arranged perpendicular to the diffractometer circle) are used to create an incident beam of X-rays that are approximately parallel. Soller slits are commonly used on both the incident and diffracted beam, but this depends on the particular system. The scatter slits (on the incident beam side) may be varied to control the width of the incident beam that impinges upon the specimen and the receiving slits may be varied to control the width of the beam entering the detector.

Interaction of X-rays with a sample creates secondary “diffracted” beams (actually generated in the form of cones) of X-rays related to interplanar spacing in the crystalline powder according to Bragg’s Law:

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

where

- \( n \) is an integer
- \( \lambda \) is the wavelength of the X-rays
- \( d \) is the interplanar spacing generating the diffraction
- \( \theta \) is the diffraction angle
At a given wavelength, the interlayer spacing is reciprocal to the diffraction angle. In the XRD pattern, the diffraction angle is represented from the appearance of the diffraction peak. In the case of a PET nanocomposite, the appearing of the diffraction peak indicates the gallery spacing of the clay platelets after mixing with PET polyester. The exfoliation morphology could be achieved only if there is a disappearance of the diffraction peak.

In this work, X-ray diffraction (XRD) patterns were obtained by using a Rigaku Ultima X-ray diffractometer with Cu Kα radiation generated at 44 kV and 44 mA, (Nickel filter, Kα (1.541Å)), by monitoring the diffraction angle 2θ from 2-8° at scan speed (0.5°/min). All the samples were ground into powders.

![Schematic diagram of diffractometer system](image)
3.2.2. Transmission Electron Microscopy (TEM)

Several studies have been conducted to investigate the behavior of polymer based composites reinforced with clay particles, which can remarkably improve the properties of the polymers. Studies using transmission electron microscopy (TEM) are necessary to understand the role of the clay mineral/particles in the reinforcing effect in the polymer based materials. Compared with a light microscope, electrons are the “light source” and their lower wavelength allows a resolution a thousand times better than with a light microscope. The possibility for high magnification has made the TEM a valuable tool in both medical, biological and materials research.

The Hitachi HD-2300A scanning transmission electron microscope was used in this research and operated at 200 KeV. The lattice resolution is approximately 0.1 mm. Imaging at this resolution requires the TEM samples to be very thin in the region of interest. As a minimum requirement, samples must be electron transparent to an extent that the electron beam penetrates the specimen. In practice, TEM specimens should be no thicker than 100 nm for low-resolution imaging, and even thinner (~60 nm) for high-resolution imaging.

Additionally, the TEM image is a two dimensional projection of a three dimensional sample. That is to say the image is an average of everything that the electron beam ‘sees’ as it penetrates the samples. Averaging leads to difficulties when interpreting those images. Therefore, the sample preparation for TEM is very challenging. The resolution and contrast of the image obtained depends on the extent of transmission, therefore, sample sections have to be thin enough to get enough transmission.
The four steps for preparation procedures include embedding, trimming, sectioning and straining, which are explained in Table 3.2. The sectioning technology also has four individual processes: specimen preparation, knife selection, sectioning and mounting grids. Figure 3-3 shows the procedure to prepare glass knife boat and comparison between glass knife and diamond knife is summarized in Table 3.3.

The diamond knife and embedded sample were fixed on the microtome. The thinner specimen after sectioning floated onto the glass knife boat which was filled with water. Under the microscope of the microtome, the thinner specimen reflected various colors due to the differences in thickness. The color of specimens selected for this work is silver, which represent a thickness of less than 100 nm. Then, transmission electron microscopy was operated on the thinner specimen with normal resolution.
Table 3.2 Four steps of preparation procedure for TEM

<table>
<thead>
<tr>
<th>Steps</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Embedding</td>
<td>Nanocomposite is placed in a small drop of resin mix into the bottom of mold. Then fill the mold to the top with resin. The molds are cured in a 45°C oven for 8-20 hrs.</td>
</tr>
<tr>
<td>2 Trimming</td>
<td>The specimen are rough trimmed by shaving the resin blocks into trapezoid having the dimensions not exceeding 0.5 mm across the base, 0.4 mm across the top and 0.3 mm along the sides.</td>
</tr>
<tr>
<td>3 Sectioning</td>
<td>Sectioning is accomplished with the use of microtome. Sections of trapezoids come off the knife and are floated onto water in the boat of glass knife.</td>
</tr>
<tr>
<td>4 Straining</td>
<td>Not necessary on my samples.</td>
</tr>
</tbody>
</table>

Table 3.3 Comparison of glass knife vs. diamond knife

<table>
<thead>
<tr>
<th>Glass Knives</th>
<th>Diamond Knives</th>
</tr>
</thead>
<tbody>
<tr>
<td>can be made easily</td>
<td>Require highly skilled user</td>
</tr>
<tr>
<td>Inexpensive</td>
<td>Expensive and fragile</td>
</tr>
<tr>
<td>Edge may last over 60 section</td>
<td>Edge may last for years</td>
</tr>
</tbody>
</table>
1. Clean prepared the glass strips
2. Store at right angles with glass knife maker

3. Break into square (25 mm)

4. Score diagonally and break into two knives

Figure 3-3 Glass knife and Glass knife boat
3.2.3. Differential Scanning Calorimeter (DSC)

DSC directly measures heat changes that occur in nanocomposite during controlled increase or decrease in temperature, and makes it possible to study materials in their natural state. This technique monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the samples and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes.

The calorimeter consists of a sample holder and a reference holder. Both are constructed of platinum to allow high temperature operation. Under each holder are a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. A flow of nitrogen gas is maintained over the samples to create a reproducible and dry atmosphere. The nitrogen atmosphere also eliminates air oxidation of the samples at high temperatures. The reference is usually an empty pan and cover [284]. The pans hold up to about 10 mg of material.

For a typical scan, the heat capacity of the sample is calculated from the shift in the baseline at the starting transient. Such as, glass transitions cause a baseline shift, crystallization is a typical exothermic process and melting is a typical endothermic process. All these features indicating the thermal and crystallinity behavior for polymer nanocomposite were determined in this research using a Perkin Elmer DSC-7 differential scanning calorimeter.
The test samples were dried under a vacuum at 140°C for 12hrs. The dried samples were set in aluminium pans and placed in the DSC cells with nitrogen flow. The differences of thermal property and crystallization behavior for adding clays could be evaluated through parameters measurement ($T_m$, $T_g$, $T_c$, $\Delta H_c$).

3.2.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000 °C. The technique can be very useful for investigating the thermal stability of a material, or for investigating its behavior in different atmospheres (e.g., in the presence of oxygen or under dry nitrogen).

The most accurate TGA experiments are to set the temperature to some constant value and follow changes in sample weight as a function of time. The results will give quantitative information about the rate of degradation at that temperature. Repeating this experiment for several temperatures will give information about the temperature range under which this polymer can be used. Monitoring weight while scanning temperature will give useful results, but it must be realized that if the degradation is slow, the polymer will appear to survive to higher temperatures than it would actually survive under long term exposure. In other words, the results will also be very sensitive to heating rate. The sensitivity is large because degradation rates may be slow when compared to typical scanning rates such as 10-20 °C/min.
Coupling the byproducts of a TGA experiment or the degradation products from the polymer to other instruments such as mass spectrometer, infrared spectrometry, gas chromatography, etc., can be useful in studying the mechanism of polymer degradation. The coupled instruments can be used to identify the structure of the degradation products. Combining structure information with kinetics information can give a complete picture of the degradation process.

A TA Instrument Q500 thermogravimetric analyzer (TGA) (New Castle, DE) was used to measure the actual weight loading of clay in the PET or MXD6 matrix. The samples with weights between 5-10 mg were heated from room temperature to 1000°C at a rate of 5 °C/min. Each scan was performed under 80 ml/min gas flow of air or nitrogen.

3.2.5. Melt Rheology (Melt I.V.)

Melt viscosities of blend samples were measured using a plate-plate type rheometrics tester, RDA III made by Rheometric Scientific. Before each I.V. measurement for the nanocomposite, the relationship between melt I.V. and viscosity for PET was calibrated with respect to different known molecular weight PET samples. As shown in the following equation:

\[
\text{I.V. (melt I.V.)} = m \ln(\eta^*) + b
\]  

For the PET calibration, constants 'm' and 'b' were 0.14616 and -0.18562 in this study. The tests conditions were:

- Environmental chamber temperature = 280°C
- Chamber environmental = Nitrogen
- Gap between parallel plates = 1 mm
- Frequency = 10 rad/sec
- Strain = 20%

It must be noted that the calibration and the Mark-Houwink equation used for the calculations of number average molecular weight of nanocomposite are all based on pure PET, so the results obtained for the nanocomposite are equivalent values with respect to pure PET rather than the actual values of the blends.

3.2.6. Density Measurement

The densities of the PET pellets were measured using a density gradient column, which was made of an aqueous calcium nitrate tetrahydrate solution. The temperature of the column was maintained at 25°C by a circulating water bath. The density of the solution in the column varies increasing from top to bottom. It has colored glass beads of standard density in the range of study floating at heights where their density matches that of the surrounding liquid in the column. All the samples take some time to reach the stable state, which usually requires 60 min and the height of each resin was measured using the cathetometer. The value of density was calculated from the equation as following

\[
\text{density}_{\text{height} \rightarrow x} = a + \frac{(x - y) \times (b - a)}{(z - y)}
\]  

(3.2)

\(a, b\) are the density is of the two standard floats between which the unknown sample lies in the column and \(x, y, z\) are the heights of unknown and the two floats \(a\) and \(b\) respectively.
3.2.7. Solid State Polymerization (SSP)

The conventional PET production process consists of two discrete sections; the melt phase reaction to lower intrinsic viscosity product that is suitable for textile applications, but not for bottle grade and other high molecular weight applications. That lower intrinsic viscosity material is then further polymerized to bottle-grade intrinsic viscosity in a solid-state polymerization section. Intrinsic viscosity (as well as molecular weight) indicates the degree of polymerization, which in turn is the main factor in setting the properties of PET. The second step raises the temperature of the solid pellets to just below the melting point in the presence of a driving force to further the polymerization. Solid stating increases the final I.V. and produces a PET with low acetaldehyde content.

Solid state polymerization in this work is utilized to increase the molecular weight (related to intrinsic viscosity) of the nanocomposite to the same level. Thus, I.V will not be the factor to affect the results on mechanical and thermal properties. Before solid stating, all the nanocomposites were vacuum-dried overnight at 140 °C. The drying process not only increased the crystallinity of the precursors, which was beneficial to prevent the pellets from sticking at the subsequent solid stating process, but also decreased the water concentration to avoid hydrolytic degradation at the initial stage of SSP.

SSP reactor (Buhler Company) with an inner diameter of 90 mm and a height of 250 mm is within a heating chamber with air circulation and independent temperature regulation. Nitrogen gas with certain flow rate was heated before entering the SSP reactor. Three thermocouples are used to monitor the product temperature at the top, middle and bottom of the reactor. For each SSP experiment, 1.5 lbs of the nanocomposite was
charged into the reactor. The reactor was heated in a range of 220 °C to 230 °C under N₂ environment (2000 liter/hr flow rate, 0.3 bar pressure). Samples were taken out of the reactor for I.V. measurement at different time intervals. The SSP reaction was continued until the I.V. of samples reached to 0.8 dL/g.

3.2.8. Twin Screw Extrusion

A Werner & Pfleiderer (ZSK-30) self-wiping co-rotating twin screw extruder (equipped with a vacuum pump) was used to prepare the PET/Na-MMT, MXD6/Na-MMT, and PET/MXD6-MMT nanocomposites by blending virgin PET, or MXD6 with Na-MMT. A uniform temperature profile of 280 °C and 200 rpm were used for the melt mixing process in order to obtain a more homogeneous dispersion of clay particles in a PET matrix.

Prior to extrusion, raw materials (PET, and MXD6) were dried using an Aircon hopper/drier for 12 hrs at 140 °C. During extrusion, dried polymer with clay slurry was loaded into the hopper of the extruder. Nanocomposite strands coming out from the extruder die were pulled through a cool water bath, then cut into pallets with a pelletizer at a rate of 45-60 rpm. The residence time in the extruder was measured by the time interval between the time of polymer enters the entrance of extruder barrel and the time of extrudate comes out of the die. The residence time in this research was 2-5 min.
3.2.9. Single Screw Extrusion

The thin films of nanocomposite were obtained from single screw extrusion. These films were used for tensile test, dynamic mechanical analysis, strain hardening behavior and oxygen permeation evaluation.

A lab scale brabender single screw extruder (screw diameter D = 19 mm, L/D = 22/1, and compression ratio = 3/1) was equipped with two different kind of dies (cylindrical and sheet) to prepare the sheets and thin films. Prior to the extrusion, pelletized samples were dried at a temperature of 140 °C in a vacuum oven for 12 hrs. The polymer pellets were melted at 280 °C in extruder with screw speed at 60 rpm. The melted polymer was pushed through a die which was filled with nitrogen. The obtained sheets were kept at 25 °C and 50% RH for the future analysis.

3.2.10. Instron Tester

Tensile testing was performed to determine elastic modulus, ultimate stress, and ultimate strain for all systems. In tensile testing, a "dog-bone" shaped sample is placed in the grips of movable and stationary fixtures in a screw driven device, which pulls the samples until it breaks and measures applied load versus elongation of the sample.

The testing process requires specific grips, load cell and extensometer for each material and sample type. The load cell is a finely calibrated transducer that provides a precise measurement of the load applied. The extensometer is calibrated to measure the smallest elongations. Output from the device is recorded in a text file including load and elongation data. Elongation is typically measured by the extensometer in volts and must
be converted to millimeters. Mechanical properties are determined from a stress vs. stain plot of the load and elongation data.

An instron 4400R tester according to ASTM D 638 type IV was used to determine the mechanical properties of PET/Na-MMT, MXD6/Na-MMT and PET/MXD6-MMT nanocomposites. All the test samples were stretched at 2 in/min crosshead speed, 50% RH and 25 °C temperature. Thickness of each sample was measured with micrometer. Samples were then clamped into the instron tensile tester. (All samples were conditioned for more than 2 days under 25 °C and 50% RH before testing.)

3.2.11. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was used to gather elastic modulus data for all the nanocomposite samples. DMA determines elastic modulus, loss modulus, and damping coefficient as a function of temperature, frequency, or time. This method is utilized to determine glass transition temperature, as well. The DMA applies torsional oscillation to the sample, while slowly moving through the specific temperature range. Experimental inputs into the equipment including the software was observed and initial static force used for dynamic testing was chosen. Given the stress limits, tensile testing only served to indicate the proper initial static load.

DMA tests were performed on a TA company instrument Q800, in tensile mode. The Temperature was varied from 25 to 100 °C with the heating rate of 3 °C/min. A static force of 0.01 N, 25.0 µm of setting amplitude, and 135% of force track were applied to the test samples. The dimensions of a sample in each case were, length = 35 ± 0.3mm and width 70 ± 0.2mm. Parameters were chosen based on review of literature and discussion
with experienced DMA researchers. In DMA, the glass transition temperature, $T_g$, of a sample can be accurately determined from the elastic and loss modulus response to temperature and stress. Results were analyzed by averaging the elastic modulus data point at a specific temperature for multiple runs of a particular system.

3.2.12. Oxygen Permeability

Nanoclay (Na-MMT) is believed to increase the barrier properties by creating a tortuous path for a diffusing penetrant through the matrix resin. The method by which a gas or vapor (the penetrant) permeates a polymer matrix is postulated to occur as follows:

- Absorption into the polymer
- Diffusion through the polymer matrix
- Desorption through the polymer wall and evaporation from the surface

Permeability tells the barrier property of a material, is the product of the permeance and thickness.

$$P = \frac{TRl}{AAP}$$

(3.4)

- $P$ = permeability of barrier
- $TR$ = transmission rate
- $A$ = area of barrier
- $l$ = thickness of the barrier
- $\Delta p$ = partial pressure difference across the barrier

The effect of clay content on oxygen permeability of the PET/Na-MMT, MXD6/Na-MMT, and PET/MXD6-MMT nanocomposite were investigated using a MoCon OxTran
1050 tester according to the ASTM D3985 standard. The values of permeability were obtained at 25 °C 45% RH for PET/Na-MMT and PET/MXD6-MMT nanocomposite, and 25°C and 0% RH for MXD6/Na-MMT. The exposed area and thickness of the films were 50 cm$^2$ and 0.06 mm respectively. A mixture of 98% N$_2$ and 2% H$_2$ was used as carrier gas to take the test gas to the detector, and the flow rate of the carrier gas was 25 cc/min. The instrument was calibrated with standard mylar polyester film before the sample measurements.

3.2.13. Injection Molding

Injection molding is one of the most important methods for processing plastics. In order to obtain a desired part by an injection molding process, consideration is given for selection of a plastic material, which has the required properties.

During the injection molding process, the polymer is melted in the extruder and then injected into a mold cavity over a chilled core pin. The polymer melt is then solidified in the cold mold until its temperature is lower than T$_g$. Finally, the mold opens and the preform is ejected, before the mold is closed for the next cycle.

The injection molding process:

1. Plasticizing
2. Injection
3. Chilling
4. Ejection
The properties of the preform are determined by both processing conditions and the nature of the materials. Minimizing the IV drop, AA generation, and ensuring optically clear preform are of great importance.

In this research, focus will be on the production of injection molded clay reinforced PET nanocomposites, which emphasize that the effects of the molecular weight of nanocomposite and cooling rate play significant role on the quality of preforms. PET 0.5wt% nanocomposite preforms were produced using a model ALLROUNDER 320 s Arburg Injection Molding Machine with 55-ton capacity, reciprocating-screw and a SELOGICA control system. Prior to the injection molding process the nanocomposites were dried at 140 °C over 12 hrs in a Conair SC 60 dehumidifier drier.

3.2.14. Stretch Blow Molding

Bottle manufacturing is one of the most significant applications of PET. Stretch blow molding is the most widely used process in the industry for manufacturing PET bottles. In this process, injection molding is performed on a blank at the pre-blow pressure. An appropriate temperature profile is applied to the preform using infrared heaters. An axial stretch rod is used for stretching the preform to a desirable depth. Then, the final pressure or the full blow pressure is applied with inflates the bottle to the desired volume. Once the bottle attains the shape of the mold, it gets solidified and cooled. It is then ejected from the mold. The simultaneous stretching and blowing process result in the biaxial orientation of PET polymer chains. As result of this orientation, strain-induced crystallization occurs and causes strain hardening of the stretched polymer. The PET will crystallize when the preform is heated to a temperature higher than Tc and cause haziness
in the bottle sidewall. Lower heating temperatures close to or below \( T_g \) will cause the appearance of pearlescence in the bottle sidewall called stress whitening.

The success of stretch blow molding in the production of PET nanocomposite bottles is largely due to PET's ability to undergo strain hardening. In this work, it is attempted to successfully produce 0.5 wt% PET nanocomposite bottles. The preforms obtained from the injection molding were stretched and blown into bottles by using a lab-scale stretch-blow molding machine, which is equipped with a Sidel type heater box. The heating temperature was controlled by adjusting the heater voltage settings, which were determined from the speed of heater box movement. The sidewall of the stretch blow molded bottle was evaluated in terms of its mechanical and oxygen barrier properties.

3.2.15. Long Extension Tester

A T.M. Long Co. Inc. Film stretcher was used to prepare the films of unconstrained uniaxial stretching at 2, 3, 3.5, and 4 stretch ratio. The three extension rates of 50%/sec, 150%/sec and 200%/sec were evaluated to establish the best conditions for preparing PET nanocomposite films. The stretcher is set at a temperature of 90 °C and stretching samples were pre-heated at 90 °C for 2 min. The influence of Na-MMT in PET matrix on yield stress and stress-strain hardening, morphology of layered silicate nanocomposite and barrier properties were evaluated.

Additionally, a mathematic model was successfully developed for the stress-strain behavior of PET nanocomposites by performing a series of uniaxial stretching experiments. This model was developed considering two important characteristics of the stress-strain curves, namely yield stress and strain hardening point. In this work, it has
been attempted to apply this methodology in order to predict the non-linear viscoelastic behavior of PET and its nanocomposites under uniaxial stretch processes.
Chapter 4

Modified Melt Blending Technology for Polymer Nanocomposite Preparation

4.1. Preliminary efforts in the preparation of Na-MMT slurries

Initially, 20 g of Na-MMT was added to 980 g of deionized water (2 wt%) while it was being stirred at room temperature. This stirring process had been performed for different time intervals in order to ensure the clay was dispersed in the water completely. It was observed that the slurry was off-white in color and contained undispersed lumps of clay particles for time intervals ranging from 2-6 hrs. After 6 hrs of continuous stirring, there was a disappearance of the clay lumps, and uniform dispersion of the clay in water was achieved. It was thought that faster clay dispersion could be achieved with the assistance of heat. Higher temperatures, such as 40 °C, and 60 °C were used in an attempt to shorten the preparation time for the clay dispersion. The higher temperature, however, was not a factor found to have significant effects on the preparation time.

As is well known, the existence of the water during the melt blending process could cause hydrolytic degradation of PET at high processing temperatures. In order to reduce the amount of water being introduced through the clay slurry into the extruder, higher weight percent of clay in the slurry were prepared at room temperature. For this purpose, 40 g of Na-MMT was added to 960 g of deionized water (4 wt%) with continuous stirring. It was found that the complete dispersion of clay slurry without lumps was
obtained after 8 hours of stirring. Another attempt was also made to further decrease the water content in the slurry. A 5 wt% clay slurry was prepared by adding 50 g Na-MMT into 950 g of deionized water. It was observed that the clay was difficult to disperse in the higher weight concentration because of the lumps that formed during the mixing process. These lumps did not disappear over several hours since the solution was very viscous.

### 4.2. Preparation of Na-MMT dispersion

It was decided that the clay water dispersion should be prepared with 4 wt% clay loading at room temperature. Na-MMT was dispersed in a water solution and stirred 15 hours overnight with a magnetic stirrer before melt blending process, as shown in Figure 4-1. This process was used to prepare clay slurry.

![Figure 4-1 Clay Slurry Preparation](image)

### 4.3. Calibration of pumps for the clay slurry and resins

The pumps for the clay slurry and extruder feeder were calibrated in order to read the actual feeding speed during the modified melt blending process. This allowed calculation of the theoretical clay loading in PET or MXD6 nanocomposites. For the calibration, the
motors of the pump and extruder feeder were operated at different speeds, at each motor speed, the clay slurry was collected for 1 min and the weight of that amount was measured. All the data are shown in Tables 4.1-4.3. The actual feeding speed of the clay slurry was plotted against the motor speed, as shown from the Figure 4-2 to 4-4, and the equations were used to obtain the actual feeding speed at specific motor setting.

Table 4.1 Relationship between motor feed speed and actual clay slurry flow rate

<table>
<thead>
<tr>
<th>Motor number (pump)</th>
<th>Actual flow rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>41.74</td>
</tr>
<tr>
<td>25</td>
<td>52.72</td>
</tr>
<tr>
<td>30</td>
<td>61.14</td>
</tr>
<tr>
<td>35</td>
<td>73.64</td>
</tr>
<tr>
<td>40</td>
<td>81.96</td>
</tr>
<tr>
<td>50</td>
<td>100.56</td>
</tr>
<tr>
<td>55</td>
<td>108.18</td>
</tr>
</tbody>
</table>
Figure 4-2 Pump Calibration for Clay Slurry

Table 4.2 Relationship between motor feed speed and actual feed speed for MXD6

<table>
<thead>
<tr>
<th>Motor number</th>
<th>Actual feeding rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>14.5</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>200</td>
<td>62</td>
</tr>
<tr>
<td>300</td>
<td>95</td>
</tr>
<tr>
<td>400</td>
<td>125</td>
</tr>
</tbody>
</table>
Figure 4-3 Pump Calibration for MXD6

Table 4.3 Relationship between motor feed speed and actual feed speed for PET.

<table>
<thead>
<tr>
<th>Motor number</th>
<th>Actual feeding rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>18</td>
</tr>
<tr>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>200</td>
<td>84.5</td>
</tr>
<tr>
<td>300</td>
<td>125</td>
</tr>
<tr>
<td>400</td>
<td>165</td>
</tr>
</tbody>
</table>
Figure 4-4 Pump Calibration for PET
4.4. Preparation of polymer nanocomposites using modified melt blending

4.4.1. Preparation of PET/Na-MMT and MXD6-MMT nanocomposites

Prior to the extrusion process, the PET and MXD6 resins were each dried in a Conair dehumidifying air dryer at 140 °C for 12 hrs.

In order to prepare PET/Na-MMT and MXD6/Na-MMT nanocomposites by the melt blending process, the polymer resin and Na-MMT slurry were fed into the co-rotating twin screw extruder (ZSF-30). The feeding speed of PET resin was 100 g/min and those for clay slurry were 12.5, 25, 50, 75, and 125 g/min for 0.5, 1, 2, 3, 5 wt% respectively. The screw speed at 200 rpm, and temperatures of zones one through five, as well as the exit die, of 280 °C were used. Figure 4-5 shows a schematic figure that illustrates the process for preparing nanocomposites. Virgin PET or MXD6 pellets and the clay slurry were fed into the hopper of the extruder at an output of 30 g/min for pellets. After the clay slurry was mixed with melted polymer, the water was evaporated from the nanocomposites and removed by the vacuum pump before the nanocomposites exited from the extruder die. Finally, PET/Na-MMT (0.5, 1, 2, 3, 5 wt%) and MXD6/Na-MMT (2, 3, and 5 wt%) strands were quenched in water at room temperature, pelletized and dried.
Figure 4-5 Schematic figure depicts the modified melt blending process using clay slurry for preparing PET/Na-MMT and MXD6/Na-MMT nanocomposites.

4.4.2. Preparation of PET/MXD6-MMT nanocomposites

The overall aim of the work described in this chapter was to investigate the possibility of using the much better understood nanocomposite technology that can be used to produce exfoliation of clay in PET. It was hoped that by blending a pre-exfoliated MXD6/Na-MMT nanocomposite, transfer of the exfoliated clay platelets into the bulk of the PET matrix could be achieved. Overall this effect would be expected to give significant improvement in the oxygen barrier of PET.

As illustrated in the Figure 4-6, the first step of this production process is to prepare 4 wt% clay slurry. Secondly, since the MXD6 nanocomposite shows better exfoliated morphology than PET nanocomposite, the clay slurry is melt blended with virgin MXD6 to form MXD6/Na-MMT nanocomposites (5 wt% and 10 wt%) using the modified melt blending technology. Prior to the third step, the produced MXD6/Na-MMT and virgin PET were mixed in a sealed container for 2 min. This mixture was dried under vacuum at
140 °C for 12 hrs before the mixtures of PET and MXD6/Na-MMT nanocomposite were loaded into the hopper of the extruder. The blended nanocomposite strands prepared from the twin screw extruder came out of the die and were then quenched through a cold water bath, cut into pellets with a pelletizer at 45 rpm.

Figure 4-6 Schematic figure depicts the modified melt blending process for preparation of PET/MXD6-Na-MMT nanocomposites.

4.5. Solid State Polymerization (SSP)

Solid state polymerization (SSP) was utilized to increase the molecular weight (as measured by intrinsic viscosity) of the nanocomposites to equivalent levels of about 0.8 dL/g. All the nanocomposites studied in this research were crystallized by being heated at 140 °C for 2 hrs to avoid the pellets sticking to each other during SSP. These crystallized nanocomposites were loaded into the SSP reactor (Buhler Company, capacity 1 kg) and heated up to 220 °C under a nitrogen environment for 5-8 hrs (2000 liter/hr flow rate, 0.3 bar pressure). During the SSP process, samples were collected at different time intervals to monitor the I.V changes. The solid stating reactions were continued until the I.V.
reached 0.8 dL/g. Table 4.4 lists the I.V. values for PET/Na-MMT and MXD6/Na-MMT resins after SSP.

Table 4.4 I.V. Values for PET/Na-MMT and MXD6/Na-MMT Resins after SSP

<table>
<thead>
<tr>
<th>Clay Loading</th>
<th>PET/Na-MMT I.V. (η) (dL/g)</th>
<th>MXD6/Na-MMT I.V. (η) (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>After SSP</td>
</tr>
<tr>
<td>0.5 wt%</td>
<td>0.67</td>
<td>0.80</td>
</tr>
<tr>
<td>1 wt%</td>
<td>0.61</td>
<td>0.78</td>
</tr>
<tr>
<td>2 wt%</td>
<td>0.56</td>
<td>0.83</td>
</tr>
<tr>
<td>3 wt%</td>
<td>0.50</td>
<td>0.82</td>
</tr>
<tr>
<td>5 wt%</td>
<td>0.45</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Chapter 5

Property Characterization on PET/Na-MMT and MXD6/Na-MMT Nanocomposites

5.1. The effects of nanoparticles on crystallinity and related thermal behavior

Crystallization behavior of polymer nanocomposites has been the focus of extensive studies [285-289]. This is because the crystallization behavior influences the semi-crystalline structure of a polymer, which in turn affects the polymer’s properties. Crystallization can be increased by the addition of nanoparticles that act as nucleating agents [285]. It is essential to study the influence of Na-MMT on the crystallization and thermal behavior of PET and MXD6 in order to understand how to optimize their processing conditions and properties of the polymer nanocomposites.

5.1.1. Clay content measurement (TGA)

Thermogravimetric analysis measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials. In this study, the clay content in PET/Na-MMT and MXD6/Na-MMT nanocomposite was measured by TGA. Figure 5-1 shows the TGA curve for a PET/Na-MMT nanocomposite. It is seen that the PET nanocomposites start the decomposition about 400 °C. As shown in Table 5.1. It can
be seen that the inorganic residuals remaining after complete combustion of the nanocomposites are lower as compared to theoretical clay loading added during processing. This was due to the clay lost during process of the mixing into polymer in the twin screw extruder. These results are in agreement with the data in the literature [290].
Figure 5-1 The TGA curve for PET/Na-MMT nanocomposite

Table 5.1 Clay content measured by TGA

<table>
<thead>
<tr>
<th>Theoretical Weight Percent</th>
<th>Actual Weight Percent (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PET/Na-MMT</td>
</tr>
<tr>
<td>0.5 wt%</td>
<td>0.42</td>
</tr>
<tr>
<td>1 wt%</td>
<td>0.9</td>
</tr>
<tr>
<td>2 wt%</td>
<td>1.6</td>
</tr>
<tr>
<td>3 wt%</td>
<td>2.3</td>
</tr>
<tr>
<td>5 wt%</td>
<td>3.9</td>
</tr>
</tbody>
</table>
5.1.2. Non-isothermal crystallization behavior on PET/Na-MMT

PET and PET/Na-MMT nanocomposite were dried in a vacuum oven at 140 °C for 12 hrs. This DSC measurements on PET pellets and its nanocomposites (0.5, 1, 2, 3, and 5 wt%) were carried out as the following procedure:

**Procedure 1**

Holding a sample at 40 °C for 3 min
Heating from 40 °C to 300 °C at 10 °C/min
Holding at 300 °C for 3 min
Cooling from 300 °C to 40 °C at 300 °C/min
Holding at 40 °C for 3 min
Heating from 40 °C to 300 °C at 10 °C/min
Holding at 300 °C for 3 min
Cooling from 300 °C to 40 °C at 10 °C/min

After the initial heating scan and quench process for removal of heat history of each test sample, additional reheating and cooling cycles were carried out in order to determine the effect of the clays under controlled conditions of heating and cooling.

DSC data in Table 5.2 and Figure 5-2 show the characteristic thermal behaviors of PET and the PET nanocomposites. All the samples have similar I.V. values which eliminate the possibility that molecular weight differences could affect the crystallization behaviors of the PET nanocomposites. In the second heating scans, as shown in Figure 5-2, the samples were heated from 40 °C to 300 °C at the rate of 10 °C/min after quenching
the samples from the melt to 40 °C at a nominal rate of 300 °C/min. Table 5.2 shows the thermal properties of the composites. The glass transition temperatures ($T_g$) of the nanocomposites were slightly increased from 78.0 °C to 79.7 °C. This may have resulted from the addition of clay into the polymer matrices, which could inhibit the mobility of chain segments and also increase the crystallinity of samples. The melting temperatures ($T_m$) of PET nanocomposites shift to slightly higher temperatures and these slight increases may also result from the hindrance caused by the nanoparticles in the PET matrix.

Mucha et al. [291] reported that the $T_m$ of polypropylene (PP) increased from 2-4 °C as a result of the addition of carbon black particles. The heats of fusion ($\Delta H_m$) of all the PET nanocomposites have been corrected (normalized) for the nominal weight of clay content and are listed in Table 5.2. All of the $\Delta H_m$ values are similar to that of neat PET, regardless of the clay contents. It can be clearly seen that most nanocomposites (2, 3, 5 wt %) crystallized during the quenching step, as these samples do not exhibit significant crystallization peaks during reheating. As shown in Table 5.2, during reheating the pure PET gives enthalpy of crystallization $\Delta H_c^m$ of 22.5 J/g and enthalpy of melting $\Delta H_m$ 32.1 J/g. The difference between the melting and crystallization enthalpies is 9.6 J/g, indicating crystallization occurred during the cooling process. For 0.5 wt% and 1 wt% PET nanocomposites, about 80% of the total crystallinity was formed in the quenching process. With increased clay contents, the disappearance of crystallization peaks result from the strong nucleating function of the clay, which enhances the crystallization rate during the quenching process [120, 131].
All the PET nanocomposites shown in Figure 5-3 were cooled from 300 °C to 40 °C at 10 °C/min. The crystallization peak temperatures ($T_c^c$) of PET nanocomposites occur at higher temperature compare to that of PET. The maximum $T_c^c$ is 195.5 °C for the 5 wt% clay incorporation. The onset of crystallization temperature ($T_{on}^c$) also shifts to higher temperatures indicating that PET starts to crystallize sooner with clay addition, indicating a stronger nucleation effect [131, 290, 292-294]. As the crystallization peaks obtained during cooling are symmetrical, half time ($t_{1/2}$) of crystallization can be obtained using the following equation [295]:

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

where $T_{on}^c$ is the onset of crystallization temperature (°C); $T_c^c$ is the crystallization temperature at the exothermic peak (°C), and $\chi$ is the cooling rate (°C/min).

The half time of crystallization is an indicator of the overall crystallization rate attributed to the combined effects of nucleation and crystal growth. Table 5.3 includes crystallization $t_{1/2}$ values for PET and its nanocomposites. The crystallization half time ($t_{1/2}$) of PET is 0.9 min. Samples in which MMT has been incorporated exhibit much lower average value 0.62 min. These results indicate that the presence of clay acts as a heterogeneous nucleating agent stimulating the crystallization to occur sooner [296-297]. Since there are no significant differences in $t_{1/2}$ among nanocomposites with different clay contents, it appears that when well dispersed structures in PET nanocomposites are formed, this leads to similar crystallization behaviors and thermal characteristics.
Table 5.2 Modified DSC data of neat PET and its nanocomposites at reheating scans

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intrinsic viscosity (dl/g)</th>
<th>Reheating</th>
<th></th>
<th></th>
<th></th>
<th>Modified ΔH_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intrinsic viscosity (dl/g)</td>
<td>T_g (°C)</td>
<td>ΔH_c (J/g)</td>
<td>T_m(°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>0.84</td>
<td>78.0</td>
<td>22.5</td>
<td>245.9</td>
<td>32.1</td>
<td></td>
</tr>
<tr>
<td>PETN 0.5 wt</td>
<td>0.80</td>
<td>78.4</td>
<td>8.2</td>
<td>245.2</td>
<td>33.5</td>
<td></td>
</tr>
<tr>
<td>PETN 1 wt</td>
<td>0.78</td>
<td>78.8</td>
<td>2.3</td>
<td>246.5</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>PETN 2 wt</td>
<td>0.83</td>
<td>79.6</td>
<td>-</td>
<td>246.9</td>
<td>33.6</td>
<td></td>
</tr>
<tr>
<td>PETN 3 wt</td>
<td>0.82</td>
<td>79.7</td>
<td>-</td>
<td>247.1</td>
<td>34.1</td>
<td></td>
</tr>
<tr>
<td>PETN 5 wt</td>
<td>0.84</td>
<td>79.7</td>
<td>-</td>
<td>247.6</td>
<td>34.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5-2 Second Heating DSC Curves of Pure PET and PET/Na-MMT

Nanocomposites at 10 °C/min
Table 5.3 Modified DSC Data of Neat PET and its Nanocomposites at Cooling Scans

<table>
<thead>
<tr>
<th>Samples</th>
<th>I.V. (η) (dl/g)</th>
<th>$T_c$ (°C)</th>
<th>$T_{on}$ (°C)</th>
<th>$t_{1/2}$ (min)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin PET</td>
<td>0.84</td>
<td>187.2</td>
<td>196.2</td>
<td>0.9</td>
<td>32.1</td>
</tr>
<tr>
<td>PETN 0.5 wt</td>
<td>0.80</td>
<td>193.5</td>
<td>199.9</td>
<td>0.64</td>
<td>33.6</td>
</tr>
<tr>
<td>PETN 1 wt</td>
<td>0.78</td>
<td>194.8</td>
<td>200.9</td>
<td>0.61</td>
<td>32.5</td>
</tr>
<tr>
<td>PETN 2 wt</td>
<td>0.83</td>
<td>192.2</td>
<td>198.4</td>
<td>0.62</td>
<td>31.5</td>
</tr>
<tr>
<td>PETN 3 wt</td>
<td>0.82</td>
<td>192.8</td>
<td>199.4</td>
<td>0.66</td>
<td>31.4</td>
</tr>
<tr>
<td>PETN 5 wt</td>
<td>0.84</td>
<td>195.5</td>
<td>201.5</td>
<td>0.6</td>
<td>29.8</td>
</tr>
</tbody>
</table>

Figure 5-3 Cooling DSC Curves of PET and PET/Na-MMT Nanocomposites at 10°C/min
5.1.3. Non-isothermal crystallization behavior on MXD6/Na-MMT

MXD6 and MXD6/Na-MMT nanocomposite were dried at vacuum oven at 140 °C for 12 hrs. DSC measurements on MXD6 and its nanocomposites (2, 3, and 5 wt%) were carried out as the following procedure:

*Procedure 1*

*Holding a sample at 40 °C for 3 min*

*Heating from 40 °C to 300 °C at 10 °C/min*

*Holding at 300 °C for 3 min*

*Cooling from 300 °C to 40 °C at 300 °C/min*

*Holding at 40 °C for 3 min*

*Heating from 40 °C to 300 °C at 10 °C/min*

*Holding at 300 °C for 3 min*

*Cooling from 300 °C to 40 °C at 10 °C/min*

Thermal properties obtained for the MXD6 and MXD6/Na-MMT nanocomposites are exhibited in Table 5.4 and Figure 5-4. In the second heating scans, as seen in Figure 5-4, the glass transition temperature ($T_g$) increases slightly in the nanocomposite samples in comparison to the value recorded for neat MXD6. This can be attributed to a higher rigidity in the amorphous phase of the polymer in the presence of the clay particles that restrict the molecular motions of the MXD6 chain segments.

Similar to the PET nanocomposites, heats of fusion (modified $\Delta H_m$) and $T_m$ for MXD6 and its nanocomposites did not vary significantly with clay loading from 2-5 wt%.
In contrast to PET nanocomposites, all MXD6 nanocomposites gave a crystallization peak during the reheating process. This occurred because most of the MXD6 matrix remained in the amorphous state during cooling. In the presence of Na-MMT, the crystallization enthalpies were reduced to about 20 J/g compared with 36 J/g for neat MXD6.

In the cooling process, as presented in Figure 5-5 and Table 5.5, Na-MMT added to MXD6 causes the crystallization peak temperature $T_c$ for all three concentrations to occur at higher temperatures with shorter $t_{1/2}$ as compared to the neat MXD6. At a 10 °C/min cooling rate, the values $t_{1/2}$ for the MXD6 nanocomposites is between 0.84-0.89 min. These are lower than that of MXD6, signifying that the addition of Na-MMT can accelerate the overall crystallization process [298-300]. The same conclusion could be observed from Figure 5-5, that the crystallization peak of neat MXD6 in the cooling scan is broader, while the nanocomposites show narrower and sharper peaks. For the MXD6 nanocomposites (2, 3, 5 wt%), both onset of crystallization temperatures and half times of crystallization are independent of clay contents, implying similar nanostructures. These observations further verify the TEM results, that all the MXD6 nanocomposites prepared in this work achieved exfoliated morphology.
Table 5.4 Modified DSC Data of Neat MXD6 and its Nanocomposite at Reheating Scans

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_h$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin MXD6</td>
<td>84.7</td>
<td>130.9</td>
<td>36.4</td>
<td>238.2</td>
<td>64.6</td>
<td></td>
</tr>
<tr>
<td>MXD6N 2 wt</td>
<td>85.4</td>
<td>131.0</td>
<td>19.4</td>
<td>245.2</td>
<td>56.9</td>
<td>59.1</td>
</tr>
<tr>
<td>MXD6N 3 wt</td>
<td>85.9</td>
<td>135.3</td>
<td>20.8</td>
<td>246.5</td>
<td>56.1</td>
<td>57.8</td>
</tr>
<tr>
<td>MXD6N 5 wt</td>
<td>85.1</td>
<td>134.6</td>
<td>29.3</td>
<td>246.9</td>
<td>61.6</td>
<td>64.8</td>
</tr>
</tbody>
</table>

Figure 5-4 Second Heating of MXD6 and MXD6/Na-MMT Nanocomposite
Table 5.5 Modified DSC data of neat MXD6 and its nanocomposite at cooling scans

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_c^s$ (°C)</th>
<th>$T_{on}$ (°C)</th>
<th>$t_{1/2}$ (min)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin MXD6</td>
<td>173.5</td>
<td>187.3</td>
<td>1.38</td>
<td>46.1</td>
</tr>
<tr>
<td>MXD6N 2 wt</td>
<td>183.9</td>
<td>192.3</td>
<td>0.84</td>
<td>46.3</td>
</tr>
<tr>
<td>MXD6N 3 wt</td>
<td>182.5</td>
<td>191.4</td>
<td>0.89</td>
<td>44.8</td>
</tr>
<tr>
<td>MXD6N 5 wt</td>
<td>183.5</td>
<td>192.2</td>
<td>0.87</td>
<td>46.2</td>
</tr>
</tbody>
</table>

Figure 5-5 Second Heating of MXD6 and MXD6/Na-MMT Nanocomposite
5.1.4. Different cooling analysis on PET/Na-MMT

The PET nanocomposite appears to have unclear crystallization behavior during the quenching process. In order to more fully investigate this point, DSC at eight of different cooling rates were studied following the procedure 2. Cooling scans were recorded for extruded PET as well as for 0.5 wt% and 3 wt% PET/Na-MMT nanocomposites.

Procedure 2

- Holding a sample at 40 °C for 3 min
- Heating from 40 °C to 300 °C at 10 °C/min
- Holding at 300 °C for 3 min
- Cooling from 300 °C to 40 °C at different cooling rates (5 °C/min, 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min, 50 °C/min, 60 °C/min, 70 °C/min, 80 °C/min)

In the reheating process, the absence of crystallization peaks for PET nanocomposites showed that different crystallization behavior occurred for PET nanocomposites, during the quenching process (Figure 5-2 and Figure 5-4). In order to fully investigate the differences of crystallization behaviors among all the PET nanocomposites. PET, 0.5 wt% and 3 wt% PET/Na-MMT nanocomposites were examined at eight different cooling rates (Figure 5-6). The work was done to further investigate the crystallization behavior observed among PET nanocomposites during the faster quenching process.
A summary of the non-isothermal crystallization behaviors of extruded PET, 0.5 wt% and 3 wt% PET/Na-MMT nanocomposites is given in Table 5.6. As expected, the crystallization enthalpies ($\Delta H_c$), normalized in terms of nominal clay contents, decrease with increased cooling rates for PET and its nanocomposites. Higher cooling rates give less time for polymer chains to fold and crystallize. The shorter times to complete the crystallization process result in the lower crystallization enthalpies. Figure 5-7 shows crystallization enthalpies $\Delta H_c$ plotted as functions of reciprocal of cooling rates. After extrapolation of the line to the X axis, as seen in Table 5.7, for extruded PET, the material is projected to remain completely amorphous at faster cooling speed (115 °C/min). Similarly, it is shown that 0.5 wt% PET nanocomposite can be quenched into the amorphous state at a cooling rate of 147 °C/min, slightly higher than that of extruded PET. In the case of 3 wt% PET/Na-MMT nanocomposite, the material already crystallizes even when quenched at an infinite rate. That is the reason for the reduction of the crystallization peaks observed during reheating process.
Table 5.6 Crystallization Enthalpy of Extruded PET (A), 0.5 wt% PET/Na-MMT (B), 3 wt% PET/Na-MMT (C) at Different Cooling Rate

<table>
<thead>
<tr>
<th>CR (min/°C)</th>
<th>ΔH_c^2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 (1/5)</td>
<td>35.2</td>
</tr>
<tr>
<td>0.1 (1/10)</td>
<td>31.9</td>
</tr>
<tr>
<td>0.05 (1/20)</td>
<td>24.2</td>
</tr>
<tr>
<td>0.025 (1/40)</td>
<td>9.1</td>
</tr>
<tr>
<td>0.020 (1/50)</td>
<td>3.7</td>
</tr>
<tr>
<td>0.017 (1/60)</td>
<td>3.6</td>
</tr>
<tr>
<td>0.014 (1/70)</td>
<td>2.8</td>
</tr>
<tr>
<td>0.0125 (1/80)</td>
<td>2.6</td>
</tr>
</tbody>
</table>

(B)

<table>
<thead>
<tr>
<th>CR (min/°C)</th>
<th>ΔH_c^2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 (1/5)</td>
<td>35.5</td>
</tr>
<tr>
<td>0.1 (1/10)</td>
<td>32.4</td>
</tr>
<tr>
<td>0.05 (1/20)</td>
<td>31.5</td>
</tr>
<tr>
<td>0.025 (1/40)</td>
<td>30.9</td>
</tr>
<tr>
<td>0.020 (1/50)</td>
<td>23.7</td>
</tr>
<tr>
<td>0.017 (1/60)</td>
<td>16.5</td>
</tr>
<tr>
<td>0.014 (1/70)</td>
<td>13.8</td>
</tr>
<tr>
<td>0.0125 (1/80)</td>
<td>2.6</td>
</tr>
</tbody>
</table>

(C)

<table>
<thead>
<tr>
<th>CR (min/°C)</th>
<th>ΔH_c^2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 (1/5)</td>
<td>32.9</td>
</tr>
<tr>
<td>0.1 (1/10)</td>
<td>30.6</td>
</tr>
<tr>
<td>0.05 (1/20)</td>
<td>29.8</td>
</tr>
<tr>
<td>0.025 (1/40)</td>
<td>27.5</td>
</tr>
<tr>
<td>0.020 (1/50)</td>
<td>26.6</td>
</tr>
<tr>
<td>0.017 (1/60)</td>
<td>22.7</td>
</tr>
<tr>
<td>0.014 (1/70)</td>
<td>20.4</td>
</tr>
<tr>
<td>0.0125 (1/80)</td>
<td>19.2</td>
</tr>
</tbody>
</table>
Figure 5-6 Relationship between Delta H versus 1/CR at Different Cooling Rate for 0.5 wt% PET/Na-MMT nanocomposite

Figure 5-7 Plots of crystallization enthalpy vs. cooling rate of extruded PET (A), 0.5 wt% PET (B), 3 wt% PET (C)
Table 5.7 The Conditions of extruded PET, 0.5 wt% PET and 3 wt% PET at fast cooling rate from DSC

<table>
<thead>
<tr>
<th>Samples</th>
<th>Intercept</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruded PET</td>
<td>0.0087 (115°C/min)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>PETN 0.5 wt</td>
<td>0.0068 (147°C/min)</td>
<td>Amorphous</td>
</tr>
<tr>
<td>PETN 3 wt</td>
<td>6.8 (Y axis)</td>
<td>Partial Crystallized</td>
</tr>
</tbody>
</table>

5.1.5. Different cooling analysis on MXD6/Na-MMT

At the same clay loading in PET and MXD6, the MXD6 nanocomposite appears to have different crystallization behavior during the quenching process compared with that of PET nanocomposite. In this case, DSC at eight of different cooling rates on MXD6 nanocomposites were also studied following the procedure 2. Cooling scans were recorded for extruded MXD6 as well as for 3 wt% MXD6/Na-MMT nanocomposites.

**Procedure 2**

Holding a sample at 40 °C for 3 min

Heating from 40 °C to 300 °C at 10 °C/min

Holding at 300 °C for 3 min

Cooling from 300 °C to 40 °C at different cooling rates (5 °C/min, 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min, 50 °C/min, 60 °C/min, 70 °C/min, 80 °C/min)
As indicated in Fig 5-2 and 5-4, the 3 wt% PET/Na-MMT and 3 wt% MXD6/Na-MMT, the MXD6 nanocomposites showed crystallization exothermic upon heating from a quenched state while the PET nanocomposite equivalent did not show an exothermic peak. To further investigate the difference between the two nanocomposites, the MXD6 nanocomposite samples were cooled from melt at different cooling rates. Figure 5-8 gives the dependence of $\Delta H_c$ on the reciprocal of the cooling rates. The data show that, an amorphous state can be reached at a cooling rate of about 130 °C/min. That is the reason for the presence of crystallization peak seen in the reheating scans for the 3 wt% MXD6 nanocomposite. This behavior is consistent with observed results from both MXD6 nanocomposite and PET nanocomposite in the reheating scans.
Table 5.8 DSC data from 3wt% MXD6 nanocomposites at different cooling rate

<table>
<thead>
<tr>
<th>Cooling Rate (°C/min)</th>
<th>1/CR (min/°C)</th>
<th>MXD6 3 wt ΔH_c (∆J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.2</td>
<td>43.7</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>43.0</td>
</tr>
<tr>
<td>20</td>
<td>0.05</td>
<td>40.8</td>
</tr>
<tr>
<td>40</td>
<td>0.025</td>
<td>35.0</td>
</tr>
<tr>
<td>50</td>
<td>0.020</td>
<td>24.5</td>
</tr>
<tr>
<td>60</td>
<td>0.017</td>
<td>12.4</td>
</tr>
<tr>
<td>70</td>
<td>0.014</td>
<td>7.6</td>
</tr>
<tr>
<td>80</td>
<td>0.0125</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Figure 5-8 DSC results on 3 wt% MXD6 nanocomposite: extrapolate curve on different cooling rate (50 °C/min, 60 °C/min, 70 °C/min, 80 °C/min)
5.2. Morphological characterization of nanoclay dispersions

5.2.1. XRD analysis on PET/Na-MMT and MXD6/Na-MMT

X-ray diffraction (XRD) patterns for the Na-MMT powder, and Na-MMT dispersions in water are presented in Figure 5-9. As can be seen, the Na-MMT exhibits a characteristic diffraction peak with a d spacing of 1.12 nm at 2θ=7.4°. When Na-MMT is introduced into distilled water, the absence of a scattering angle peak suggests that the natural clay platelets are exfoliated due to their hydrophilic nature. Figures 5-10 and 5-11 give X-ray diffraction patterns for the PET/Na-MMT nanocomposites (0.5, 1, 2, 3, and 5 wt%) and MXD6/Na-MMT nanocomposites (2, 3, and 5 wt%). The absence of basal reflections in the X-ray patterns for both types of nanocomposites indicate the formation of exfoliated nanostructures. Similar behavior, in which the disappearance of the clay diffraction peak showed strong evidence for the exfoliation of composites, has also been reported by Cho and Paul [301]. They described the preparation of nylon 6/Na-MMT by melt blending and investigated its morphological properties. They concluded that the absence of a clay diffraction peak was strong evidence for the formation of an exfoliated nanocomposite. In the work of Zhao et al. [302], XRD was used to indicate the d-spacing of poly (methyl methacrylate) and polystyrene/clay nanocomposites. Their results showed that the clay was nearly exfoliated in both polymers based on the characteristic peak disappearance.
Figure 5-9 XRD Patterns of Na-MMT and Clay Dispersion
Figure 5-10 XRD Patterns of PET/Na-MMT nanocomposites (0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 5 wt%)
Figure 5-11 XRD Patterns of PET/Na-MMT nanocomposites (0.5 wt%, 1 wt%, 2 wt%, 3 wt%, 5 wt%)

MXD6/Na-MMT nanocomposite (5 wt%)

MXD6/Na-MMT nanocomposite (3 wt%)

MXD6/Na-MMT nanocomposite (2 wt%)
5.2.2. TEM analysis on PET/Na-MMT nanocomposite

In order to verify the results obtained from the XRD data, transmission electron microscopy (TEM) was used to image the structures of samples. The black lines in the photomicrographs correspond to the clay layers while lighter background represents the polymer matrices. Figure 5-12 to 5-16, show TEM photomicrographs of PET with 0.5 wt%, 1 wt%, 2 wt%, 3 wt% and 5 wt% Na-MMT, respectively. As can be seen, the Na-MMT is highly dispersed in the PET matrix indicating exfoliated morphology of the clay layers. The morphologies of Figure 5-15 and 5-16 show mixtures of high level of intercalated and partially exfoliated features. In contrast to the PET/Na-MMT nanocomposites based on other approaches, when clay dispersion method is used, the clay platelets appear more randomly dispersed in the PET matrix.

5.2.3. TEM analysis on MXD6/Na-MMT nanocomposite

Figure 5-17, 5-18 and 5-19 display TEM images of MXD6/Na-MMT nanocomposites, respectively, containing 2, 3, and 5 wt% of the clay component. The micrographs of all of the MXD6 nanocomposites, reveal well exfoliated structures. The TEM results indicate that XRD observations cannot be the only route to confirm the morphology of nanocomposites. The disappearance of diffraction peaks may indicate intercalation or exfoliation of the clay [285-286]. Eckel et.al [285] evaluated the organo-clay dispersion in polymer nanocomposites using XRD and TEM. XRD was found to be limited to quantify the clay dispersion. Mixed layering, and other peak broadening factors can cause the disappearance of the diffraction peak as has been discussed by Morgan et.al [286]. The important result from this morphological study is that the Na-MMT has been
effectively exfoliated in both PET and MXD6 matrices at a nanometer levels. At lower clay loading, exfoliated morphology has been achieved for both PET and MXD6 nanocomposites. These results also indicate that XRD should be combined with TEM in order to obtain clear picture of actual clay dispersion within the polymer.
Figure 5.12 TEM Image of 0.5 wt% PET/Na-MMT Nanocomposite.
Figure 5.13 TEM Image of 1 wt% PET/Na-MMT Nanocomposite
Figure 5-14 TEM Image of 2 wt% PET/Na-MMT Nanocomposite
Figure 5-15 TEM Image of 3 wt% PET/Na-MMT Nanocomposite
Figure 5.16 TEM Image of 5 wt% PET/Na-MMT Nanocomposite
Figure 5.17 TEM Image of 2 wt% MXD6/Na-MMT Nanocomposite
Figure 5-18 TEM Image of 3 wt% MXD6/Na-MMT Nanocomposite
Figure 5-19: TEM Image of 5 wt% MXD6/Na-MMT Nanocomposite
5.3. Mechanical Properties Improvement

5.3.1. Tensile analysis on PET/Na-MMT nanocomposite

All the nanocomposite samples were measured with an Instron 4400R tester according to ASTM D 638 type IV. Test samples were stretched at 2 in/min crosshead speed after store in a room with 50% humidity and 23°C. 5~10 specimens were measured per sample at each conditions.

Tensile modulus, the maximum stress and the strain at break of PET/Na-MMT nanocomposite are summarized in Table 5.9. It has been seen that with an increase in the clay to 2 wt%, an increase of 24% in modulus is obtained for PET nanocomposite. With further increase in nanoclay from 3-5 wt%, a decrease in tensile strength and modulus of nanocomposites has been observed.

The effect of clay loading on the elongation at break of polymer matrix and the nanocomposite is also given in Table 5.9. The elongation at break decreased drastically with the incorporation of the clay loading. The materials show the brittleness due to the presence of Na-MMT.

Table 5.9 Tensile properties of PET/Na-MMT nanocomposite
5.3.2. Tensile analysis on MXD6/Na-MMT nanocomposite

The Young’s modulus, tensile stress and the strain at break of MXD6/Na-MMT nanocomposites are shown in Table 5.10. It is observed that the presence of Na-MMT in the MXD6 matrix has no effect on elongation at break. MXD6 nanocomposite having 2 wt% MMT gives the maximum improvement in tensile strength (15%) and Young’s Modulus (21%) compared to neat MXD6. With more clay addition into MXD6 matrix, both tension strength and young’s modulus decrease.

If one compares tensile properties of MXD6 nanocomposites with PET nanocomposites, neither of them gives significant improvements on Young’s Modulus. The results obtained from this study were close to the values in the article. It is pointed out tensile modulus increased by 30% at 5 wt% clay in twin screw extruder. This is different from the original expectation that the well dispersed structure would double the tensile properties, as shown in the literature. The reason for this may due to weak interfacial interaction force between the Na-MMT and polymer matrix.

Table 5.10 Tensile properties of MXD6/Na-MMT nanocomposite

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tension Strength (MPa)</th>
<th>Strain at Break (%)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MXD6</td>
<td>69.3</td>
<td>6±0.3</td>
<td>1111</td>
</tr>
<tr>
<td>2 wt% MXD6/Na-MMT</td>
<td>79.0</td>
<td>7±0.5</td>
<td>1349</td>
</tr>
<tr>
<td>3 wt% MXD6/Na-MMT</td>
<td>70.1</td>
<td>7±0.6</td>
<td>1310</td>
</tr>
<tr>
<td>5 wt% MXD6/Na-MMT</td>
<td>66.5</td>
<td>7±0.5</td>
<td>1242</td>
</tr>
</tbody>
</table>
5.3.3. DMA analysis on PET/Na-MMT nanocomposite

Figure 5-20 shows the dynamic mechanical spectra (storage modulus) as a function of temperature for PET nanocomposites with different clay loading. The values of storage modulus and $T_g$ are presented in Tables 5.11 and 5.12. As the temperature increases to 30 °C, the first significant improvement is given by 0.5 wt% PET nanocomposite, which is 2640 MPa while neat PET is 1640 MPa. And the storage modulus doubles at 5 wt% PET nanocomposite, which is 3240 MPa.

The glass transition temperatures $T_g$ of the PET nanocomposites were obtained from the peak of the loss factor curve (Table 5.12). It can be seen from table that the material with 0 wt% clay content shows lower $T_g$, which is 72.6 °C. The nanocomposite with 5 wt% clay content exhibits a $T_g$ of 76.7 °C. As the clay loading increases, the $T_g$ shifts to higher temperatures.

![DMA](image)

Figure 5-20 Storage modulus curves of PET/Na-MMT nanocomposite vs. temperature
Table 5.11 Storage modulus (at 30 °C) of PET/Na-MMT nanocomposite vs. temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1639.9</td>
</tr>
<tr>
<td>0.5 wt% PET/Na-MMT</td>
<td>2638.1</td>
</tr>
<tr>
<td>1 wt% PET/Na-MMT</td>
<td>2846.8</td>
</tr>
<tr>
<td>2 wt% PET/Na-MMT</td>
<td>2594.1</td>
</tr>
<tr>
<td>3 wt% PET/Na-MMT</td>
<td>2799.0</td>
</tr>
<tr>
<td>5 wt% PET/Na-MMT</td>
<td>3239.4</td>
</tr>
</tbody>
</table>

Table 5.12 $T_g$ of PET/Na-MMT nanocomposite at peak of tan δ

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>72.6</td>
</tr>
<tr>
<td>0.5 wt% PET/Na-MMT</td>
<td>74.2</td>
</tr>
<tr>
<td>1 wt% PET/Na-MMT</td>
<td>76.0</td>
</tr>
<tr>
<td>2 wt% PET/Na-MMT</td>
<td>75.2</td>
</tr>
<tr>
<td>3 wt% PET/Na-MMT</td>
<td>74.9</td>
</tr>
<tr>
<td>5 wt% PET/Na-MMT</td>
<td>76.7</td>
</tr>
</tbody>
</table>
5.3.4. DMA analysis on MXD6/Na-MMT nanocomposite

Table 5.13, gives the temperature dependence of the storage modulus of MXD6 and its nanocomposite. The storage modulus decreases with temperature increases, in that temperature range, and there was a sharper decrease near $T_g$. Similar behavior was observed the value of modulus increased with increased clay loading. For the 5 wt% MXD6 nanocomposite, the modulus, which is 6172 MPa, is almost 1.5 times that for neat MXD6.

The dependence of $\tan \delta$ on the temperature is provided the temperature at the peak point corresponds to $T_g$. Compare to neat MXD6, as shown in Table 5.14, the peak of the nanocomposite slightly shifts to a higher temperature, from 78 °C to 81 °C, which means $T_g$ increased with the addition of the clays.
Table 5.13 Storage modulus of MXD6/Na-MMT nanocomposite vs temperature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Storage Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MXD6</td>
<td>4206.6</td>
</tr>
<tr>
<td>2 wt% MXD6/Na-MMT</td>
<td>4418.9</td>
</tr>
<tr>
<td>3 wt% MXD6/Na-MMT</td>
<td>5269.5</td>
</tr>
<tr>
<td>5 wt% MXD6/Na-MMT</td>
<td>6172.5</td>
</tr>
</tbody>
</table>

Table 5.14 $T_g$ of MXD6/Na-MMT nanocomposite at peak of tan δ

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MXD6</td>
<td>78.1</td>
</tr>
<tr>
<td>2 wt% MXD6/Na-MMT</td>
<td>81.2</td>
</tr>
<tr>
<td>3 wt% MXD6/Na-MMT</td>
<td>82.5</td>
</tr>
<tr>
<td>5 wt% MXD6/Na-MMT</td>
<td>81.7</td>
</tr>
</tbody>
</table>
5.4. Barrier Property Improvement

5.4.1. Oxygen barrier of PET/Na-MMT nanocomposite

The gas barrier property is a very important factor for food and beverage packaging. The gas barrier property is evaluated by measuring the oxygen permeability though the PET/Na-MMT nanocomposite films. The PET/Na-MMT resins were melted extruded and then made into thin films of which thickness was about 0.06 mm. The oxygen permeability tests were carried out at 23°C and 45% relative humidity. The results of O₂ permeability are listed in Table 5.15.

Table 5.15 gives the oxygen permeability values for PET and the PET/Na-MMT nanocomposites. It can be seen that the oxygen permeability of PET/Na-MMT decreased with increased clay loading. The largest reduction was observed at 2 wt% PET/Na-MMT, which gave a 52% improvement in its oxygen barrier compared to neat PET resin. The 5 wt% composition only resulted in a reduction about 37%. This difference may have been related to tactoid structures shown in the TEM image. In work described by Frounchi et al. [303], two different organoclays (Closite and Nanolin) were prepared as PET nanocomposites using a melt blending method. The nanolin nanocomposite showed a permeability which is about half that of the pure PET, and the Closite nanocomposite gave a 30% improvement in its barrier property.
Table 5.15 Oxygen permeability values of PET and its nanocomposites

[cc*mil/(100*in²*day*atm)]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Permeability (%) decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>8.7 ± 0.4</td>
</tr>
<tr>
<td>0.5 wt% PET/Na-MMT</td>
<td>6.2 ± 0.3 (28.7%)</td>
</tr>
<tr>
<td>1 wt% PET/Na-MMT</td>
<td>5.1 ± 0.3 (41.4%)</td>
</tr>
<tr>
<td>2 wt% PET/Na-MMT</td>
<td>4.2 ± 0.3 (51.7%)</td>
</tr>
<tr>
<td>3 wt% PET/Na-MMT</td>
<td>5.2 ± 0.4 (40.2%)</td>
</tr>
<tr>
<td>5 wt% PET/Na-MMT</td>
<td>5.5 ± 0.5 (36.8%)</td>
</tr>
</tbody>
</table>

5.4.2. Oxygen barrier of MXD6/Na-MMT nanocomposite

Comparisons of the oxygen permeability (PO₂) values of pure MXD6 and its nanocomposites are given in Table 5.16. The PO₂ value of the pure MXD6 film was 0.512 cc*mil/(100*in²*day*atm) and all the MXD6/Na-MMT nanocomposite had lower PO₂ values than the neat MXD6, indicating improvement in the oxygen barrier properties of MXD6. With 2 wt% clay loading in the MXD6 matrix, PO₂ was decreased to 0.225 cc*mil/(100*in²*day*atm). The highest improvement was achieved with the 3 wt% MXD6/Na-MMT, giving 70% reduction in the PO₂ value. All the results are consistent with the observation obtained from TEM, showing the higher degree of exfoliation. Ammala et al [304] reported effects of different organo-modifiers (Cloisite 30B, 10A and 93A) on oxygen barrier properties of MXD6. They found that the Cloisite 10A additive provided the best oxygen barrier, indicating a reduction of PO₂ of 66% compared to the neat MXD6.
Table 5.16 Oxygen permeability values of MXD6 and its nanocomposites

[cc*mil/(100*in²*day*atm)]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>MXD6</td>
<td>0.512±0.01</td>
</tr>
<tr>
<td>2 wt% MXD6/Na-MMT</td>
<td>0.225±0.03</td>
</tr>
<tr>
<td>3 wt% MXD6/Na-MMT</td>
<td>0.153±0.02</td>
</tr>
<tr>
<td>5 wt% MXD6/Na-MMT</td>
<td>0.160±0.02</td>
</tr>
</tbody>
</table>

Summary of Key Observation:

1. A modified melt blending method is developed to prepare exfoliated nanocomposite in the absence of organic modifiers.
2. The presence of Na-MMT in PET/MXD6 matrix acts as nucleating agent, which accelerates the rate of crystallization.
3. WXRD and TEM indicate that the exfoliated morphology were achieved by using the modified melt blending methods.
4. Mechanical property is enhanced by adding small amount of clay into polymer matrix.
5. PET oxygen barrier is increased by 50% at 2 wt% clay loading. MXD6 oxygen barrier is enhanced by 70% at 3 wt% clay loading.
Chapter 6

Exfoliation Transfer Blends of MXD6/Na-MMT Nanocomposite with PET

In the previous chapters, the PET/Na-MMT and MXD6/Na-MMT nanocomposites prepared by modified melt blending are discussed related to various properties, such as crystallization behavior, clay dispersion, Young’s modulus, and oxygen barrier properties. The results reveal that the improvement of clay dispersion is obtained in the PET and MXD6 matrices. It is also found that exfoliated morphology is observed in MXD6 nanocomposites and low clay content PET nanocomposites. There is dramatical reduction on oxygen permeability of PET nanocomposite at 2 wt % clay.

Since it has been recognized that both PET/MXD6 blends and PET/Na-MMT, MXD6/Na-MMT nanocomposites have given good results in terms of the barrier properties, and the use of polyamide blended with PET has been demonstrated to improve the barrier properties considerably with a loading of 5 wt%. The most effective materials of the polyamides investigated were clearly MXD6 which resulted in a barrier improvement of ~1.9 cc*mil/(100*in²*day*atm). Previous work in chapter 5 revealed that MMT was better dispersed in MXD6 then in PET. Therefore, the aim of the section is to combine these two approaches, thus developing a PET/MXD6- Na-MMT nanocomposite with low oxygen permeability by transferring well dispersedMXD6/Na-
MMT into PET. Particular attention has been paid to the relationship between nanostructure and mechanical, oxygen barrier property improvements.

6.1. Preparation process & conditions

As discussed in chapter four, PET/MXD6-Na-MMT nanocomposites were prepared by using modified melt blending. First of all, a clay slurry was added into the twin screw extruder to be blended with melted MXD6 at a temperature of 280 °C. Two kinds of MXD6 nanocomposites were produced which contained 5 wt% as well as 10 wt% Na-MMT. A final approach was undertaken when 5 wt% MXD6/Na-MMT and 10 wt% MXD6/Na-MMT were extruded with PET resin to produce PET/MXD6-Na-MMT nanocomposites as an addition step. After extrusion, all the materials were dried at 140 °C for 12 hrs before further processing or characterization.

The nanocomposite can be added to virgin PET in the correct ratio and the compositions of the nanocomposites are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PET (wt %)</th>
<th>MXD6 (wt %)</th>
<th>Na-MMT (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/MXD6-Na-MMT&lt;sup&gt;1&lt;/sup&gt; (0.5 wt%)</td>
<td>90</td>
<td>9.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PET/MXD6-Na-MMT&lt;sup&gt;2&lt;/sup&gt; (1 wt%)</td>
<td>90</td>
<td>9</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.1 The composition of PET/MXD6-MMT.

(1 indicates 5 wt% MXD6/Na-MMT, 2 indicates the 10 wt% MXD6/Na-MMT)
6.2. Morphological characterization of PET/MXD6-MMT nanocomposites

Followed the routine analysis methods described in chapter 5, the PET/MXD6-MMT (0.5, and 1 wt%) nanocomposites were studied by XRD and TEM, in order to observe the morphological structure of MXD6 in PET, and Na-MMT in MXD6/PET blends.

The XRD pattern was obtained only for 10 wt% MXD6/Na-MMT and PET/MXD6-MMT (1 wt%) in current work since it was previously evaluated for 5 wt% MXD6/Na-MMT in the chapter. As seen in Figure 6-1, the XRD spectrum shows there is no appearance of a diffraction peak for 10 wt% MXD6/Na-MMT nanocomposite. The result for PET/MXD6-MMT nanocomposite (1 wt%) given in Figure 6-2 is similar. It is expected that intercalation or exfoliation of the clay has been achieved in these samples.

Further investigations were carried out by TEM, which was used to evaluate nanocomposite blend structures, showing phase separation of matrix, clay dispersion, and the presence of clusters. The TEM image of the PET/MXD6 matrix (Figure 6-3) gives the isolated domains of the MXD6 phase dispersed into the PET phase. It is observed that the blend had spherical or slightly ellipsoidal MXD6 particles dispersed in the continuous PET matrix. The MXD6 domains range from 0.1 to 0.4 µm in diameter. This result is consistent with other research on PET/MXD6 blends.

Since both the dimensions and dispersion of these domains as well as clay layers have a role to improve barrier properties, both these features have been analyzed by TEM for all nanocomposite blends prepared. For 10 wt% MXD6/Na-MMT nanocomposite, shown in Figure 6-4, the dark line in the figure represents MMT clay sheet having 1 nm thickness and 100 nm aspect ratio. Also, some agglomerated clay particles were detected
which gives mostly like interaction structure. Compared with this TEM analysis, the 5 wt% MXD6/Na-MMT nanocomposite reveals higher exfoliation levels than 10 wt% clay addition in MXD6 matrix.

The PET/MXD6-Na-MMT (1 wt%) nanocomposite prepared from 10 wt% MXD6 nanocomposite was studied by TEM. As shown in the Figure 6-6 and Figure 6-7, it was found that there are two kinds of morphologies present. Figure 6-7 shows a preferential dispersion of clay into MXD6 domain instead of PET continuous phase. The clay seems to be mainly intercalated although some small tactoids can be seen. In another side, few clay diffuse from MXD6 into PET matrix, as evident in Figure 6-5. This may be due to the higher affinity of clay toward MXD6 indeed, when clay is dispersed first in MXD6, the diffusion of clay towards PET phase during the second step of melt blending is hindered by the low affinity of clay towards PET itself. In summary, it seems that an important feature in processing of polymer nanocomposites blends is first dispersing clay in the low-affinity phase, since, in the second step, due to the better thermodynamic interactions, clay tends to diffuse easily toward the higher affinity phase.

Considering that the 5 wt% MXD6/Na-MMT nanocomposite provides better exfoliated structure than that of 10 wt% MXD6/Na-MMT, PET/MXD6-MMT (0.5 wt%) nanocomposite was prepared by 5 wt% MXD6/Na-MMT nanocomposite in order to compared with the PET/MXD6-MMT nanocomposite (1 wt%). In the Figure 6-6, it clearly shows the higher dispersion level and better morphological structure that that of PET/MXD6-MMT nanocomposite (1 wt%).
Figure 6-1 XRD Patterns of MXD6/Na-MMT nanocomposites (10 wt%)
Figure 6-2 XRD Patterns of PET/MXD6-MMT nanocomposites (1 wt)
Figure 6-3 TEM Image of PET/MXD6 Nanocomposite
Figure 6-4 TEM Image of 10 wt% MXD6/Na-MMT Nanocomposite.
Figure 6-5 TEM Image of PET/MXD6-MMT Nanocomposite (0.5 wt%) (PET domain)
Figure 6.6 TEM Image of PET/MXD6-MMT Nanocomposite (0.5 wt%)
Figure 6-7: TEM Image of PET/MXD6-MMT Nanocomposite (1 wt%)
6.3. Tensile Property Improvement

The tensile properties for PET/MXD6-Na-MMT nanocomposites are listed in Table 6.2. It was observed that by blending MXD6 nanocomposites with PET, there is an improvement of the mechanical properties in relationship to those of virgin PET. For all the samples, the MXD6 nanocomposite content is 10% by weight. Therefore, the only difference between two kinds of PET/MXD6-Na-MMT is the utility of MXD6/Na-MMT nanocomposite (5 wt%) or MXD6/Na-MMT nanocomposite (10 wt%).

As seen in Table 6.2, both PET/MXD6-Na-MMT nanocomposites indicates the better mechanical properties than that of PET. However, the maximum improvement was achieved in the case of PET/MXD6-Na-MMT (0.5 wt%), which was prepared by blending with high exfoliated 5 wt% MXD6/Na-MMT nanocomposite. It reveals that the tensile strength is increased to 62.8 MPa, which is a 25.6% improvement and the Young’s modulus is improved by 38.7% (Figure 6-8). Based on these results, it claims that the mechanical properties of the PET/MXD6-Na-MMT are directly related to the morphology of the MXD6/Na-MMT nanocomposite. As mentioned, 5 wt% MXD6/Na-MMT showed better exfoliated morphology than the 10 wt% MXD6/Na-MMT nanocomposite. Therefore, the PET/MXD6-Na-MMT (0.5 wt%) gives better mechanical properties even with lower MMT content. It is expected that the mechanical property data is consistent with what is seen in TEM analysis.
Table 6.2 Tensile properties of PET/MXD6-MMT nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tension Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>50.0</td>
<td>914.0</td>
</tr>
<tr>
<td>PET/MXD6 (10 wt %)</td>
<td>56.2</td>
<td>949.3</td>
</tr>
<tr>
<td>PET/MXD6-Na-MMT (0.5wt %)</td>
<td>62.8</td>
<td>1267.9</td>
</tr>
<tr>
<td>PET/MXD6-Na-MMT (1 wt %)</td>
<td>59.4</td>
<td>1018.2</td>
</tr>
</tbody>
</table>

Figure 6-8 Young’s modulus of PET/MXD6-MMT nanocomposite

6.4. Oxygen barrier property of PET/MXD6-MMT nanocomposite

The effect on barrier properties arising from PET/MXD6-Na-MMT nanocomposite is evaluated by O₂ permeability evaluations. Comparison of the different clay loading in the PET/MXD6 blends has been carried out, as reported in Table 6.3.

The oxygen permeability value of PET obtained here is 8.7 cc*mil/(100*in²*day*atm). Known improvements are given by blending 10 wt% MXD6
into PET, owing to the high barrier properties of MXD6 itself. The result obtained for PET/MXD6 blend is similar to those reported in the literature for unoriented film. Addition of clay to PET/MXD6 blend results in a further reduction of the oxygen permeability constant by about 20-30%. The PET/MXD6-Na-MMT (0.5 wt%) nanocomposite and 1.67 cc*mil/(100*in²*day*atm) for the PET/MXD6-Na-MMT (1 wt%) nanocomposite have been calculated. From the results it is clear that the PET/MXD6-MMT nanocomposite considerably improves the oxygen barrier compared to the PET control. According to the TEM analysis, the clay has remained incorporated in the MXD6 domain due to low levels of ester-amide interchange, which indicates the improved barrier properties are predominantly due to the presence of the polyamide and the clay has little influence. Additionally, it is found that the oxygen barrier is directly related to nanocomposite morphological structure, this is shown by the fact that the PET/MXD6-Na-MMT (0.5 wt%), which shows better exfoliated nanostructure, gives the most improvement on oxygen barrier properties.

The variations of the PET/MXD6-MMT (0.5 wt%) and PET/MXD6-MMT (1 wt%) are related to the different degree of intercalation and distribution of the clay in polymer matrix. When the clay is more homogeneously distributed between the two polymeric phases and more exfoliated, the permeability is lower.

Finally, regarding optical transparency, which is a very important property for barrier applications: all filled samples show low yellowness, due to the clay impurities, although they still transparent.

As a conclusion, both mechanical and barrier properties of nanocomposites are determined mostly based on the level of mixing morphology in the blends.
Table 6.3 Barrier properties of PET/MXD6-MMT nanocomposite

[cc*mil/(100*in²*day*atm)]

<table>
<thead>
<tr>
<th>Samples</th>
<th>Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>8.70 ± 0.4</td>
</tr>
<tr>
<td>PET/MXD6-MMT (0.5wt %)</td>
<td>0.91 ± 0.02</td>
</tr>
<tr>
<td>PET/MXD6-MMT (1 wt %)</td>
<td>1.67 ± 0.16</td>
</tr>
</tbody>
</table>

Summary of Key Observation:

1. It is assumed that by blending pre-exfoliated MXD6 based nanocomposites, transfer of exfoliated clay platelets into the PET matrix can be achieved. However, TEM indicates majority clay stay inside the MXD6 domain.

2. 5 wt% MXD6 nanocomposites gives high degree exfoliation than 10 w% MXD6 nanocomposites.

3. 37% and 87% improvements were achieved for Young’s modulus and oxygen barrier of PET/MXD6-MMT. (0.5 wt%)

4. Experimental results strongly indicate that the morphology structure plays important role on property enhancement.
Chapter 7

Properties of Oriented PET Nanocomposites

It has been shown that the orientation can strongly influence the morphology of layered silicate nanocomposites and thus influence the mechanical, and barrier properties. Previous work was carried out by Ansari [305-306] to develop a model for the stress-strain behavior of bottle grade PET by performing a series of biaxial stretching experiments. This model was developed considering two important characteristics of the stress-strain curve, namely yield stress and strain hardening point. In this work, we attempt to apply this methodology in developing the stress-strain model in order to study the non-linear viscoelastic behavior of PET and its nanocomposites under the orientation processes. In this case, the stress-strain relationship for PET nanocomposites can be obtained by modifying the significant parameters, which can indicate the effects of the nanoparticles in the PET matrix.
7.1. Uniaxial stress-strain relationship for PET/Na-MMT nanocomposite

As shown in Figure 7-1, to obtain a typical stress-strain behavior for stretching PET film, PET is stretching above $T_g$, around 90°C. At first, the stress rises rapidly up to a yield point. Most chain deformation occurs in this region is recoverable. With further elongation, the curve shows a flat region, named strain softening region. In this region, three things usually happen: A. chain alignment B. chain relaxation C. at high strain, when the alignment exceeds the relaxation, the polymer starts to crystallize. The formation the crystals acts as cross-linking. After some point, the materials become stiffer, leading to the strain-induced crystallization, observed by an upswing in the stress-strain curve [305-306].

![Figure 7-1 Typical Stress-strain curve of PET](image-url)
A uniaxial stretch test was conducted using the long extension tester (LET). A stretching specimen (4 in*2 in) were cut from the PET nanocomposite sheet and clamped into the LET. The specimen was then heated for 3 min using a pair of hot-air blowers positioned above and below the specimen so that the heat applied to the specimen was uniform. After 3 min the heating was stopped and uniaxial force was applied to the specimen immediately in order to deform the specimen. The extruded PET nanocomposite sheets were stretched unconstrained to a stretch ratio up to 4. The stretching temperature was 90 °C and the stretched samples had an average thickness of 0.1 mm.

From Figure 7-2, it is clear that the addition of Na-MMT to the PET, even at loading of 1%, has an effect on the strain-hardening behavior leading to much earlier strain hardening and with much higher stress. One explanation is that the presence of Na-MMT in the matrix possibly leads to a greater degree of molecular knotting and entanglement with in turn leads to earlier strain hardening.

The effect of increasing the natural clay content is to increase the stress required to deform the sheet. With different applied extension rates (50%, 150%, 200%), as shown from Figure 7-2 to Figure 7-4, they exhibited differences between stress-strain curves, especially at large applied strains. Hence, although the initial morphology has a relatively minor impact on the small strain behavior, the evolution of morphology can influence the reproducibility of the results at larger strains.
Figure 7-2 stress-strain as a function of different clay loading at T=90°C and extension rate =50%/s, uniaxial extension
Figure 7-3: Stress-strain curve of PET/Na-MMT at different clay loadings at T=90°C and extension rate = 150%/s, uniaxial extension.
Figure 7-4 stress-strain as a function of different clay loading at T=90°C and extension rate =200%/s, uniaxial extension.
7.2. The 4-parameter stress-strain model

After review of several models, it is difficult to find an accurate way to describe the stress-strain behavior of PET at both low and high extension ratios. In the work of Ansari [305-306], a strictly mathematical approach was adopted to find such a model for the stress-strain relationship of PET. Here we attempted to apply and modify this methodology to develop a model for PET/Na-MMT nanocomposite.

As described in the stress-strain curves, four parameters were chosen to build the prediction curve for PET nanocomposites in Ansari’s work [305-306]. A model contains these four parameters can be expressed in the equation 7.1 [305]. \( G \) represents the yield stress, while \( n \) relates to the rate of increase of initial stress levels. The strain hardening point and the slope of the strain hardening region were described as \( H \) and \( S \). After characterization of the modes of orientation, the relationship between the 4 parameters and the factors which affect the stress-strain curve were investigated.

By using the techniques of nonlinear regression and empirical modeling, correlations were developed for each parameter according to the format given in Eq. (7.2-7.5). A statistical software call “Matlab”, was used for the purpose. The correlations developed for the case of uniaxial extension are given below, and \( \lambda \) is extension ratio.

\[
\sigma = G(1 - \frac{1}{\lambda^n}) + 100 \times S[(\lambda - H)\tan^{-1}(\lambda - H) - \frac{1}{2} \log_e (1 + (\lambda - H)^2)]
\]

(7.1)
Table 7.1 The four parameters from stress-strain curve of PET nanocomposite

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th></th>
<th>G</th>
<th></th>
<th>H</th>
<th></th>
<th>S</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50%</td>
<td>150%</td>
<td>200%</td>
<td>50%</td>
<td>150%</td>
<td>200%</td>
<td>50%</td>
<td>150%</td>
</tr>
<tr>
<td>0</td>
<td>3.2</td>
<td>3.4</td>
<td>4.2</td>
<td>125.1</td>
<td>140.1</td>
<td>85.4</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td>1</td>
<td>3.3</td>
<td>3.1</td>
<td>5.1</td>
<td>126.5</td>
<td>167.3</td>
<td>170.8</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
<td>3.3</td>
<td>5.8</td>
<td>121.7</td>
<td>187.7</td>
<td>236.3</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>3.4</td>
<td>6.5</td>
<td>130.1</td>
<td>213.2</td>
<td>308.8</td>
<td>2.8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Uniaxial Extension,

\[ G = 50.76 \times \exp (20 \times w + 0.4 \times (ER - 1.80) + 1) \] \hspace{1cm} \text{Equation 7.2} \\
\[ n = \exp (9.8 \times w + 0.29 \times ER + 0.85) \] \hspace{1cm} \text{Equation 7.3} \\
\[ S = 810.75 \times \exp (-30 \times w - 0.2 \times (ER - 1.99) + 1) \] \hspace{1cm} \text{Equation 7.4} \\
\[ H = 2.41 \times \exp (-6.25 \times w - 0.01 \times ER + 0.35) \] \hspace{1cm} \text{Equation 7.5}

Where: G, n, S and H are the 4-parameters

W is the weight percent of clay in the PET matrix

ER is extension ratio, %/s
Figures 7-5, 7-6, and 7-7 show comparisons between the experimental stress-strain curves and those predicted by the Model. The value of the 4 parameters is obtained using the equation. Each plot in turn has more than one set of data. These figures, therefore, cover a wide range of data. Experimental values and the values obtained by the model are shown in different color and it was found that the curves created by this 4-parameter model fit the experimental curves very well.
Figure 7-5 stress-strain as a function of different clay loading at T=90°C and extension rate =50%/s, uniaxial extension.

Comparison between experimental and model values.
Figure 7. Stress-strain as a function of different clay loading at T=90°C and extension rate = 150%/s, uniaxial extension.

Comparison between experimental and model values.
Figure 7-7 stress-strain as a function of different clay loading at T=90°C and extension rate =200%/s, uniaxial extension.

Comparison between experimental and model values
7.3. Morphology of nanoclay in stretched PET nanocomposites

A brief review of the stretching effect on the clay dispersion has already been summed up in Chapter 6. In this section, we will focus on the effects of different MMT loading and the subsequent stretching on the morphology and the macroscopic properties.

Figure 7-8 and 7-9 show the morphology of PET nanocomposites after uniaxial stretching to a stretch ratio of 4. From TEM images, it can be observed that the nanoclays are more aligned after uniaxial stretching. It is speculated that stretching has pulled and oriented the nanoclay until the platelet can slip past each other. Comparing the exfoliation level found with different clay loading, an increase MMT loading percentage caused increased particles thickness after stretching. The increased thickness after stretching indicates the formation of intercalation or tactoid structures, because it is speculated that at high clay loading, the MMT particles have a greater chance of forming agglomerates with neighboring particles.

The deformation structures reveal developed microvoids, around the exfoliated layers. As shown in Figure 7-8, in the oriented nanocomposite, the microvoids, elongated in the tensile direction, are homogeneously distributed in the whole range of specimen and appear in the range of micrometers; even the larger microvoids can be clearly seen in Figure 7-10.

Formation of microvoids in the nanocomposite is mostly resulted from the interfacial debonding between MMT and polymer matrix or from the delamination of clay aggregates. The surface property of MMT is hydrophilic and polymers are hydrophobic in nature, the applied stress during the stretching process could break the bonding between the surface phase and the polymer matrix because of weak interfacial
interactions. Once microvoiding occurs, similarly, the connectivity of molecular network is in part destroyed due to decreasing physical crosslinks from the clay platelet. As shown in previous studies and references, microvioding sets in around yield point and become more significant in the composites with further straining.
Figure 7-8: TEM Image of uniaxially stretched PET/Na-MMT Nanocomposite (1 wt%)
Figure 7.9 TEM Image of uniaxial stretched PET/Na-MMT Nanocomposite (2 wt%)
Figure 7-10 TEM Image of uniaxial stretched PET/Na-MMT Nanocomposite (Microvoids)
7.4. Demonstration of the formation of microvoids during stretching

7.4.1. Clarity Evaluation

- **Uniaxially Stretched PET/Na-MMT nanocomposite bottle**

Figure 7-11 showed the uniaxially stretched PET and its nanocomposite. From left to right, each represents (A) PET, (B) PET/Na-MMT (1 wt%), (C) PET/Na-MMT (2 wt%), and (D) PET/Na-MMT (3 wt%). Stretched PET was still transparent after stretching, however, this result changes with introduction of the clay into PET. It was found that the samples with clay become hazy compared to PET. The value of haze increases with increased MMT loading in PET. For the 3 wt% PET/Na-MMT nanocomposite, it was observed that the stretched sample was complete opaque.
• **Stretch Blow Molded PET/Na-MMT Nanocomposite Bottle (0.5 wt%)**

In this work, PET performs are made by injection molding of SSP resin and then bottles are produced from the preforms by stretch-blow molding. The crystallinity of PET preforms and bottles has to be controlled in order to get the desired properties. The preform’s body and neck are usually transparent and nearly amorphous, but the injection point is opaque. While a transparent, amorphous performs is sought initially, after stretch blow molding, one aim to get as high a crystallinity as possible in the final bottle, which improves the gas barrier and superior mechanical properties. The final PET bottle is semicrystalline, yet very transparent. The crystallinity in the bottle is not uniform, but is regional- the neck can be amorphous, while the bottle sidewall has the highest crystallinity.

The PET and PET nanocomposite bottles are produced from same conditions during stretching blow molding. Figure 7-12 represents the sidewall from PET/Na-MMT bottles containing 0.5 wt% of clay. Compared with a sidewall from a PET bottles, the sidewall of PET/Na-MMT bottles felt like more stiff and rigid. The color comparison between these two kinds of bottles are shown in Figure 7-13. It can be seen that there is a complete loss of transparency after stretched blow molding process. The orientation process results in the white color for PET/Na-MMT nanocomposites, while PET bottles still give excellent clarity. This disappearance of transparency is due to the formation of the microdomain structures, which causes strong light scattering.
Figure 7-12 Sidewall of PET/Na-MMT bottle (0.5 wt%)
Figure 7-13 Stretched Blow Bottles: left, PET; right, PET/Na-MMT (0.5 wt%)
7.4.2. Density Evaluation

A typical stress-strain behavior for PET involves three major processes: firstly, PET deforms under small amount of strain. In this region PET will relax to its original state if the strain is removed. This is followed by a plateau region, where increasing the strain results in the polymer chain alignment along the stretching direction. The crystals are formed when the polymer chain alignment exceeds the chain relaxation. The presence of crystals acts as cross-linking, which makes the PET chain more stiff and rigid. In the stress strain relationship curve, the strain induced crystallization gives an upswing, which indicates that stress increases rapid with strain. Starting from the formation of crystals, the density of PET increases with increased the stretching ratio.

In this work, PET has a density of 1.33 g/cc and the density of MMT is 2.6 g/cc. Generally, the cast nanocomposite resin density increases with increased the MMT loading and also increased by the larger the extension ratio. From Table 7.2, however, the density has no direct relation in terms of extension ratio. At given extension ratio, the density shows a reduction in terms of increased clay loading. Also, the differences of density between PET and 3 wt% PET nanocomposite is 0.016 g/cc, while this density difference is larger at high extension ratio (λ = 4), which gives a value of 0.026 g/cc. These numbers indicate that increased extension ratio plays a negative role on the density increase of PET nanocomposites. The maximum density reduction occurs at 3 wt% clay loading at extension ratio about 4. This can be explained by the combination of two effects: the decrease in the density due to void forming on the one hand being to a
substract by the increase in the crystallinity of the polyester matrix due to stretching on the other.

From Figure 7-14, it is clearly shown that the density values of PET are directly proportional to the extension ratio. However, for 1 wt% and 2 wt% PET nanocomposite, the density increases until $\lambda = 3.5$, which is stain-hardening point (SHP) of PET, after SHP the density value drops significantly. With high clay loading in PET (3 wt%), the density starts to decrease sooner, which at $\lambda = 3.0$. The final density value is given by crystallization factor and microvoiding factor. Therefore, before strain hardening point, the crystallization factor dominate the result of density which the microvoiding factor dominates after the extension ratio of 3.5, in the case of 1 wt% and 2 wt% PET nanocomposite. For 3 wt% PET nanocomposite, the microvoids factor effect becomes significant after extension of 3.
Table 7.2 Density Measurement (g/cm³) of Oriented PET Nanocomposite (1, 2, 3 wt%)

<table>
<thead>
<tr>
<th></th>
<th>$\lambda=1$</th>
<th>$\lambda=2$</th>
<th>$\lambda=3$</th>
<th>$\lambda=3.5$</th>
<th>$\lambda=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.340</td>
<td>1.345</td>
<td>1.359</td>
<td>1.364</td>
<td>1.372</td>
</tr>
<tr>
<td>SPETC 1 wt</td>
<td>1.333</td>
<td>1.340</td>
<td>1.351</td>
<td>1.363</td>
<td>1.356</td>
</tr>
<tr>
<td>SPETC 2 wt</td>
<td>1.329</td>
<td>1.332</td>
<td>1.346</td>
<td>1.349</td>
<td>1.346</td>
</tr>
<tr>
<td>SPETC 3 wt</td>
<td>1.324</td>
<td>1.324</td>
<td>1.339</td>
<td>1.338</td>
<td>1.336</td>
</tr>
</tbody>
</table>

Figure 7-14 Density Measurement of Oriented PET Nanocomposite (1, 2, 3 wt%)
7.4.3. Properties evaluation on stretch blow PET nanocomposite bottles

- **Mechanical properties of the sidewall of PET nanocomposite bottle**

  The mechanical properties of the bottles made from PET and those of the bottles made from 0.5 wt% PET nanocomposite were measured. The result obtained for Young's modulus and yield stress of axial and hoop direction are shown in Table 7.3.

  There is no improvement on the yield stress and Young's modulus of PET nanocomposite bottles compared with that of pure PET bottles. The date shows that the Young's modulus and yield stress in both axial and hoop directions decreased with the introduction of MMT clay. In Cheng’s work [307], it was concluded that in order to enhance the mechanical properties of PET nanocomposite bottles, an important issue to consider in preparing polymer nanocomposite is polymer-clay affinity, which can be as important as particle dispersion. The complete exfoliation and improved adhesion of clay to PET will provide superior mechanical properties for nanocomposite.
Table 7.3 Mechanical Properties of sidewall of PET Nanocomposite bottle (0.5 wt%)

<table>
<thead>
<tr>
<th></th>
<th>Yield Stress (MPa)</th>
<th>Max Strain (%)</th>
<th>Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET bottle (axial)</td>
<td>80.2</td>
<td>161.6</td>
<td>1385.0</td>
</tr>
<tr>
<td>PET bottle (hoop)</td>
<td>170.0</td>
<td>21.0</td>
<td>2683.0</td>
</tr>
<tr>
<td>PETC 0.5 bottle (axial)</td>
<td>78.6</td>
<td>214.4</td>
<td>1302.8</td>
</tr>
<tr>
<td>PETC 0.5 bottle (hoop)</td>
<td>148.0</td>
<td>64.6</td>
<td>2465.2</td>
</tr>
</tbody>
</table>

- **Oxygen barrier of sidewall of PET nanocomposite**

The barrier properties of packaging materials are critical in determining the shelf life of the contained products. In the chapter 5, it is discussed that by introducing Na-MMT clay into a PET matrix the barrier properties of PET nanocomposite are given 50% enhancement. Increasing the clay loading in PET lowers the oxygen permeability. Several studies showed the result stretch blow molded PET bottles gave lower oxygen permeability than that of the non-oriented PET films. This work was been utilized to evaluate whether these is an improvement by on oxygen barrier property by applying the orientation.

The oxygen permeability values of the 2-liter bottles made from PET/Na-MMT nanocomposite (0.5 wt%) are collected in the Table 7.5. It is seen that the oxygen permeability of stretch blow molded PET bottle is 50% lower than that of unstretched PET films. With the introduction of 0.5 wt% clay into PET, there is a 26% enhancement in oxygen barrier properties. However, there is no difference in the oxygen barrier properties between stretch blow molded PET bottles and stretch blow molded PET
nanocomposite bottles. These two kinds of bottles give oxygen permeability values of 4.2 cc*mil/(100*in²*day*atm) and 4.1 cc*mil/(100*in²*day*atm) respectively, as seen in the Figure 7-15.

As know, a good adhesion between the matrix and the silica is evident as no voids are present. Indeed, when the adhesion between the filler and the matrix is poor, the fragile fracture creates typical fracture at the borderline of the filler aggregates and some holes, due to the detaching of the unembedded particles are created. These holes will allow the gas to defuse through the PET matrix easily and thus provide a negative effect on oxygen barrier property.

Summary of Key Observation:

1. The incorporation of MMT into PET enhances the modulus, particular above the glass transition temperature, and results the strain hardening occur earlier.

2. Computational model tool is successful developed enable the prediction of the effect of processing parameters on mechanical properties of PET nanocomposite.

3. Microvoids were generated during stretching due to the weak interfacial attraction between MMT and polymer.

4. For the stretched blown PET bottles, the strain-induced crystallization causes the enhanced oxygen barrier property for PET. However, the presence of voids results less improvements between PET bottle and PET nanocomposite bottles.
Table 7.4 Density Measurement of the sidewall of PET Nanocomposite bottle

<table>
<thead>
<tr>
<th></th>
<th>PET resin</th>
<th>PET bottle</th>
<th>0.5 wt% PET Nanocomposite</th>
<th>0.5 wt% PET bottle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cc)</td>
<td>1.340</td>
<td>1.3675</td>
<td>1.3413</td>
<td>1.3670</td>
</tr>
<tr>
<td>Actual 0.42 wt%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modified Density (g/cc)</td>
<td></td>
<td></td>
<td>1.3360</td>
<td>1.3618</td>
</tr>
</tbody>
</table>

Table 7.5 Oxygen permeability of PET Nanocomposite Bottle (0.5 wt%)

<table>
<thead>
<tr>
<th></th>
<th>Permeability (cc.mil/100 in². atm.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PET</td>
</tr>
<tr>
<td>films</td>
<td>8.7</td>
</tr>
<tr>
<td>Stretch blow bottles</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Figure 7-15 Oxygen Barrier of PET nanocomposite and its bottles (0.5 wt%)
Chapter 8

Conclusion & Future Work Recommendation

8.1. Conclusion

A novel processing technology was developed to prepare exfoliated PET/Na-MMT, MXD6/Na-MMT and PET/MXD6-Na-MMT nanocomposites in this research. The effect of Na-MMT on thermal properties, morphological structure, mechanical and barrier properties of PET and MXD6 were studied separately. Additionally, a numerical model was developed for stretching PET/Na-MMT nanocomposite in order to predicate the strain hardening behavior of PET nanocomposite under different extension ratio during uniaxial stretch process. For the final product PET/MXD6-MMT nanocomposite, morphology of Na-MMT in PET/MXD6 blends, mechanical properties and oxygen barrier properties were also investigated in this research.

With the purpose of preparing exfoliated nanostructure in the absence of organic modifiers, the hydrophilic nature of Na-MMT allow it to be exfoliated in water to form a clay dispersion. Then melt blending of PET with MXD6 nanocomposite containing different clay loading were performed in twin screw extruder separately. The clay from
the clay slurry would be fixed into the melted polymer chains as it was exfoliated in the water in the extruder, which helps to exfoliate the clay into PET and MXD6 during the melt blending process.

Wide angle X-ray diffraction (WXRD) and transmission electron microscopy (TEM) were used as indicators of the extent of the dispersion state of clay platelets within each polymer matrix. The micrographs of PET/Na-MMT nanocomposites as well as MXD6/Na-MMT nanocomposites, reveal well exfoliated structures in both materials. The 5 wt% MXD6/Na-MMT nanocomposites and 5 wt% PET/Na-MMT nanocomposites, however, show a mixture of morphologies, which is a combination of smaller partial intercalation and exfoliation. These studies strongly indicate that the WXRD needs to be combined with TEM on the morphology study of polymer nanocomposite.

All of the nanocomposite samples (PET/Na-MMT, MXD6/Na-MMT) were subjected to thermal analysis by differential scanning calorimeter (DSC). It was found out that the introduction of Na-MMT hinders the mobility of polymer chains, which results in slight increases of the glass transition temperature. In addition, the presence of Na-MMT in the PET or MXD6 matrix acts as a nucleating agent, which accelerates the rate of crystallization. Among the nanocomposites with different weight percent of Na-MMT, no significant differences in crystallization behavior based on the exfoliation morphological structure was achieved for the polymer nanocomposites.

Tensile tests show that the maximum improvement in Young’s modulus is around 24% at 2 wt% clay addition in PET and 21% at 2 wt% MXD6 nanocomposite. The polymer becomes brittle due to the presence of Na-MMT. DMA data showed that the
storage modulus doubled at 5 wt% clay addition in the case of PET/Na-MMT nanocomposites, and was 1.5 times larger than recorded for neat MXD6. Moreover, it is observed that PET nanocomposites had a lower permeability value than that of the pure PET. When introducing 2 wt% Na-MMT into a PET matrix, the value of permeability dropped to 4.2 cc*mil/(100*in²*day*atm) with decreasing to 52%. And for MXD6/Na-MMT nanocomposite, optimum oxygen barrier was given by 3 wt% clay loading, showing 70% enhancement. Therefore, it is conclude that nanocomposites showed better oxygen barrier properties compared to neat PET by using a modified melt blending method.

It has been studied that the orientation can strongly influence the morphology of layered silicate nanocomposite and thus influence their mechanical, and barrier properties. In the presence of Na-MMT in PET, strain hardening occurs sooner than in pure PET during uniaxial orientation. In order to describe the stress-strain behavior of PET nanocomposite under uniaxial stretching, a computational model was successfully developed to enable the prediction the effect of clay loading and varies extension ratio on the mechanical properties. For the biaxially stretched blown PET bottles, the strain-induced crystallization resulted in an the enhanced oxygen barrier property for PET. The presence of voids, however, gave less improvement between PET and PET nanocomposite bottles.

When the exfoliated MXD6 nanocomposite was transferred into a PET matrix, it was found that the majority of the clay remained to stay inside the MXD6 domain. Meanwhile, 37% and 87% improvements were achieved for Young’s modulus and the
oxygen barrier of PET/MXD6-MMT. These were obtained for the 5 wt% MXD6 nanocomposite blended with PET, which shows high degree of exfoliation, and indicates that morphology structure plays a significant role on property enhancement.

For extruded films and sheets of PET/Na-MMT, MXD6/Na-MMT nanocomposites, exfoliated nanostructure was found to enhance the oxygen barrier properties. This improvement, however, was not shown when we try to study the mechanical properties in the tensile test. A common feature of all polymer composites is the existence of an interface between the matrix and filler, where the properties can differ dramatically from the bulk and influence the mechanical properties of the nanocomposite. The exfoliated polymer nanocomposite with weak interfacial property would lead to a lower level of enhancement for mechanical properties. The consequence of this poor interfacial property for the orientation PET/Na-MMT nanocomposite results into the phase separation, which creates the micro-voids in the polymer clay nanostructure. These micro-voids defects remove the advantage of increased the tortuous path obtained from clay addition, thus limits the oxygen barrier property for stretched blown bottles.

In conclusion, PET/Na-MMT nanocomposites prepared by modified melt blending technology could be applied for extruded films/sheet, or any product without orientation, for example, extrusion blown molded products. The compatibility between the organic polymer and silica has a great effect on the mechanical properties and oxygen barrier properties of PET. In order to achieve optimum property enhancement of oriented PET, this high adhesion strength and good clay dispersion need to be present in the PET nanocomposite system.
8.2. Summary and Future Work Recommendation

**Summary:**

PET nanocomposites consisting of nanometer-sized materials in PET matrix have been shown to exhibit improved gas barrier characteristics and mechanical properties. The benefits of PET nanocomposites as a packaging material have been well investigated in the previous work, including PET/OMMT nanocomposite as well as PET/Na-MMT nanocomposite by using melt blending and in situ polymerization.

Ideally, the nano-material particle should have a high aspect ratio (length/thickness) to provide significant enhancements in mechanical and barrier properties. To achieve maximum compatibility with organic PET polyester, the surfaces of the individual nanoclay are mostly organically modified by using organic surface cations (alkyl ammonium or alkyl phosphonium). In addition to rendering the surface hydrophobic, the surface treatment can expand the spacing between the layers, further facilitating penetration of the PET and individual nanoclay. The previous work revealed that the high compatibility of organic modified clay leads to a higher exfoliation dispersion in PET compared to that of natural nanoclay. The issue in previous study is caused by the decomposition of the organic modifier from modified nanoclay at high processing temperature, creating a possibility of re-agglomeration of nanoclay.

Another nanotechnology was selected in the previous work is to prepare PET/Na-MMT using in situ polymerization. Natural Na-MMT was chosen in the study in order to avoid the thermal degradation of clay in melt phase polymerization process. Nanoclay is
mixed with monomer reactant then following by esterification and polycondensation reactions. The dispersed clay in monomer reactant step results in the formation of intercalation morphology, but limited with only low clay addition (0.5 wt%).

A novel method have been developed in this study to continue the previous work on PET nanocomposite. Clay slurry is prepared while the clay is fully exfoliated in the water, then the exfoliated clay platelet is fixed into melted polymer matrix using melt blending technology. This novel method effectively prepares the exfoliated PET nanocomposite, with the indications from XRD, TEM studies. Also, exfoliated PET nanocomposites have shown to exhibit significant enhancement on PET barrier indicated by oxygen permeation test. The poor interfacial interaction between clay and PET substracts the benefits which could be obtained from the oriented PET nanocomposite. The formation of microvoids observed in the stretching process not only reduces the mechanical and barrier properties compared with that of pure PET, but also gives a total opaque PET nanocomposite bottles.

This modified melt blending technology can be applied to produce PET nanocomposite with excellent mechanical and barrier properties, which is a potential packaging usage. Since the orientation could result in a poor properties materials compared with non-oriented PET nanocomposite. Therefore, PET nanocomposite in this study is suggested to be applied in extrusion blow molded containers, and films. A further study need to be carried out base on the improvement of compatibility of PET and natural clay, in a way to provide the possibilities that PET nanocomposite will be excellent packaging materials for oriented sheets/film, and stretching blow molded bottles.
Future Work Recommendation:

In order to improve the compatibility between clay and PET, coupling agents have been used to modify the clay. Rather than using modified clay, a second approach is to modify the polymer before preparing the polymer clay nanocomposite. PET ionomer could be used to enhance the polarity of the polymer and hence improve compatibility with the clay surfaces.

Alternatively, AQ55 polyester ionomer from Eastman Chemical Company has been studied in polymer nanocomposite research. It has been demonstrated that the compatibility of PET with clay can be considerably improved by the incorporation of small qualities of these ionomer moieties and the dispersion improves further as the ionomer content increases. These improvements can be obtained with various organo-clays and even unmodified sodium clay.

My recommendations for the further research on PET/Na-MMT nanocomposite are summarized as follows:

- PET ionomer should be synthesized by replacing a small quality of terephthalic acid with sulfoisophthalic acid to yield copolymers with ionic content. Modified/unmodified clay could be introduced into the reactor to prepare the PET nanocomposite with different clay loading.
- AQ55 polyester ionomer should be dispersed in water after preparing the clay slurry. In the solution, the well dispersed clay will be coated with AQ55 ionomer. This mixture then could be pumped into the extruder when the PET is fed into the
hopper. PET nanocomposite could be prepared after removing the water from extruder during this melt blending process.

- Also, AQ55 polyester ionomer could be dispersed in water after preparing the clay slurry. Then the solution could be poured onto PET and the water removed by mechanical agitation and heat to leave coated PET pellets. Finally, polymer nanocomposite could be processed using conventional melt processing techniques.
References


PET/MXD6 blends by modifying PET with isophthalate. *Polymer, 46*, 5202-5210.
(ethylene terephthalate) by incorporating isophthalate. I. Effect of orientation. *Journal of
[86] Hernandez, R. J. (2004). Plastics packaging- properties, processing, applications and
of biaxially stretched engineering thermoplastics with emphasis on PET, a book chapter
in “film processing”. *Progress in Polymer Processing Series, 8, Hanser Publishers*.
oriented polyimide 12 films. *Journal of Polymer Science B Polymer Physics, 40*, 1189-
1200.
modelling of polymer film orientation processes. *Chemical Engineering Research and
Design, 76*, 38-44.
role of in-plane crystalline orientation distribution on the film properties. *Journal of
Applied Polymer Science, 48, 1635-1648.


[99] Boykin, T. L.; and Moore, R. B. (1998). The role of specific interactions and transreactions on the compatibility of polyester ionomers with poly (ethylene terephthalate) and nylon 6, 6. Polymer Engineering & Science, 38, 1658-1665.

terephthalate)/polyamide-6 alloys: mechanical, thermal and morphology characterization. *Polymer, 40*, 4811-4819.


Fibers by In Situ Polymerization: The Thermomechanical Properties and Morphology.  
*Journal of Applied Polymer Science, 98, 2009-2016.*


and mechanical properties on gas permeability. *Polymer, 41, 5461-5470.*


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