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TITANATE AND SILANE COUPLING AGENTS BASED SURFACE MODIFICATION OF CLAY AND THEIR EFECTS ON THE PERFORMANCE OF POLY(TRIMETHYLENE TEREPHTHALATE) NANOCOMPOSITES

By

Dhiraj Hasija

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Submitted to
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2008

ABSTRACT

TITANATE AND SILANE COUPLING AGENTS BASED SURFACE MODIFICATION OF CLAY AND THEIR EFFECTS ON THE PERFORMANCE OF POLY(TRIMETHYLENE TEREPHTHALATE) NANOCOMPOSITES

By

Dhiraj Hasija

In this study, titanate and silane coupling agents modified montmorillonite clay was embedded in PTT, poly(trimethylene terephthalate) through a melt processing technique to study the effect of such chemical modification of clay on the mechanical, thermo-mechanical and barrier properties of PTT clay nanocomposites. PTT (trade name Sorona® from DuPont) is an engineering polymer, which can be partially derived from biomass. Montmorillonite clay was organically modified with a titanate based coupling agent and a silane coupling agent and were characterized by different analytical techniques, which validated the successful modification of montmorillonite clay. In this study, petroleum-based Sorona® was used. The outcome of this study can be applied to biobased Sorona®. The tensile modulus, storage modulus and heat deflection temperature (HDT) of PTT were improved through organo-clay reinforcements. Extruded cast film of neat PTT had low percent elongation while PTT-clay nanocomposites showed quite ductile behavior with no break. The barrier properties of PTT film were also investigated in extruded cast film nanocomposites. The PTT/titanate modified clay nanocomposite film was characterized through transmission electron microscopy (TEM) and polarized light optical microscopy (PLOM).

Dedicated to my family and friends

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

After invention of plastics during 19th century and a rapid growth in last century, plastics have become the most versatile materials ever developed in history of mankind. Plastics are the major contributor for modern society in various fields. Plastics can be seen anywhere such as automobile industry, aircrafts, packaging, computers, grocery bags and so many. Major contribution of plastics is manufactured for packaging industry most because of their wide range of properties, ease of processing and their versatility. Plastic has become prevalent because these are affordable and can be engineered with a wide range of properties. Plastics can be tailored for various uses, such as high-density polyethylene for milk bottles, low-density polyethylene for plastic bags, polyethylene terephthalate for soda and water bottles, polypropylene for ketchup bottles, expandable polystyrene for egg crates, and polyvinyl chloride for water pipes. Plastics can be molded into variety of shapes and sizes including complicated small parts, and can be drawn into thin fibers. Plastics are strong but lightweight, resistant to being degraded by chemicals, sunlight, and bacteria, and are thermally and electrically insulating. Plastics that can be remolded again and again are called thermoplastics, which contribute a major part in packaging. In this study we will be discussing thermoplastics, which are termed as plastics everywhere in this study. Plastics have become a critical material in the modern economy, especially in packaging industry. Plastics can be shaped into thin

flexible films as well as rigid bottles. In earlier stage plastics were developed as synthetic substitutes for natural materials, such as rubber, which were once widely used for consumer goods. Most of the plastics, which are used, are non-biodegradable in nature, which means they remain persistent for long time. The non-biodegradable nature of conventional polymers and dwindling petroleum resources are driving forces for extensive research and development in the field of biobased polymers and their applications. Bio-based and biodegradable polymers can substitute these conventional polymers and can help in building an environment friendly world [1-4].

Most of the commercially available plastics are conventional petroleum derived plastics. Conventional petroleum poses certain environmental challenges because of their non-biodegradable nature and problems related to disposability. These conventional petroleum based plastics are widely used in packaging and other industries by virtue of their good properties but these are not friendly to environment because they are non-biodegradable. This means that these plastics don't degrade for years. Plastics play a dominant role in the packaging applications. Most of the commercially available plastics are non-biodegradable in nature. In the present scenario, conventional plastics are suffering from higher resin cost, depleting resources and disposing problems. The incineration of plastic wastes poses environmental concerns by adding green house gases to our atmosphere. For these reasons there is lot of thrust on the development of sustainable, environmentally benign and biodegradable polymers. Biodegradable

polymers are emerging as promising alternatives to conventional polymers. Most of the biodegradable plastics are produced in batch process. It is a challenge to find new as well as emerging applications of such biodegradable polymers that would demand high volume production. The increase in their production volume can bring down the cost of biodegradable polymers. Biodegradable polymers are designed to be stable in their intended lifetime and decompose under composting conditions. Materials made from renewable resources are attaining augmented importance as world-leading industries and manufacturers seek to replace dwindling petrochemical-based feedstock with agricultural and biomass based materials. The best examples of biopolymers derived from renewable resources are polylactides, polyhydroxyalkanoates, cellulosic plastics and starch plastics.

To develop a bio-polymer from 100% renewable resources is highly desirable, however, the cost - performance attributes are also major criteria to take into account when applying biopolymers to real world applications. It may not be desirable to have new materials derived completely from renewable resources or from biomass if they show inferior performance. To find new materials containing the maximum permissible content of bio-derived materials while still maintaining cost-performance attributes is quite challenging as well as rewarding. One of the best examples of such a 'green' polymer is poly(trimethylene terephthalate) (PTT), DuPont's Sorona®. Biobased PTT is an example of polymer, which can be partially derived from biomass. DuPont has discovered an alternate synthesis of 1,3- propanediol (PDO), which is one of the

raw materials for PTT that can be derived from corn. In petroleum-based PTT both of the raw materials, 1,3 propanediol and terephthalic acid are made from petroleum resources. Because they have the same chemical structure, petroleum-based and biobased PTT are expected to exhibit similar properties with that of biobased Sorona®. DuPont received the 2003 Presidential Green Chemistry Challenge Award for biobased Sorona®. This polymer has potential uses as fibers, films and as an engineering resin [5-7].

Conventional fillers such as minerals, metals, and fibers have been added to polymers for decades to produce composites with improved mechanical and thermal properties. High-aspect ratio nano-fillers also provide improvements in barrier performance and clarity without a significant increase in density, which is not feasible with conventional composites. The advantage of nanocomposites over macro composites is that low level of nanoparticle (2-5 wt%) is needed to enhance the properties of matrix as compared to 30-50 wt% of macro sized fillers such as glass & wood fibers. This is because of exceptionally high aspect ratio that is length/diameter of nano-sized fillers as compared to macro-sized fillers [8-12].

The development of polymer/clay nanocomposites (PCN) is one of the latest evolutionary steps in polymer technology. Nanocomposites offer the potential for the diversification and application of polymers due to their excellent properties such as high heat distortion temperature, dimensional stability,

improved barrier properties, flame retardancy, and enhanced physico/thermo-mechanical properties. The concept of nanocomposites was first introduced by researchers from Toyota who made nanocomposites from polyamide 6 and organophilic clay [13].

For this research study our basic aim is to improve the mechanical, thermo-mechanical and barrier properties of PTT by incorporation of organically modified clays. The objectives of this study can be summarized as:

- To surface modify MMT clay with titanate and silane coupling agents and characterize the modified clay through X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), hydrophilic-hydrophobic balance and thermo-gravimetric analysis (TGA).
- Micro-compounding processing (extrusion followed by injection molding) to fabricate Sorona®/organoclay nanocomposites. Such micro-compounding (compounding that needs materials for processing at the level of few grams) experiments target to screening/optimization studies that would lead to semi-pilot scale experiments.
- To fabricate semi-pilot scale extruded cast films from neat Sorona® as well as Sorona®/organoclay nanocomposites.
- Characterization of nanocomposites for their tensile and thermo-mechanical properties, barrier properties and morphologies through XRD and transmission electron microscopy (TEM).

These objectives will be derived in three phases. In the first phase MMT clay will be modified with titanate and silane based coupling agent. This study will mainly focus on the modification of MMT clay with titanate coupling agent. The ratio of titanate coupling agent and MMT clay in the system will be evaluated for surface characteristic studies to choose the suitable clay for nanocomposites.

In the second phase, the above selected clay will be used to fabricate the PTT based nanocomposites using melt intercalation technique and optimized for the right composition based on their mechanical and thermo-mechanical properties. In this phase micro-compounder will be used for fabrication of nanocomposites.

In third phase selected composition will be fabricated in twin-screw extruder followed by cast film extrusion. Finally cast film nanocomposites will be studied for mechanical, thermo-mechanical and barrier properties.

Chapter 2

Background and Literature Review

Biodegradable and bio-based polymer products, which are produced from renewable agricultural and biomass feedstock, can make the base for green and environment friendly, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock. This is the reason why US government agencies are making the agendas for using green and environment friendly products as an alternate for petroleum based sources. On the basis of origin we can divide biopolymers in three classes: Renewable resource based, Petroleum based biodegradable and Petro-bio mixed (which are not biodegradable). Figure 2.1 shows classification of biodegradable polymers on the basis of their origin [3, 14, 15].

Bionanocomposites are gaining lot of attention from last few years due to the sustainable approach. Bionanocomposites are usually termed for nanocomposites involving a biopolymer in blend with an organic or inorganic moiety of nanometric dimensions (at least one dimension in range of 1-100nm). Darder et al [16] has listed various areas in which biocomposites can be used. There are lots of areas where biocomposites are being used and can be used in future in place of conventional petroleum plastic based nanocomposites. Bionanocomposites are currently being used in life sciences, functional areas and packaging and have numerous potential for other applications [16-18].

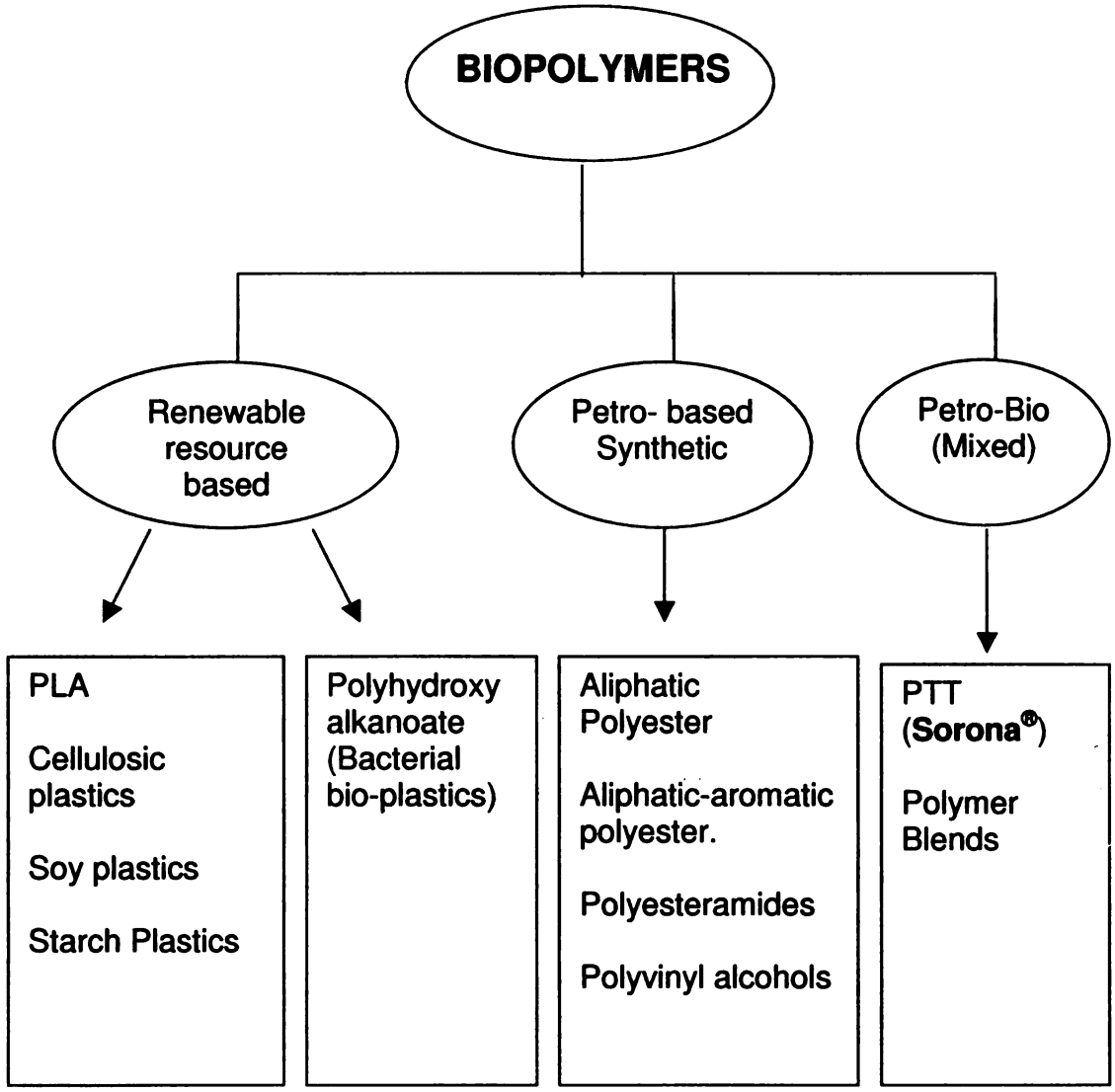

Figure 2.1 *Classification of Biopolymers. After Reference [3]*

In this study we focused on Poly(trimethylene terephthalate) (PTT) which can be obtained partially from biomass. This polymer has potential uses as fibers, films and as an engineering resin [6].

PTT has been widely used as textile fibers. Typical physical properties of Sorona® are listed in Table 2.1 [19].

Sorona® or 3GT (3-Glycol Terephthalate) polymer is one member of a family of polymers based on fiber-grade 1,3-propanediol. It is a linear crystallizable polymer having a melting temperature of about 228 °C and a glass transition temperature (Tg) of about 50 °C. The structure of PTT has been studied extensively [20-22]. The valuable properties of Sorona® polymer are derived from a unique, semi-crystalline molecular structure having a kink. The polymer shape is an outcome of the convolutions of the bonds in the trimethylene constituent [6].

Table 2.1 *Physical properties of Sorona®. After Reference [6]*

Property	**Semi-dull**	**Bright**
Intrinsic Viscosity (IV), dl/g	1.02	1.02
Hunter B Color	6.7	9.0
Hunter L Color	81	68
Melting Point (°C)	229	229
TiO_2, wt%	0.3	0
Mositure, ppm (as packaged)	120	120
Pellet Size, wt of 50 pellets, g	0.6	0.6

This zigzag shape means that tensile or compressive forces interpret at the molecular level to bending and twisting of bonds, rather than simply stretching. When the polymer is cooled from a liquid state to solid state it forms crystalline and amorphous regions. With 3GT, the modulus of the crystalline regions is significantly lower than that of other commercial polymers, such as PET. Sorona® can be cast into films at settings comparable to polypropylene or Nylon 6 but process optimization is required to eliminate film brittleness of cast films. Biaxially oriented films of Sorona® can also be prepared. Modified 3GT polymers or blends of 3GT with other commercially available polymers (2GT, 4GT, etc.) can be successfully used in films to obtain desirable property advantages and increased value. For example, the combination of properties of 3GT (oxygen and water vapor barrier and heat sealability) means that in many food packaging applications a single 3GT or modified 3GT layer may replace several layers of presently manufactured laminated films [6, 23].

There are various literatures available on poly(trimethylene terephthalate) (PTT) related to its structure and synthesis [24-26]. There are also literatures for PTT nanocomposites focused on improvement of properties of PTT by incorporation of organically modified nanoclays [27, 28]. There are also lot of studies done on rheology, interaction and chemistry of polymer blends and nanoparticles [29-36]. These literatures are reviewed for this study to get an in depth knowledge of behavior of PTT and its nanocomposites.

In a study by Drown et al [5], researchers focused on improving mechanical and barrier properties of poly(trimethylene terephthalate) by incorporation of commercial nanoclays via melt compounding. In this study fully petroleum based Sorona® was used. Biobased PTT-clay nanocomposites are also expected to exhibit exactly similar properties with that of petroleum based PTT-clay nanocomposites. Nanocomposites of Sorona® containing organo-clays were produced using melt compounding, e.g. extrusion, followed by injection molding. The researchers used five commercially available organo-clays at 5 wt% loadings to find the organic modification that achieved the best balance of mechanical and thermal properties. The increase in tensile modulus of the nanocomposites versus neat PTT ranged from 31 to 37%. The tensile stress at yield and break for the neat PTT were 58.5 and 38.5 MPa, respectively. The increase in the tensile stress at break of the nanocomposites versus neat PTT ranged from 2 to 53%. The heat deflection temperature (HDT) of the neat PTT was 88°C, and incorporation of the organo-clays produced increases in HDT up to 38%. From these results, the organo-clay Cloisite® 25A was selected for detailed study over the range of loading from 0 to 5 wt%. The thermo-mechanical properties as measured by the HDT increased monotonically with increasing organo-clay content. The barrier properties of Sorona® were improved by addition of Cloisite® 25A, and a loading of 3 wt% was effective in reducing the oxygen and water vapor permeation. The modulus of biobased and petroleum derived PTT was compared and found to be essentially identical.

Kelsey et al [37] studied the first-order thermal degradation rates of poly(trimethylene terephthalate) (PTT) at 240–280°C under non-oxidative conditions. They observe increase in allyl end groups by ^1H NMR (Nuclear Magnetic Resonance Spectroscopy) which is similar to the rates determined from the decrease in molecular weight which was measured by intrinsic viscosity. In this study these researchers found that there is little or no effect on PTT thermal degradation rates under non-oxidative environments. The thermal stability of poly(butylene terephthalate) [PBT] was also determined from butenyl end groups by NMR studies and molecular weight by intrinsic viscosity. They also found that activation energies (E_a) for both PTT and PBT thermal chain scission are similar to the reported E_as for poly(ethylene terephthalate) [PET] degradation. However, PTT and PBT endure molecular weight decrease faster than PET. But catalysts, additives or the type of synthesis does not manipulate thermal degradation of PTT.

There are lot of studies done on crystal structure, mechanical and other properties of PTT which shows the effect of nanoclays on the crystallization and properties of PTT which are essential to review for this study in order to gain knowledge about crystallization kinetics of PTT and its nanocomposites [38-45].

Hu and Lesser [46] also studied the morphology of intercalated poly(trimethylene terephthalate) (PTT)/clay nanocomposites prepared by the melt mixing of PTT with quaternary or ternary ammonium salt-modified clays. The

researchers studied the morphology and structure, crystallization and melting behavior, and the dynamic mechanical behavior and were characterized by X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and dynamic mechanical thermal analysis. The results of the study showed that the preparation of successful PTT nanocomposites. They found more regular stacking of the silicate layers at higher clay concentrations and shorter blend times. As per researchers' observations as compared with conventionally compounded composites, the nanoscale-dispersed organophilic clays were more effective as crystal nucleation agents. The influence of the nanosilicates on the crystallization and melting behavior of PTT became distinctive when the concentration of clay was around 3wt %. They concluded from their study that changes in the crystallization behavior of the polymer/clay nanocomposites are not only dependent on the size of the silicates but also on the intrinsic crystallization characteristics of the polymers.

The non-isothermal crystallization of intercalated PTT/clay nanocomposites was also investigated by Hu and Lesser [47] by different methods. They described non-isothermal crystallization of pure PTT by the Ozawa equation, but found that Ozawa theory is not valid for PTT/clay nanocomposites. As per their study, addition of clay into PTT decreases the crystallization half-time whereas increasing the crystallinity and crystallization rate. The PTT/modified clay nanocomposites have a higher crystallization rate parameter and a lower crystallization half-time as compared to unmodified

clay/PTT composites. They calculated the crystallization activation energy from Kissinger equation for PTT and PTT clay based nanocomposites, which were found to be 100 to 230 $kJ.mol^{-1}$. As per their study, addition of clay increases the crystallization activation energy but the clay still acts as an effective nucleating agent and this effect increases the crystallization rate and crystallinity of PTT. Further, they observed that modified nanoclays are more effective nucleating agents than the unmodified nanoclays, and found the most effective nucleating concentration of nano-clay is between 1–3 wt%. The crystallization half-time, $t^{1/2}$, decreases as a function of cooling rate, Q, and decreases with an increase in clay concentration.

Chang et al [48] studied and compared the PET and PTT clay based nanocomposites. Authors synthesized the nanocomposites; one with poly(ethylene terephthalate) (PET) and the other with poly(trimethylene terephthalate) (PTT), by using organically modified clay. They prepared organically modified clay and polyesters nanocomposites by in-situ interlayer polymerization method at different organoclay contents and at different draw ratios to produce monofilaments. They found that thermal stability and tensile mechanical properties increased with increasing organoclay content at a draw ratio of 1. However, they also observesd at the same time that values of the tensile mechanical properties of the hybrid fibers decreased with increasing draw ratio. They also find that reinforcing effects of the organoclay of the PET hybrid fibers were higher than those of the PTT hybrid fibers.

Chang et al [49] also studied the effect of different kind of clays in properties of PTT fibers. They observed a significant impact on thermal stability and tensile properties in PTT nanocomposites. The increase in draw ratio also impacted the initial modulus and ultimate strength of PTT hybrid fibers[49].

Liu et al [50] studied the crystallization, morphology and dynamic mechanical properties of PTT clay based nanocomposites. These researchers successfully prepared exfoliated PTT/clay nanocomposites via melt intercalation using a co-rotating twin-screw extruder. They found by their study on crystallization kinetics that the addition of clay changes the crystallization behaviors of PTT and enhances the crystallization of PTT, which in turn indicates of clay as nucleation agents. The morphology of spherulites was observed using polarized light microscopy, which also agrees with the results of crystallization kinetics. These researchers pointed that due to the strong interaction between the specific clay and the PTT matrix, Tg of the nanocomposite was considerably higher than that of pure PTT. As per their DMA studies they observed the higher modulus of nanocomposite than neat PTT. They find that temperature higher than Tg, storage modulus value of the nanocomposite is higher about ten times than that of neat PTT because of increase in crystallization rate of the PTT.

Mishra et al [31] studied the properties of rubber toughened PTT nanocomposites. Researchers prepared these nanocomposites using melt

mixing technique and observed a percolated network of clay. They also observed the increase in non-isothermal crystallization by incorporation of clay particles.

For future packaging innovations nanotechnology is the path forward in the flexible film and rigid plastic industries offering enhanced properties such as greater barrier protection, increased shelf life and lighter-weight materials. Polymer nanocomposites can be defined as polymers blended with nano-particles to produce materials with enhanced properties. They have been in subsistence for many years, but recently gaining momentum in mainstream commercial packaging use. Nano materials refers to materials that can be measured in nanometers i.e. have at least one dimension in nano-metric scale. In the metric system of measurement, a "nano" equals a billionth so a nanometer is one-billionth of a meter [51].

Polymer nanocomposites are fabricated by dispersing a filler material i.e. polymer matrix into nanoparticles such as nanoclays, carbon nanotubes, nanosilica etc. Nanoparticles have platelets like structure and during nanocomposites fabrications, these platelets are distributed into a polymer matrix, creating multiple, parallel layers that form "tortuous path," forming complex barriers to gases and water vapor [52]. The increase in barrier properties of polymer by adding nanoclays can be explained by two theories:

(a) Creating "tortuous path" in polymer matrix, (Nielsen model) [53] i.e. filling up free volume of polymer thus making permeants difficult to pass through the polymer matrix.

(b) Change in local permeability by nanocomposites, as per studied by Gusev and Lusti [54].

(a) Tortuous path theory: Nanocomposites increase the gas barrier properties by creating a "tortuous path" that reduced the progress of gas molecules through the polymer matrix. As per Nielsen Model [53], for platelets of length L and width D, which are dispersed parallel in polymer matrix, the tortuosity factor (τ) can be expressed as:

$$\tau = 1 + (L/2D)\,\varphi$$

where φ is volume fraction of dispersed layered silicate particles.

And relative permeability coefficient of nanocomposites and neat polymer can be expressed as:

$$Pnc/Pn = 1/[1 + (L/2D)\,\varphi]$$

where Pnc is permeability coefficient of nanocomposites

and Pn in permeability coefficient of neat polymer [53]

(b) This factor explains that presence of silicate layers (nanoclays) changes the local permeability because of the molecular level of alteration within the polymer

matrix. So if clay is more exfoliated (thoroughly dispersed) in polymer matrix it will decrease the permeation of gases through polymer matrix [54] .

Effectively, when there is more dispersion i.e exfoliation of nano-particles throughout a polymer, the permeability is significantly reduced.

Nanoparticles can be used for much lower loading levels than traditional fillers to achieve optimum performance. Usually, additional levels of nanofillers are less than 5%, which significantly impacts the weight reduction of nanocomposite films. This dispersion process results in a high aspect ratio and surface area, in turn creating higher-performance plastics than with conventional fillers.

Diverse types of fillers are utilized; the most common is a nanoclay material called montmorillonite-a layered, smectite clay. These clays in a natural state are hydrophilic, while polymers are hydrophobic. Montmorillonite (Referred as MMT hereafter) clay should be organically modified in order to be compatible with organic polymer. One way to modify clay is by exchanging organic ammonium cations [positively charged ions] for inorganic cations from the clay surface. Additional nanofillers include carbon nanotubes (CNT's), graphite platelets and carbon nanofibers. Carbon nanotubes are more expensive than nanoclay fillers, which are readily available and offer superb electrical and thermal conductivity properties. Two major suppliers of nanoclays in US are

Southern clay Products and Nanocor. There are three common methods used to enhance polymers with nanofillers to produce nanocomposites: melt compounding, in-situ polymerization and the solvent method. Melt compounding of the nanofillers into a polymer is done simultaneously when the polymer is being processed through an extruder, injection molder or other processing machine. The polymer pellets and filler (clay) are pressed together using shear forces to help with exfoliation (the process of separating the particles into the right shape and layer structure) and dispersion. With in-situ polymerization, the filler is added directly to the liquid monomer during the polymerization state. Using the solution method, fillers are added to a polymer solution using solvents such as toluene; chloroform etc to disperse the polymer and filler molecules. As the use of solvents is not environmentally friendly, melt processing and in-situ polymerization are the most widely used methods of nanocomposites production. Possible morphologies of polymer/clay nanocomposites are shown in Figure 2.2 [55].

The advantages of nanocomposite films are numerous, and the possibilities for application in the packaging industry are continual. Because of the nanocomposite process's dispersion patterns, the platelets result in largely improved performance in gas, oxygen, water barrier, high mechanical strength, chemical and thermal stability, heat resistance, good optical clarity, dimensional stability.

A greater part of consumer products that are using nanocomposite packaging are in the beverage and also food industry. Many different types of commercial plastics are used for nanocomposites including PP, Polyamides, PET and PE.

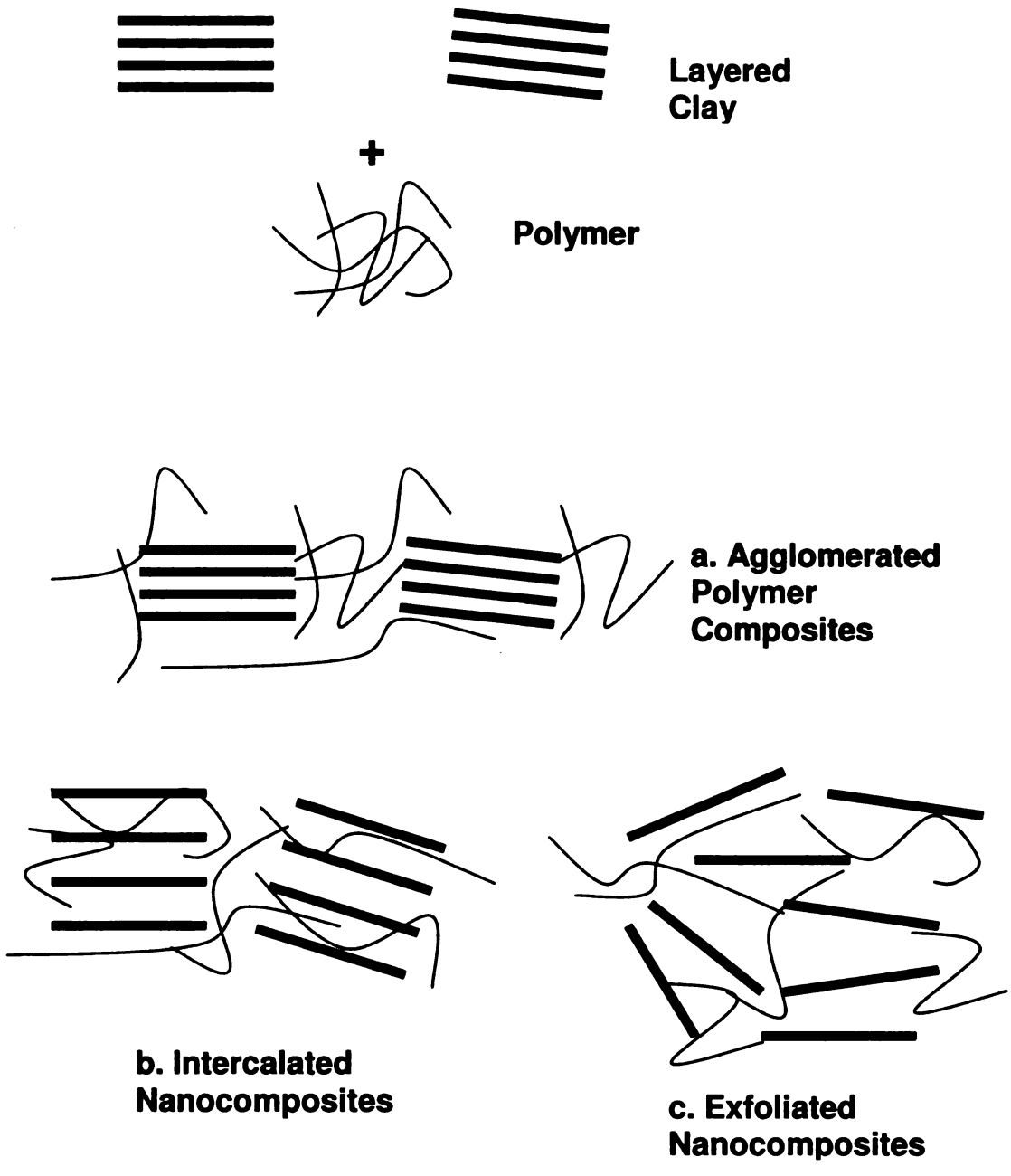

Figure 2.2 *Possible morphologies of polymer/clay nanocomposites. After Reference [55]*

An example of commercial nanocomposites is Nylon nanocomposites, used as barrier layers for multilayer PET containers which performed much better than the traditional ethylene vinyl alcohol barrier layers, as nylon has a 50°F higher melt temperature. Studies show that nylon 6 nanocomposites can achieve an oxygen transmission rate (OTR) much lower than unfilled nylon 6 as shown in Figure 2.3. In the case of Honeywell's Aegis™ OX barrier nylon resins, which were designed for multilayer bottle applications, the nanoclay layers also retain the active oxygen scavengers in the polymer meanwhile reducing OTR drastically. Aegis™ OX oxygen-scavenging compounds provides 6 to 12 months shelf life for plastic beer bottles which is comparable to glass bottles [51].

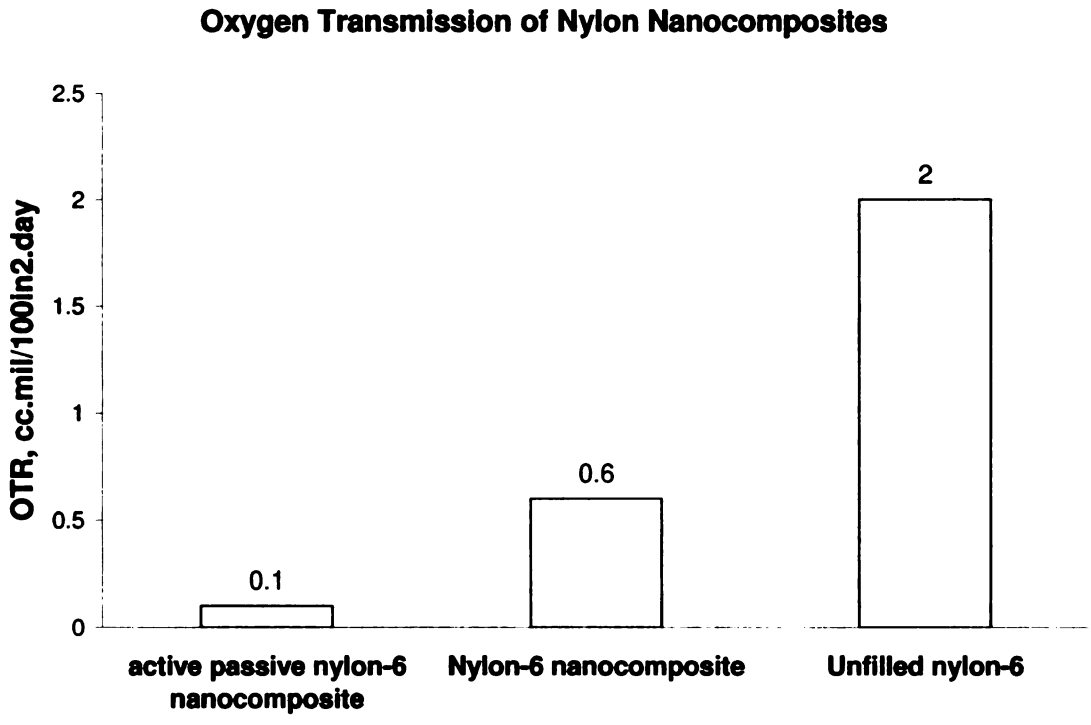

Figure 2.3 *Oxygen Transmission Rate of Nylon and its nanocomposites [51]*

Orientation of nanoparticles also has an effect on the success of nanocomposites. Nanoparticles need to be dispersed throughout polymer so they are parallel to the material's surface. This position ensures a maximum tortuous path for the gasses when migrating through the polymer. Compatibility between the nanofillers and the polymer substrate is also an important factor that is how they interact with each other. Certain nanofillers need to be modified so they can interact well with the matrix. A study done by Bhardwaj and Mohanty confirms the interaction of modified nanostructured dentritic polymer with brittle renewable based polymer matrix [56]. Another concern is that during the processing state, there is a possibility of reaggregation, where the particles clump together. In that case, the creation of the nanocomposites is ineffective [57].

Polymer nanocomposites are the future for the global packaging industry. Once production and materials costs decrease, companies will use this technology to increase their product's stability through the supply chain to deliver higher quality to their customers while saving money. Research is also continuing into other types of nanofillers, allowing new nanocomposites structures with different, improved properties that will further advance their use in many diverse packaging applications.

Imperm®, produced by Nanocor is an example of commercial avialbale nanocomposites. It showed similar results when it is added to a multilayer PET structure. It requires no adhesion tie layers to PET and is recyclable. When used in a 16-oz beer bottle, Imperm® can provide almost seven-month shelf life [58].

The four areas in food industry that will be significantly improved by nanotechnology are development of nanoscale processing, product development, new functional materials, design of methods and instrumentation for food safety and biosecurity [59].

Chapter 3

Materials and Methods

3.1 Materials

3.1.1 Poly(trimethylene terephthatale) (PTT)

The poly(trimethylene terephthalate),PTT was obtained from DuPont (Wilmington, DE) under trade name of Sorona®. In this study, petroleum based Sorona® was used. PTT comes under the family of conventional aromatic polyesters like poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The PTT was supplied as pellets and dried in a forced-air desiccant drier at 125℃ for 4 hours prior to use. The chemical structure of PTT is shown in Figure 3.1.

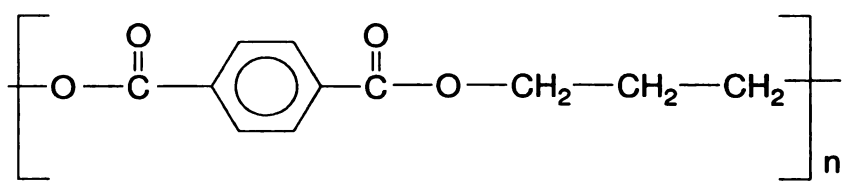

Figure 3.1 *Chemical Structure of Poly(Trimethylene Terephthalate)*

PTT has melting point of 228℃ and glass transition temperature of about 50℃ with density of 1.33 g/cc. It is bright transparent in color without odor containing 0.3 wt% of TiO_2 as additive. It has an intrinsic viscosity of 1.02 mlg^{-1} . PTT was kept in air tight jar after drying for 4 hours in convection oven because it is hygroscopic in nature like other polyesters.

3.1.2 Montmorillonite Clay (MMT)

The unmodified montmorillonite clay denoted by MMT was supplied by Southern Clay Products, Inc. (Gonzales, TX) under trade name of Cloisite® Na^+. Table 3.1 shows the cation exchange capacity, specific gravity and d-spacing of this clay. It is natural montmorillonite clay without any modifier. Clay was predried at 80℃ for about 12 hours before its surface modification. Surface modified clay was dried at 60℃ for about 4 hours prior to fabrication of nanocomposites.

Table 3.1 *Physical properties of natural montmorillonite clay (Cloisite® Na^+). After Reference [60]*

MMT Clay	Cation Exchange Capacity (CEC) (meq/100g of clay)	Specific Gravity (g/cc)	Basal Spacing (001)-d_{001} (nm)
Cloisite® Na^+	92.6	2.86	1.17

3.1.3 Titanate Based Coupling Agent

The titanate-based surface modifier (Kenreact® LICA-38) as used in this work is *neopentyl (diallyl)oxy tri(dioctyl) pyrophosphato titanate,* (Figure 3.2), a product of Kenrich Petrochemicals, Inc. (Bayonne, NJ). Chemical structure of titanate modifier sourced from [61].

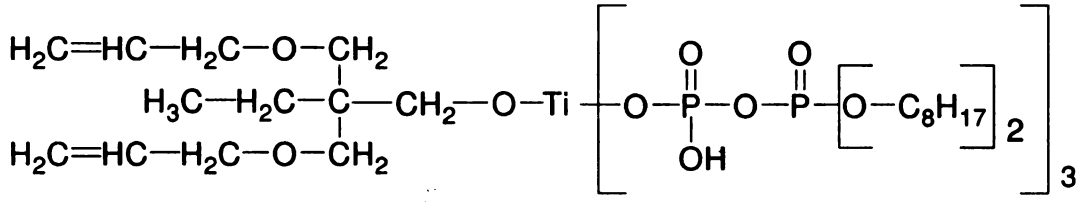

Figure 3.2 *Chemical Structure of Neopentyl (diallyl)oxy tri(dioctyl) pyrophosphato Titanate. After Reference [61]*

3.1.4 Silane Coupling Agent

The silane coupling agent (Dow Corning® Z-6040) selected from various silane coupling agent based on its functionality was *γ-Glycidoxypropyltrimethoxysilane* (Figure 3.3). This was purchased from Sigma-Aldrich and was used as received.

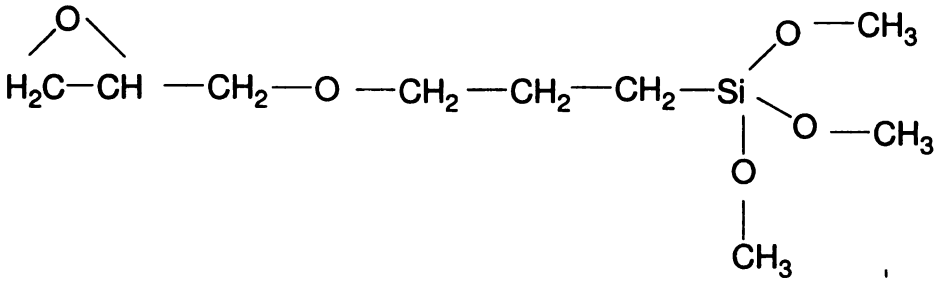

Figure 3.3 *Chemical Structure of γ-Glycidoxypropyltrimethoxysilane*

The non-aromatic solvent i.e. an aliphatic hydrocarbon solvent (Kwik-Dri® 66) was purchased from Ashland Distributions Inc. (Columbus, OH). Toluene was obtained from Aldrich and was used as received. Laboratory grade ethanol was purchased from Aaper Alcohol and Chemical Co. (KY).

3.2 Methods

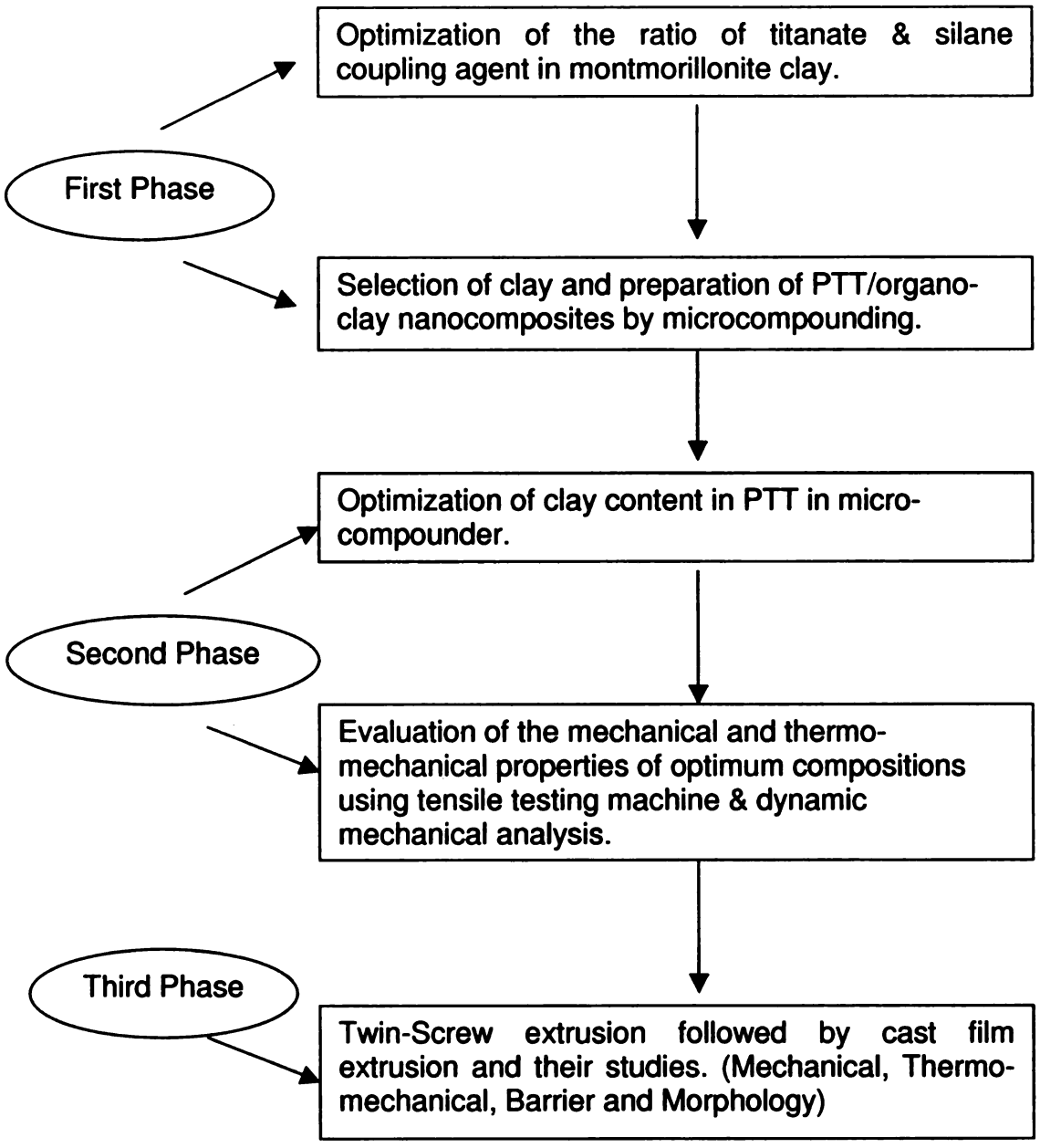

Figure 3.4 *Schematic representation of steps followed for this research work*

3.3 Surface Modification of Montmorillonite Clay

3.3.1 Surface Modification of Clay with Titanate Based Coupling Agent

The surface modification of clay with titanate based coupling agent has been reported by Monte[62] and in our previous studies [61]. MMT clay (Cloisite® Na^+) was modified with titanate coupling agent. In the surface modification process, the amount of titanate coupling agent was varied in order to get modified clay with varying titanate contents.

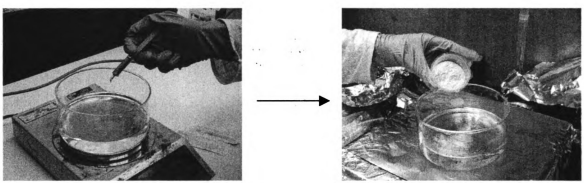

Figure 3.5 *Titanate surface modifier (in syringe) added to toluene in crystallizing dish (left) and clay added to the toluene and modifier in continuous mode (right).*

Two different solvents, toluene and Kwik-Dri® 66 were used to carry-out the surface modification of clay. The MMT clay was dried overnight in vacuum oven at 80℃. Approximately 300 ml of solvent (toluene or Kwik-Dri® 66) was placed in a crystallizing-dish and the requisite amount of titanate modifier was added to the solvent and dispersed using a magnetic stirrer at ambient temperature. The calculated amount of dried MMT clay was added to the solution incrementally and stirred for 3 hours. The clay was allowed to settle and the excess solvent was decanted, followed by several washings in order to remove the unreacted and excess modifier and possible byproducts. The schematic representation of the surface treatments are shown in Figure 3.5 and Figure 3.6. Finally, the excess solvent was decanted and the clay dried overnight at ambient conditions followed by drying in a vacuum oven for 5 hours at 55℃ before use.

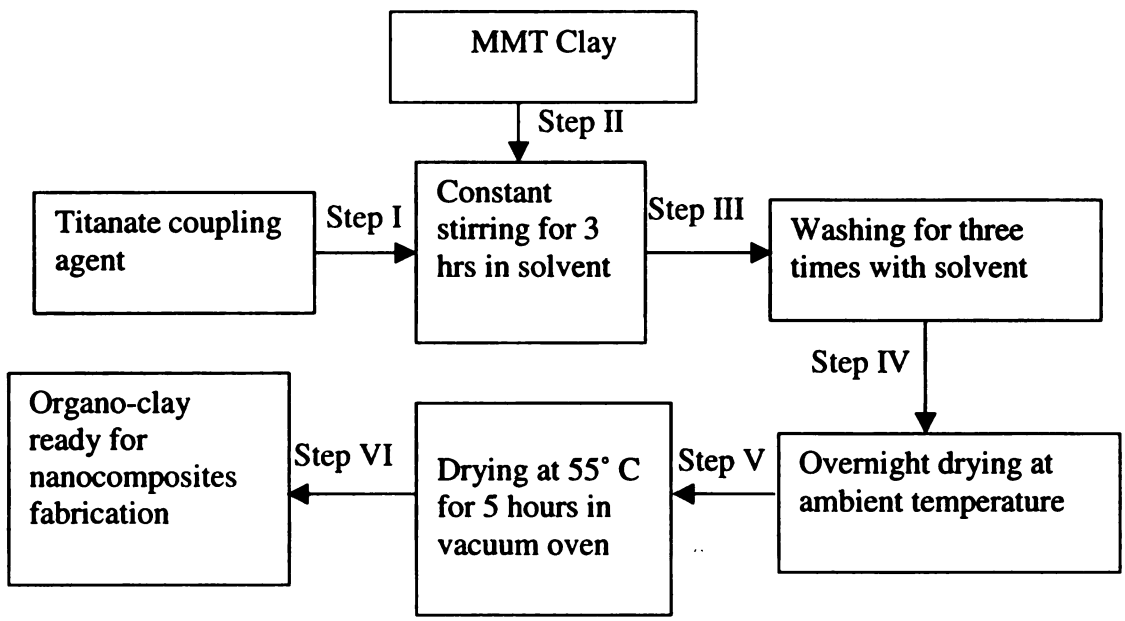

Figure 3.6 *Schematic of Surface Modification of MMT Clay*

3.3.2 Surface Modification of Clay with Silane Coupling Agent

The surface modification of clay with a silane coupling agent has been reported by Hongping et al [63]. In the adopted process, an ethanol/water mixture was used as the solvent to carry-out the surface modification of clay, the amount of silane coupling agent was kept at a constant ratio with aqueous solution of ethanol and clay. Prior to treatment, MMT clay was dried overnight in a vacuum oven at 80℃. A solution of ethanol and deionized (DI) water was prepared in ratio of 95:5 and the calculated amount of acetic acid was added to the solution to maintain its pH in the range of 4.5-5.5. Then, the silane coupling agent was added and stirred for 10 minutes using a magnetic stirrer at ambient temperature; dried MMT was added to the solution incrementally and stirred for 1 hour.

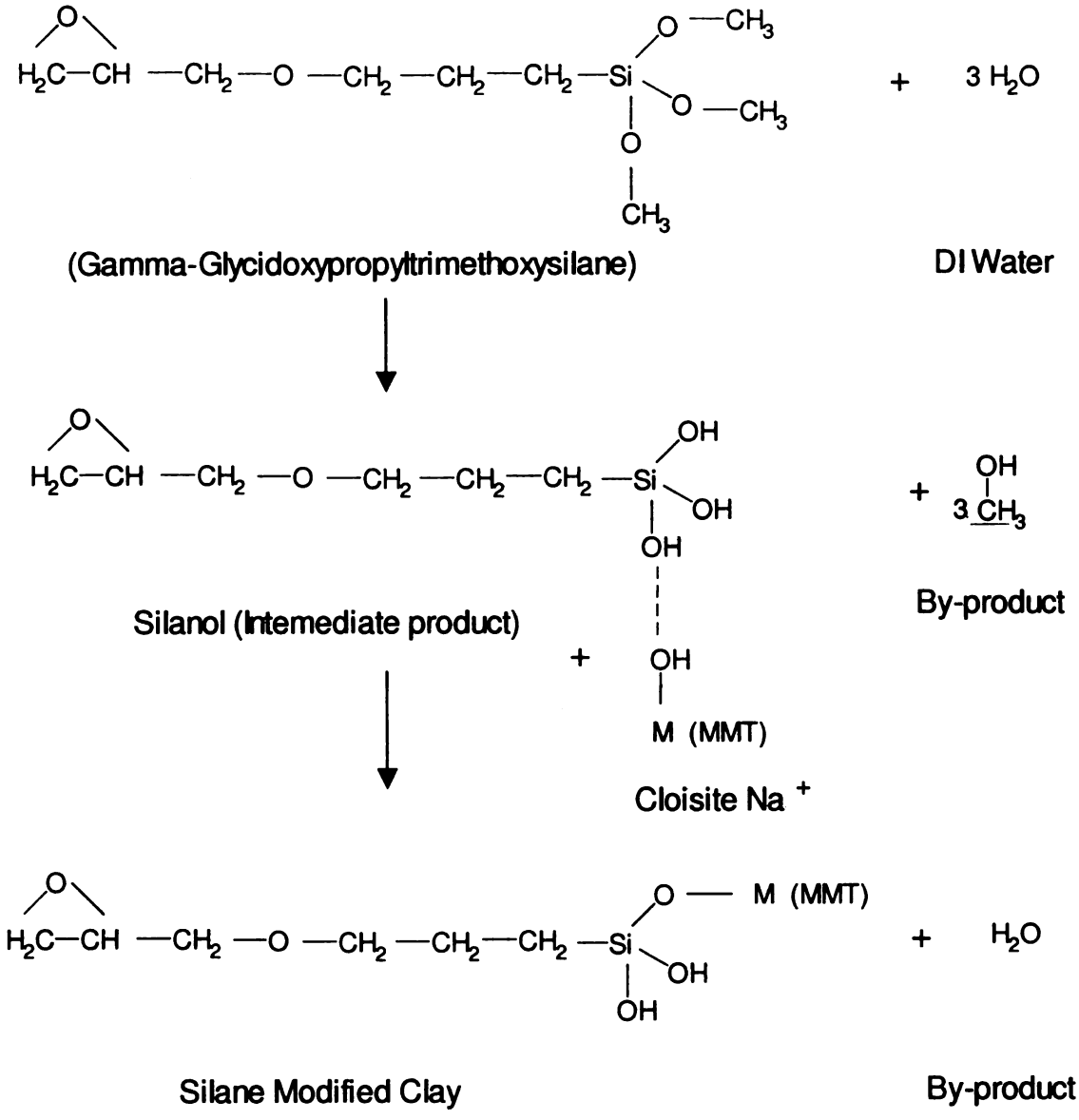

Figure 3.7 *Silane Coupling Agent Reaction Scheme*

The excess solvent was decanted followed by several washings in order to remove the unreacted and excess modifier and possible byproducts. The silane coupling agent reaction with the clay surface is shown in Figure 3.7 and a schematic representation of the surface treatment process is shown in Figure 3.8. The excess solvent was then decanted; the clay was dried overnight at ambient conditions and then dried in a convection oven for 5 hours at 80°C, ground and subsequently dried in a vacuum oven at 80°C for 1 hour.

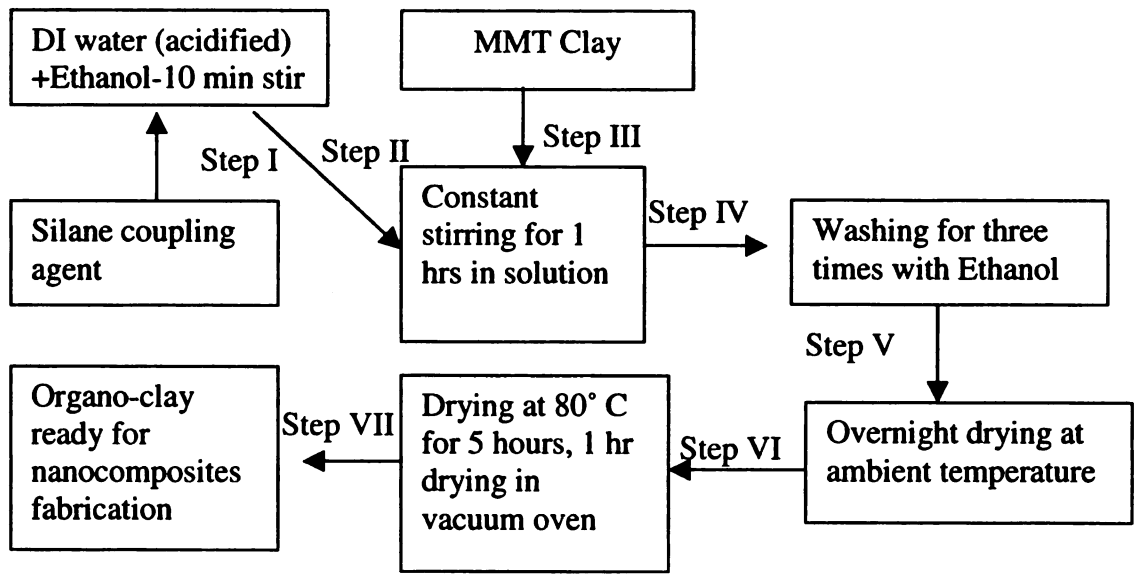

Figure 3.8 *Schematic Representation of Clay Modification with Silane Coupling Agent*

3.4 Processing Equipments

3.4.1 DSM Microcompounder

Polymer melt compounding was done using micro compounding equipment (TS/I-02, DSM, Netherlands). Photographs of the mini compounding system are shown in Figure 3.9.

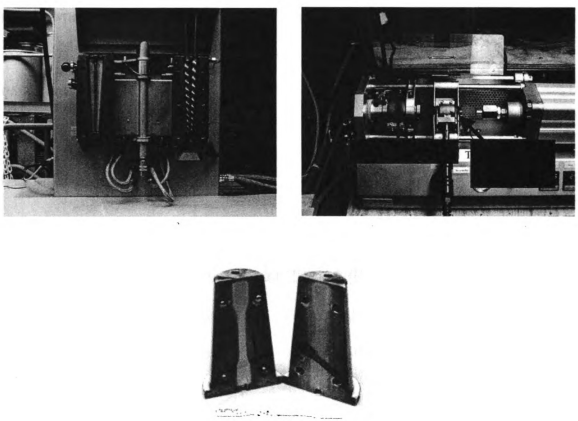

Figure 3.9 *DSM mini-extruder (top left), mini injection-molder (top right), tensile mold and tensile beam (bottom)*

The mini extruder is equipped with conical co-rotating screws having length of 150 mm, L/D ratio of 18 and net capacity of 15 cc. The attached injection-molding unit is capable of 160-psi injection force. PTT and modified clay were weighed as per calculated compositions for specific processing conditions and fed into mini extruder. After extrusion, the melted materials were transferred through a preheated cylinder to the mini injection molder which was preset to a mold temperature of 85℃ to obtain the desired specimen samples for various measurements and analysis. Neat PTT and PTT based nanocomposites were processed at 250℃ and 150 rpm for cycle times of 3 minutes and 6 minutes, respectively.

3.4.2 Twin Screw Extruder

The pilot-scale (may also be termed "semi pilot-scale") blending was carried out using a twin screw extruder ZSK-30 (Figure 3.10). PTT pellets were placed into the blend resin feeder. For the nanocomposites, clay was placed into the clay feeder. Small feeding screws were used to control the feed rate for resin and clay. The materials were melted and mixed in the extruder section and forced through the die as strands. Initially, a master batch containing 20 wt.% modified clay was prepared.

These melt compounded strands were then cooled in water bath and the strands were cut into pellets using a pelletizer. After drying in a vacuum oven at

100℃ overnight, the master batch pellets were added to neat PTT resin to obtain 3 wt.% and 5 wt.% clay nanocomposites. The temperature profile of the ZSK-30 twin-screw extruder was 235, 240, 240, 240, 245, 245 ℃ corresponding from Zone1 to Zone 6; the screw speed was 100 rpm. The torque of extruder was kept at 60%. A photograph showing a schematic view of master batch followed by nanocomposites fabrication at the desired clay content is shown in Figure 3.11.

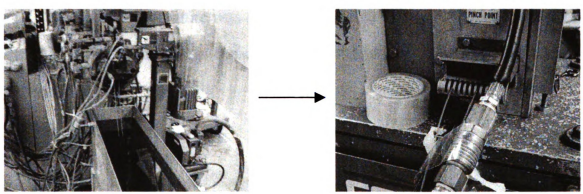

Figure 3.10 *ZSK-30 twin-screw extruder nanocomposites strands in water bath on left and Pelletizer on right*

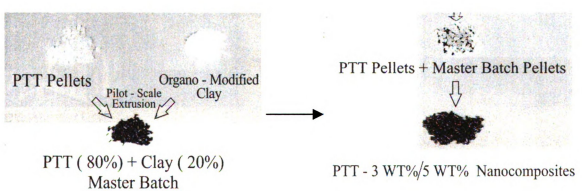

Figure 3.11 *Pilot-scale extrusion schematic diagrams*

3.4.3 Single Screw Cast Film Extruder

Cast films of neat PTT and PTT based 3 wt.% and 5 wt.% clay nanocomposites were prepared using a single screw extruder, Killion KLB-100, Figure 3.12. The temperature of the extruder was kept at 260,265 and 260℃ for Zone1 to Zone 3 respectively. Temperature of clamp ring, adapter and external die was kept at 265, 260 and 250℃ respectively.

The melt temperature was 250℃. The temperature of chill-roll was kept at 12° C and take-off speed of the chill-roll was 18 rpm. The average thickness of film was 3.5 mils.

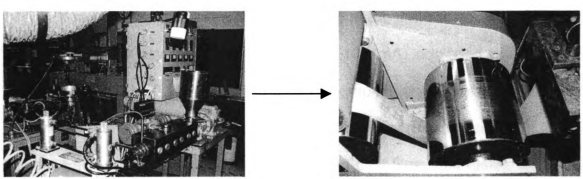

Figure 3.12 *KLB-100 Single-screw Extruder (left) and Chill-roll (right)*

3.5 Characterization

3.5.1 X-ray Photoelectron Spectroscopy (XPS)

Surface elemental analysis of the clays was performed using XPS. The XPS measurements were performed using a Physical Electronics PHI-5400 ESCA workstation. The X-ray source was a polychromatic magnesium anode (1254 eV). The analyzer was operated in the fixed energy mode employing a pass energy of 89.45 eV for survey scans and 17.9 eV for utility scans. Clay samples were affixed to the specimen holder with double-sided tape. Semi-quantitative information was obtained by measuring the C1s and O1s peak areas and applying the appropriate sensitivity factors. Each composition of clay was tested for single sample.

3.5.2 X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) patterns of the clays were obtained using a Rigaku 200B X-ray diffractometer (45 kV, 100 mA) equipped with a CuKα radiation source (λ= 0.1541 nm) and a curved graphite crystal monochromator at a scanning rate of 0.5°/min. The d_{001} basal spacings were calculated from the 2θ values. Each composition of clay and extruded cast films was tested for single sample.

3.5.3 Hydrophobic-Hydrophilic Balance

To determine the relative moisture uptake of the various clays, they were first prepared by drying in a convection oven at 80℃ for 8 hours followed by 4 hours under vacuum at 80℃. Samples of each were placed into plastic weighing dishes and introduced into a conditioning chamber held at 43% relative humidity by the use of a saturated potassium carbonate solution, ASTM E-104. The dishes were weighed periodically to determine when equilibrium (saturation of the clay) had occurred. Once equilibrium had been reached, the clays were dried in triplicate in a convection oven at 110℃ for 8 hours. Samples of each composition of clay were tested in triplicate.

3.5.4 Dynamic Mechanical Analyzer (DMA)

Storage modulus measurements of samples were obtained using a TA Instruments Q800 dynamic mechanical analyzer, (TA Instruments, DE). Single cantilever mode was used for injection-molded samples whereas tension mode was used for film samples. Samples were tested at a frequency of 1 Hz and 15 μm amplitude over the temperature range of 30 to 140℃ at a ramp rate of 2℃/min. Samples of each composition of injection molded specimen of PTT and PTT nanocomposites were tested in triplicate.

Beam specimens of dimension 2 x 12 x 60 mm were fabricated using the DSM mini-extruder and mini injection molder. A dynamic mechanical analyzer

DMA Q800 (TA Instruments, DE) with 3-point load fixture was used for HDT (Heat Deflection Temperature) measurements. The HDT was measured according to ASTM D-648. The support span was 50 mm, the mid-point stress was fixed at 0.455 MPa and HDT was measured at 0.195% strain. The samples were heated from 30 to 160℃ at a ramp rate of 2℃/min. Five samples of each composition of injection molded specimen of PTT and PTT nanocomposites were tested to calculate HDT.

3.5.5 Universal Testing Machine

A United Testing System model SFM-20 test frame was used for measuring tensile strength and percent elongation of the extruded cast films following ASTM D882-02 standard. A sample width of 1 inch and gage length of 4 inches with a grip separation speed of 0.4 in/min were used. The samples were conditioned for 48 hours at 23℃ and 50% relative humidity prior to testing. The tensile properties of the injection-molded materials were measured using the SFM-20 according to ASTM D 638 for the measurement of the modulus of elasticity, tensile strength and percent elongation. A sample width of 0.19 inches and gage length of 1 inch with crosshead speed of 0.1 in/min were used. Flash was removed from the edges of the coupons using 1200 grit silicon carbide coated abrasive paper prior to testing. Five samples of each composition of injection molded specimen and extruded cast films of PTT and PTT nanocomposites were tested for tensile properties.

3.5.6 Thermal Behaviors (DSC & TGA)

Differential Scanning Calorimetry (DSC) technique was used to measure the melting and crystallization temperatures and crystallinity of PTT and PTT nanoclays based nanocomposites. A Q100 (TA instruments, DE) differential scanning calorimeter was used for these behaviors. The testing was carried out at the temperature range of 30°C to 270°C at scanning rate of 20°C/min. Samples of each composition of extruded cast films were tested in triplicate.

Thermogravimetric analysis (TGA) of the titanate and silane coupling agents and organically modified clays was carried out using a 2950 TGA (TA Instruments, DE) to measure the weight loss with respect to temperature. Approximate 20 mg of sample was placed in aluminum pans and heated to 600°C at 20°C/min with a nitrogen purge. Each composition of clay and coupling agents were tested for single sample.

3.5.7 Barrier Properties

The water vapor and oxygen permeability of neat PTT and nanocomposite films were measured using a MOCON® Permatran-W® 3/33 MG and Ox-Tran® 2/21, respectively. Extruded cast films of nominal thickness of 3.5 mils were tested for their water vapor and oxygen permeabilities. The temperature and relative humidity (RH) of Permatran-W® 3/33 MG was 37°C and 100% respectively and operated in continuous mode. The temperature and RH used in the Ox-Tran® 2/21 was 23°C and 0% respectively and permeant

concentration was kept at 100% and operated in continuous mode. 50 cm^2 area films were tested for oxygen and water vapor permeation. Samples of each composition of extruded cast films of PTT and PTT nanocomposites were tested in triplicate.

3.5.8 Transmission Electron Microscopy (TEM)

A transmission electron microscope (TEM) (Jeol 100 CX) was used to analyze the morphology of extruded cast films nanocomposites at an acceleration voltage of 100 kV. Film samples were embedded in an epoxy resin and cured for 24 hours followed by sectioning using an ultra-microtome. Thin-film specimens with a thickness of 70 nm were used for TEM observation. Single sample of PTT nanocomposites was observed under TEM

3.5.9 Polarized Light Optical Microscopy (PLOM)

Micrographs of neat PTT and PTT nanocomposites were taken using an Olympus BH-2 optical microscope and images were captured using a RT Color Spot digital camera. A single sample of each composition of extruded cast films of PTT and PTT nanocomposites were observed under PLOM.

Chapter 4

Results and Discussion

The detailed nomenclature of the clays is given in Table 4.1.

Table 4.1 *Nomenclature of the Surface Modified Clays*

Clay Designation	Solvent	Modifier	Ratio of Clay to Titanate Modifier
MMT	**N/A**	**N/A**	**N/A**
Ti,90:10(Tol)	**Toluene**	**Titanate**	**90:10**
Ti,85:15(Tol)	**Toluene**	**Titanate**	**85:15**
Ti,95:5(KD)	**Kwik-Dri® 66**	**Titanate**	**95:5**
Ti,90:10(KD)	**Kwik-Dri® 66**	**Titanate**	**89.8:10.2**
Ti,85:15(KD)	**Kwik-Dri® 66**	**Titanate**	**85:15**
Si (Et)	**Ethanol+ Water**	**Silane**	**98:2**

4.1 Studies on Surface Modified Clays

4.1.1 XPS Analysis

The MMT clay was modified with the titanate coupling agent using varied loadings and two solvents. The modified clays were studied by XPS elemental analysis to gain more information about the modification process. There are various available literatures which report clay exfoliation and nanocomposites with enhanced properties due to clay surface modification [13, 64, 65]. X-ray photoelectron spectroscopy utilizes photoelectrons emitted from the sample and energy-dispersive analysis to determine elemental composition. The XPS elemental analysis of MMT and modified clays is shown in Table 4.2.

The analysis of as received MMT clay shows the presence of silicon, aluminum, oxygen and sodium – which are components of the clay's structure. The surface also contains carbon and nitrogen. Some of the oxygen is present as hydroxyl groups on the surface of clay. These hydroxyl groups are targeted to exchange with alkyl-titanate complex of the titanate surface modifier during treatment. The XPS analysis shows a reduction in the oxygen concentration of the modified clays. The presence of titanium and phosphorous on the modified clays indicates that modifier has reacted with clay surface. The increase in carbon content is due to alkyl chains of the modifier which reacted with the MMT clay surface. There is also reduction of silicon and aluminum in modified clays as modifier layer is covering the surface of clay. XPS analysis shows that there is an increase in the carbon content in titanate modified clays as compared with

MMT clay, possibly due to an increased amount of grafted titanate modifier present on the clay. The silane modified clay, Si (Et) also shows an increase in silicon (as shown in Table 4.2) due to surface grafting of silane coupling agent with clay.

Table 4.2 *XPS Elemental Analysis of Montmorillonite Clay and Modified Clays*

Element	**MMT**	**Ti, 90:10 (Tol)**	**Ti, 85:15 (Tol)**	**Ti, 90:10 (KD)**	**Ti, 85:15 (KD)**	**Si (Et)**
Carbon	22.81	28.51	31.97	29.20	34.80	21.21
Nitrogen	0.71		0.50			
Oxygen	51.94	47.82	45.08	47.39	44.37	53.29
Sodium	1.99	2.87	2.39	2.81	2.04	2.09
Aluminum	6.74	5.53	5.06	5.45	5.25	6.72
Silicon	15.80	13.12	12.53	13.16	11.68	16.69
Phosphorous		1.66	1.56	1.67	1.56	
Titanium		0.49	0.91	0.33	0.30	

4.1.2 Hydrophobic-Hydrophilic Balance

The clays treated with the titanate modifier were examined to determine the reduction of the hydrophilicity of the clay surfaces, as gauged by their moisture uptake at 43% relative humidity. Both solvent systems were examined. The unmodified clay adsorbed 61.4 mg H_2O/g clay, the treated clays adsorbed from 50.7 to 61.8 mg H_2O/g clay. Figure 4.1 shows the percent change in the moisture uptake of the modified versus MMT clay.

The system using toluene as the solvent had decreased moisture uptake as the concentration of the titanate coupling agent increased, which is indicative of the clay's surface becoming more hydrophobic with increased coverage by the modifier. On the other hand, the system with Kwik-Dri as the solvent had erratic behavior with respect to modifier concentration. Whether this is due to the nature of the solvent is unclear.

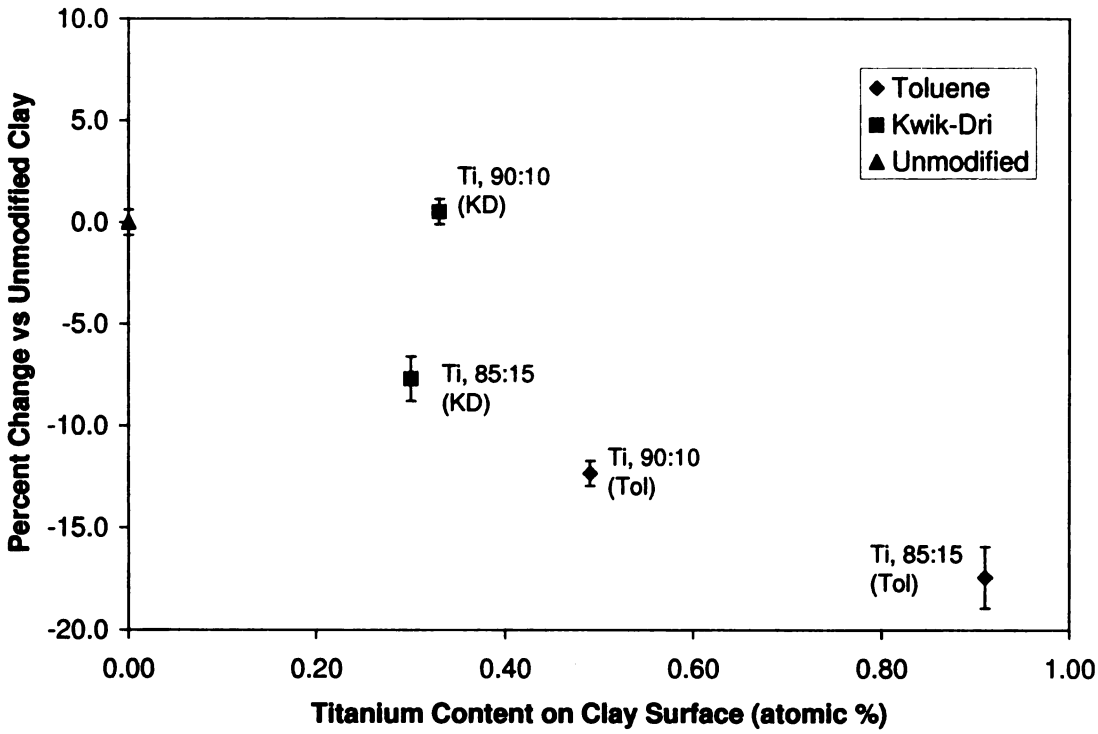

Figure 4.1 *Reduction in Hydrophilicity as a Function of Modifier Content*

4.1.3 XRD Analysis

X-ray diffraction (XRD) analysis was performed on the MMT clay and modified clays. The XRD results show an increase in d-spacing of up to 21% in Ti, 90:10 (Tol) as well as Si (Et) clay. Table 4.3 provides the basal spacings of MMT clay and the titanate modified clays. Figure 4.2 shows the corresponding XRD curves for powder clays.

Table 4.3 *Basal Spacings of Raw Montmorillonite and Modified Clays*

Material	2θ°	d spacing(Å)
MMT	7.90	9.71
Ti, 90:10 (Tol)	7.55	11.70
Ti, 85:15 (Tol)	7.80	11.33
Ti, 85:15 (KD)	8.7	10.16

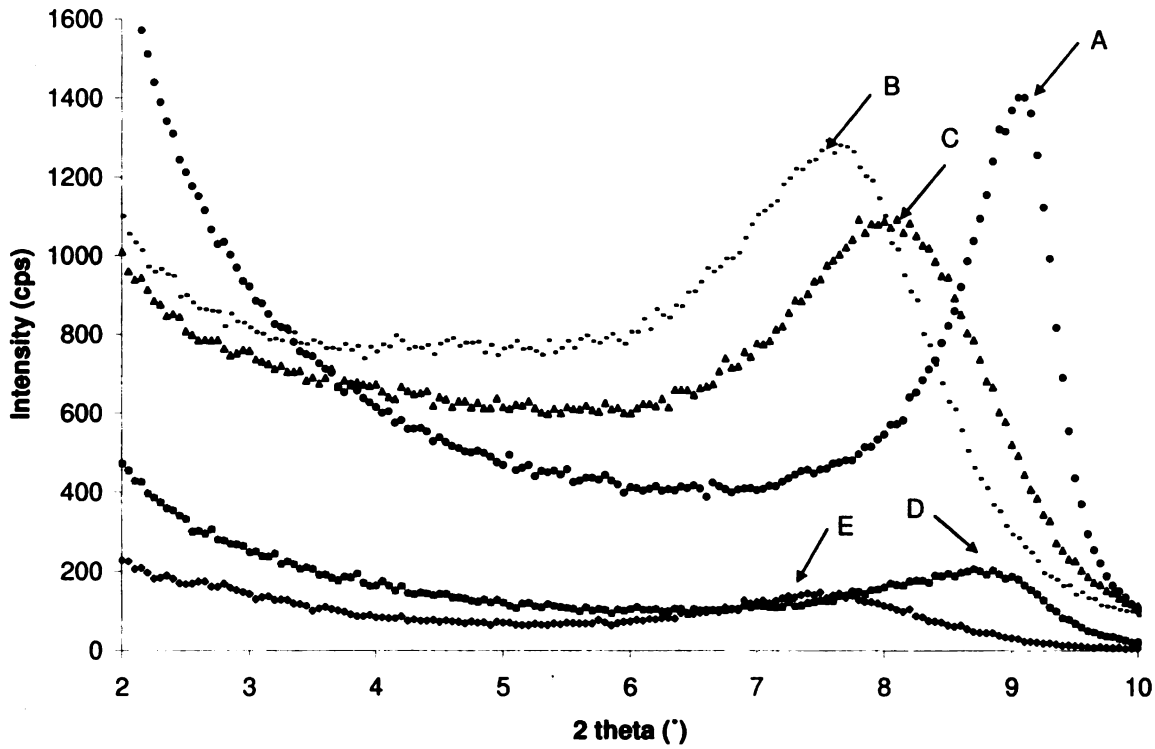

Figure 4.2 *X-ray diffraction pattern of raw MMT and modified clays*
A: MMT; B: Ti, 90:10 (Tol); C: Ti, 85:15 (Tol); D: Ti, 85:15 (KD)
E: Si (Et)

4.1.4 TGA analysis

The weight loss of titanate modifier, MMT clay and organically modified clays was measured using TGA. Table 4.4 shows the weight loss of MMT, organically modified clays and titanate modifier between 100° C and 600°C. This table shows the uncorrected weight change of organically modified clays because there is some weight change in MMT clay also due to the dehydroxylation of Si-OH groups.

Table 4.4 *Weight Change of MMT, Organically Modified Clays and Titanate Modifier*

Clay	Wt @ 100°C (mg)	Wt @ 600°C (mg)	Wt change
MMT	5.402	5.317	0.016
Ti,85:15 (Tol)	3.034	2.964	0.024
Ti,85:15 (KD)	4.011	3.891	0.031
Si (Et)	2.399	2.347	0.022
Titanate Modifier	32.547	11.339	1.870

Table 4.5 shows the corrected weight change values of organically modified clays by subtracting their uncorrected weight change values from the weight change value of MMT clay. Weight change of organically modified clays is given as loss of modifier per gram of clay.

Table 4.5 *Weight Change (Corrected) of MMT, Organically Modified Clays and Titanate Modifier*

Clay	Wt @ 100℃ (mg)	Wt @ 600℃ (mg)	Wt change	Wt change (corrected)
Ti,85:15 (Tol)	3.034	2.964	0.024	0.008
Ti,85:15 (KD)	4.011	3.891	0.031	0.015
Si (Et)	2.399	2.347	0.022	0.006

MMT clay shows a decrease of 16.0 mg per gram of clay whereas organically modified clays shows decrease of up to 14.8 mg loss per gram of clay as given in table 4.5. Figure 4.3 shows the weight loss curves of titanate modifier, MMT clay and organically modified clays and figure 4.4 shows the expanded curves of MMT clay and organically modified clays in range of 100 ℃ to 600 ℃ to evaluate the extent of dehydroxylation and loss of modifier. As shown in figure 15 MMT clay shows a smooth weight loss whereas organically modified clays showed onset points where the organic modifier began to decompose. Clays Ti,85:15 (Tol) and Ti,85:15 (KD) have a decomposition temperature of around 260 ℃ which is the decomposition temperature of titanate modifier. Figure 4.5 and 4.6 shows the derivative weight curves for titanate modifier, MMT clay and organically modified clays.

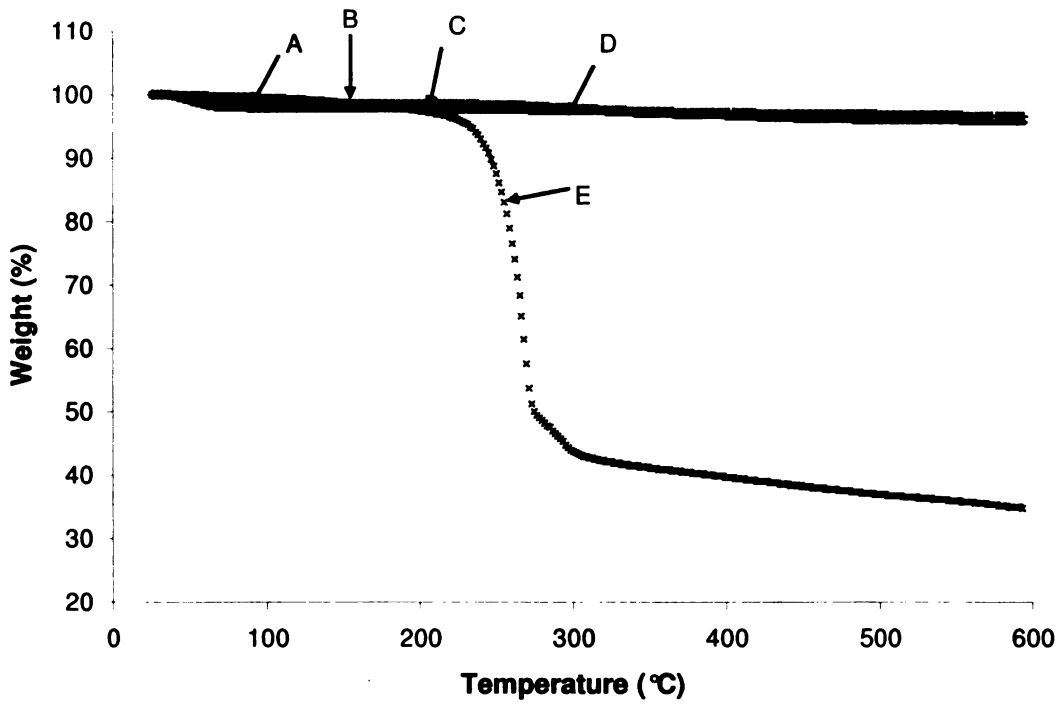

Figure 4.3 *TGA curves of MMT and modified clays and titanate modifier A: MMT, B: Ti,85:15 (Tol), C: Ti,85:15 (KD), D: Si (Et), E: Titanate Modifier*

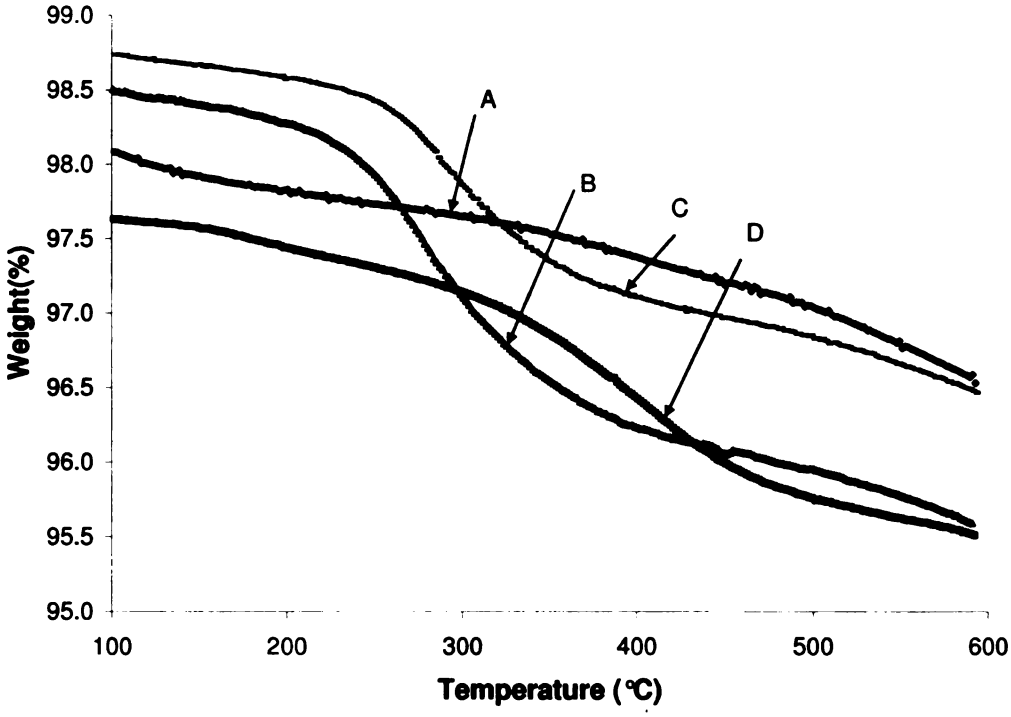

Figure 4.4 *Expanded TGA curves of MMT and modified clays A: MMT, B: Ti,85:15 (Tol), C: Ti,85:15 (KD), D: Si (Et)*

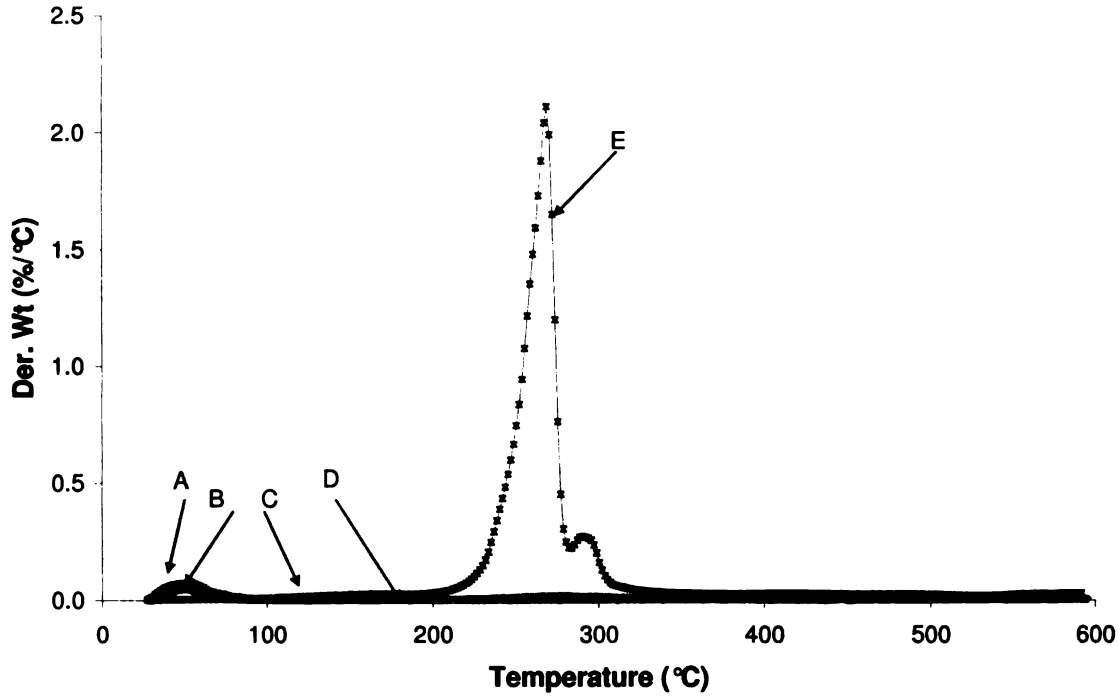

Figure 4.5 *TGA curves for derivative weight of MMT and organo- modified clays and titanate modifier*
A: MMT, B: Ti,85:15 (Tol), C: Ti,85:15 (KD), D: Si (Et), E: Titanate Modifier

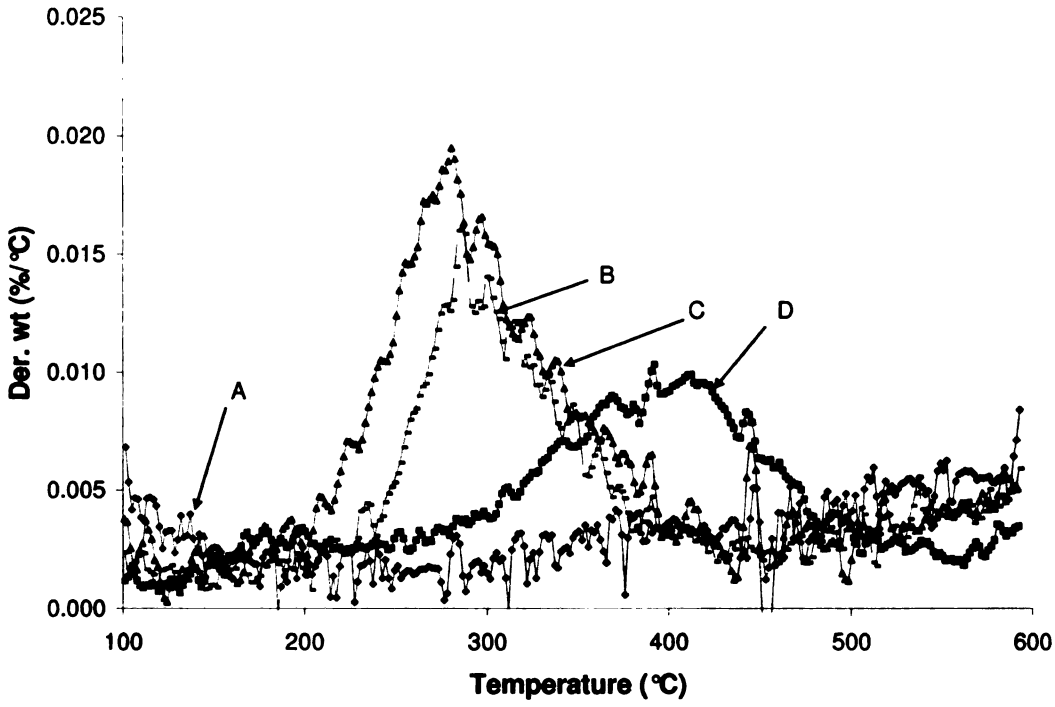

Figure 4.6 *Expanded TGA curves for derivative weight of MMT and modified clays*
A: MMT, B: Ti,85:15 (Tol), C: Ti,85:15 (KD), D: Si (Et)

4.2 Injection Molded Nanocomposites

4.2.1 Tensile Properties

As discussed earlier, two different solvents; toluene (an aromatic organic solvent) and Kwik-Dri® 66 (a non-aromatic, aliphatic hydrocarbon solvent) were used in the surface modification process. We studied the effect of such two solvent-based modifications on the performance of the resulting nanocomposites.

The tensile modulii data of neat PTT and its nanocomposites are shown in Figure 4.7. The 3 wt.% loading of Ti,90:10 (Tol) clay and Ti,90:10 (KD) clay showed an improvement in modulus versus the neat PTT by 8.5 and 4.3% respectively. The 5 wt.% loading of Ti,90:10 (Tol) clay increased the modulus of PTT by around 18%. PTT containing 3 wt.% Ti,90:10 (Tol) clay nanocomposites exhibits the maximum increase of 6% of tensile strength as compared to neat PTT from 57.3 MPa to 60.6 MPa and maximum elongation at break of 10.5 % among the three nanocomposites (Figures 4.8 and 4.9).

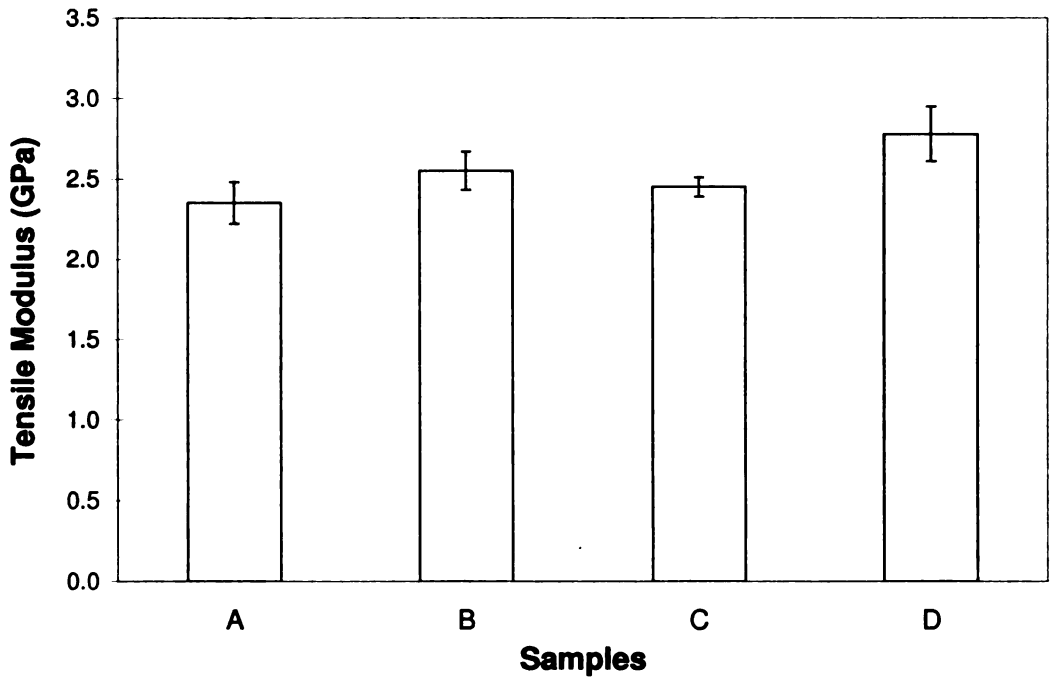

Figure 4.7 *Tensile Modulus of PTT/organoclay nanocomposites*
A: Neat PTT, B: PTT-3 wt% Ti,90:10 (Tol), C: PTT-3 wt% Ti,90:10 (KD), D: PTT-5 wt% Ti,90:10 (Tol)

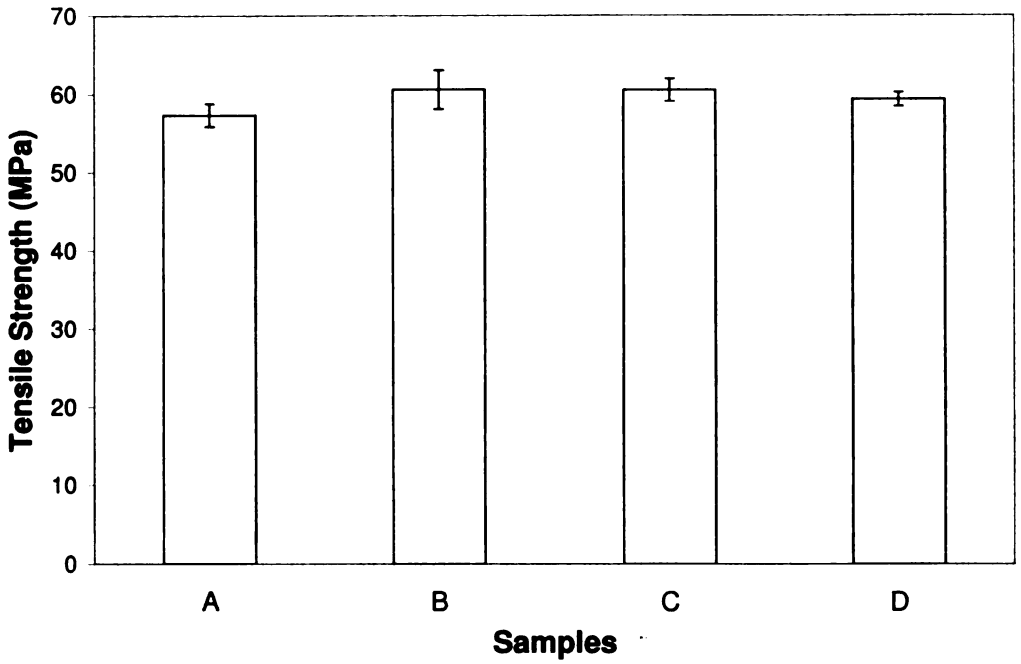

Figure 4.8 *Tensile Strength of PTT/organoclay nanocomposites A: Neat PTT; B: PTT-3 wt%Ti,90:10 (Tol); C: PTT-3 wt%Ti,90:10 (KD;, D: PTT-5 wt%Ti,90:10 (Tol)*

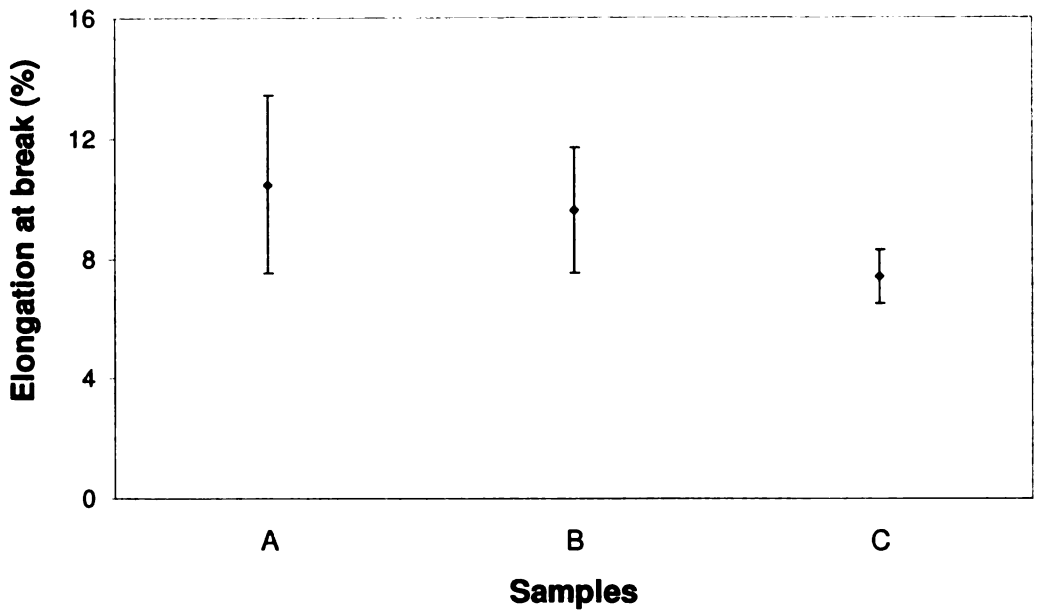

Figure 4.9 *Elongation at break of PTT/organoclay nanocomposites A: PTT-3 wt%Ti,90:10 (Tol); B: PTT-3 wt%Ti,90:10 (KD); C: PTT-5 wt%Ti,90:10 (Tol)*

4.2.2 Thermo-mechanical Properties

Storage modulus measurements were performed on injection-molded samples. The storage modulus of neat PTT and its nanocomposites are reported at 30℃ to determine the effect of organo-modified clays on the thermomechanical properties of PTT. Of the four nanocomposites studied, PTT containing 5 wt.% Ti,90:10 (Tol) clay exhibited the maximum storage modulus of 3.01 GPa, which is 28% more the storage modulus of neat PTT which is 2.35 GPa. PTT with 5 wt.% Ti,90:10 (KD) exhibits an increase of 23%. The storage modulus results indicate that toluene and Kwik-Dri® 66 exhibit similar results,

The heat deflection temperature of PTT and its nanocomposites were measured using DMA Q-800 analyzer. The specimens were heated from 30 to 160℃ at rate of 2℃/min. The PTT with 5 wt.% Ti,90:10 (KD) clay nanocomposites exhibit the maximum HDT of the materials studied, 106℃, an increase of 21% over neat PTT with HDT of 88℃. PTT 3 wt.% Ti,90:10 (Tol) and Ti,90:10 (KD) clay nanocomposites exhibited an increase of 16 and 10% respectively, Figure 4.11. HDT plays an important role in deciding the thermal applications of polymers. Due to high HDT of PTT and its nanocomposites it can be used for thermal resistant packaging applications such as microwavable packaging. As compared with PLA (polylactides) which is 100% biobased polymers has a low HDT of around 60℃ is not suitable for such kind of applications.

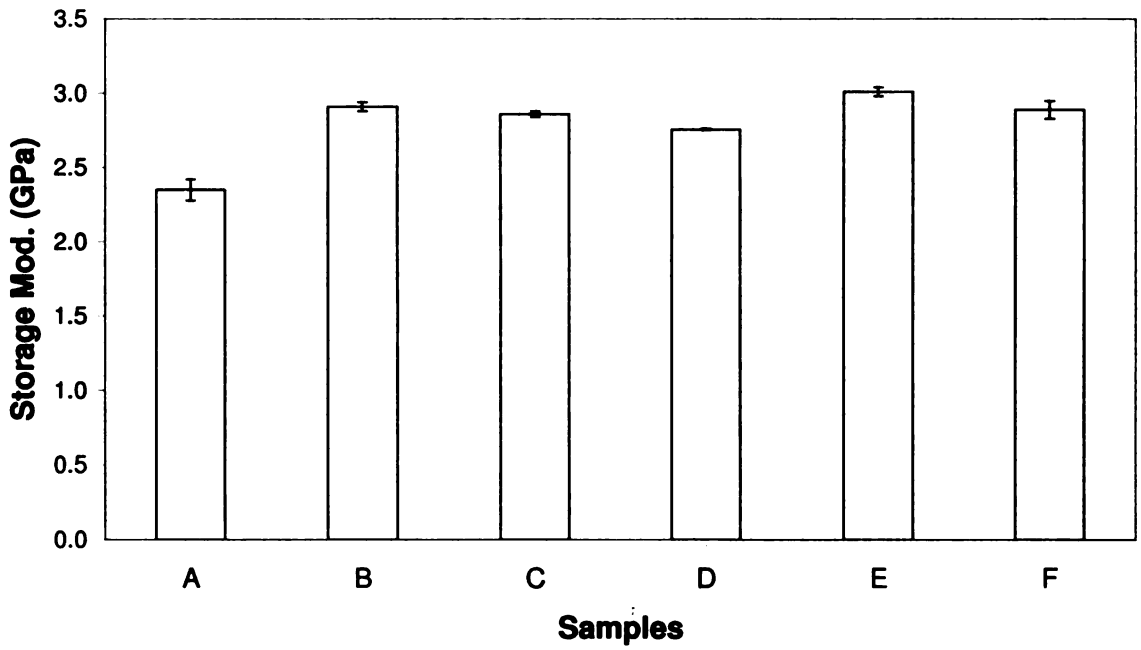

Figure 4.10 *Storage Modulus of PTT/ organoclay nanocomposites*
A: Neat PTT; B: PTT-3 wt% Ti,90:10 (Tol); C: PTT-3 wt% Ti,90:10 (KD); D: PTT-3 wt% Ti,85:15 (KD); E: PTT-5 wt% Ti,90:10 (Tol);F: PTT-5 wt% Ti,90:10 (KD)

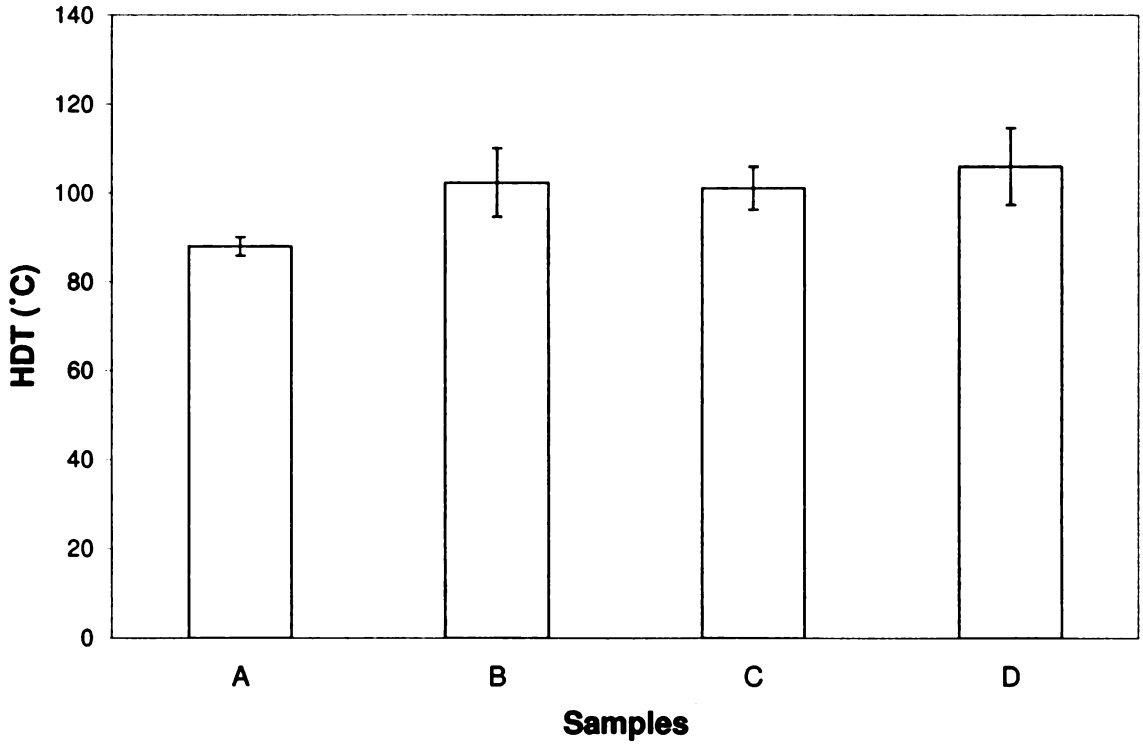

Figure 4.11 *HDT of PTT and its Nanocomposites*
A: Neat PTT; B: PTT-3 wt% Ti,90:10 (Tol); C: PTT-3 wt% Ti,90:10 (KD); D: PTT-5 wt% Ti,90:10 (Tol)

4.3 Extruded Cast Films Nanocomposites

Titanate modified clays of varying titanate modifier and silane coupling agent contents were used to study their effectiveness on the performance of the resulting nanocomposites films. The nomenclature of nanocomposites extruded cast films made from the above listed clays is represented as:

NC-1: PTT w/ 3 wt.% Ti, 90:10 (Tol) clay

NC-2: PTT w/ 3 wt.% Ti, 85:15 (Tol) clay

NC-3: PTT w/ 3 wt.% Ti, 85:15 (KD) clay

NC-4: PTT w/ 5 wt.% Ti, 85:15 (KD) clay

NC-5: PTT w/ 3 wt.% Si (Et) clay

NC-6: PTT w/ 5 wt.% Si (Et) clay

4.3.1 Tensile Properties

The results on tensile properties of the nanocomposites are summarized in Table 4.6 and Figures 4.12 and 4.13.

Table 4.6 *Tensile properties of PTT/organo- modified clay nanocomposites extruded cast films (Value given in parentheses is Standard Deviation)*

Material	Tensile Strength at yield (MPa)	Elongation at break (%)
Neat PTT	42.5 (0.6)	5.7 (0.8)
NC-1	33.4 (1.6)	No break
NC-2	34.5 (1.3)	No break
NC-3	32.9 (3.0)	No break
NC-4	35.9 (1.6)	3.3 (0.3)
NC-5	31.1 (1.1)	No break

The tensile properties of neat PTT film and PTT/titanate modified clay nanocomposites films were measured at 0.4 inch/min cross head speed. It is quite interesting to observe that neat PTT film breaks while nanocomposites films show quite ductile behavior with no breakage, Figure 4.12. Neat PTT film showed a brittle failure whereas nanocomposites exhibit no failure. The tensile strengths of nanocomposites films were found to be inferior versus the neat PTT film, Figure 4.13. The major achievement in this project is ductile behavior of PTT 3 wt.% nanocomposites films. To strengthen our view we observed the nanocomposites films under microscope and found there were voids in films which can help in improving elongation. There are some literatures available which explain the behavior of voids on tensile properties. It was found that due to lack of interaction between nano-reinforcement and polymer, nano-reinforcement can act as void. The decrease of strength may be attributed to poor interfacial adhesion of organoclay with the PTT matrix under the present conditions of nanocomposite fabrication. The voids present in 3 wt% nanocomposites films can allow a larger volume of the matrix in the deformation zone and thereby increasing the elongation to break [66, 67].

As evident from the stress-strain curves toughness of 3wt% nanocomposites films was drastically improved. Toughness is the area under stress-strain curve. Due to such increase in toughness these films can be good choice for high impact films in packaging. The main concern was the color of film which is not consumer appealing which may be improved but that can be used

for military based packaging. Due to voids the barrier is not expected to improve but some high barrier polymers such as EVOH can be co-extruded with PTT based nanocomposites films to improve the performance and thus can be used for extended shelf life packaging films.

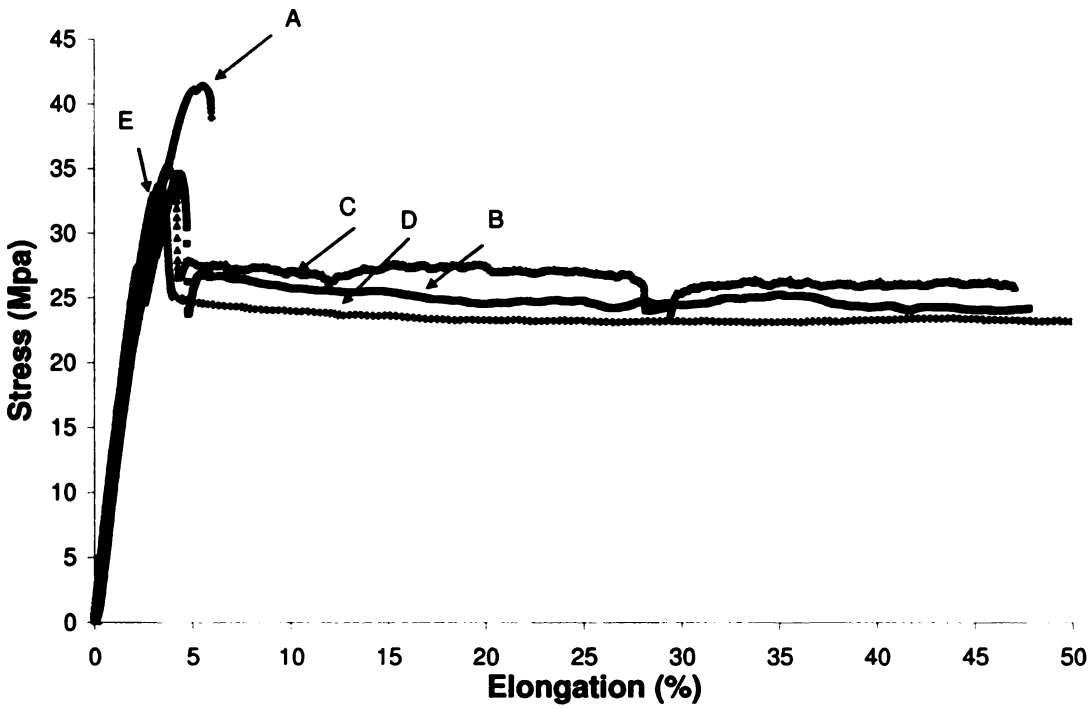

Figure 4.12 *Stress-Strain Curves of PTT and its Nanocomposite Films*
A: Neat PTT, B: NC-1, C: NC-2, D: NC-3, E: NC-4

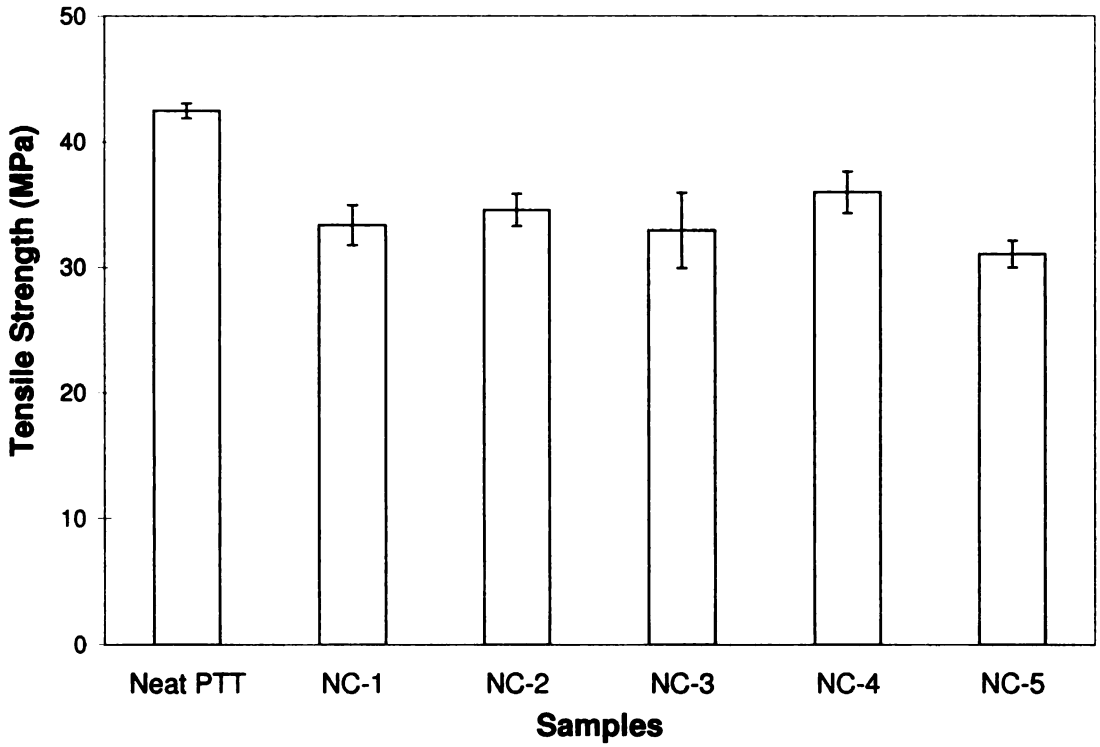

Figure 4.13 *Tensile Strength of PTT and its Nanocomposite Films*

4.3.2 Thermo-mechanical Properties

Storage modulus measurements were obtained using a dynamic mechanical analyzer in the tension mode for the film samples. The storage modulus of neat PTT and its nanocomposites were measured at 30℃ to determine the effect of the organoclays on thermo-mechanical properties of PTT films. Of the two nanocomposites films, NC-4 had the highest storage modulus of 1.99 GPa. The data of DMA studies are shown in Table 4.7 and Figure 4.14. The storage modulus of nanocomposites showed marginal improvement and the maximum tan delta peak was nearly same for both neat PTT and its nanocomposites. Tan delta peak represents the glass transition temperature (Tg) of polymer which was around 60℃ for PTT and its nanocomposites.

Table 4.7 *Storage Modulus and Tan Delta Peak of PTT/organoclay nanocomposites extruded cast films (Value given in parentheses is Standard Deviation)*

Material	Storage Modulus (GPa)	Tan Delta Maximum (°C)
Neat PTT	1.63 (0.06)	59.9 (0.3)
NC-1	1.77 (0.08)	59.3 (0.6)
NC-2	1.74 (0.05)	61.2 (0.3)
NC-3	1.82 (0.10)	58.8 (0.4)
NC-4	1.99 (0.05)	59.6 (0.9)

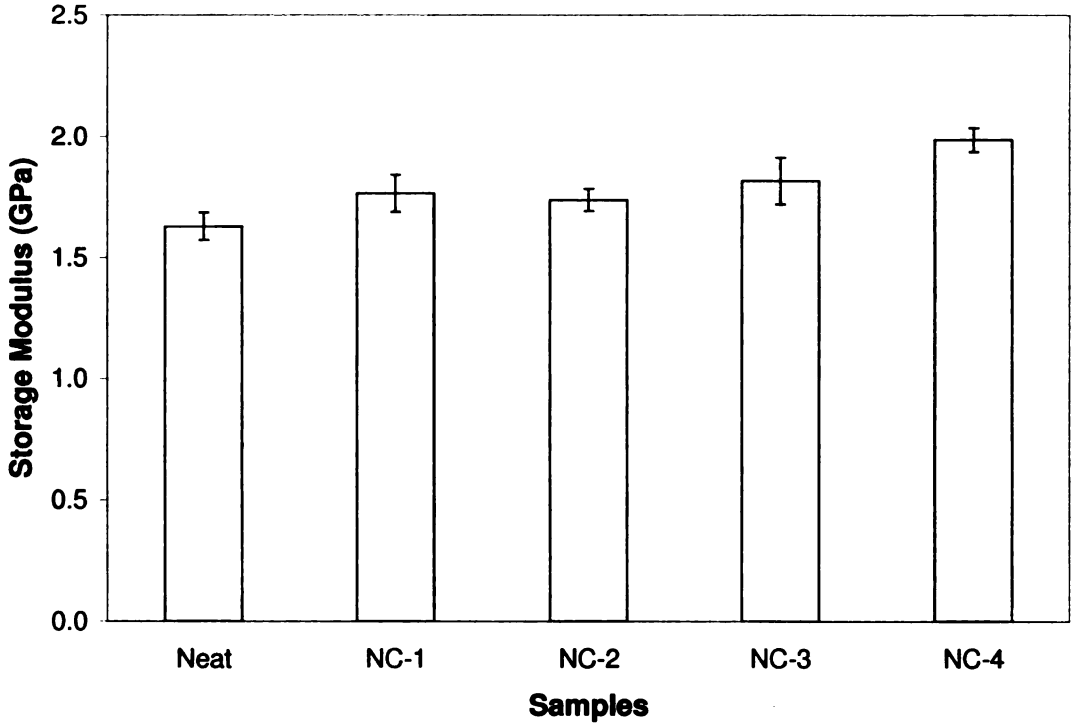

Figure 4.14 *Storage Modulus of PTT and PTT/organo-clay nanocomposites films*

4.3.3 Thermal Properties

Differential Scanning Calorimetry (DSC) was used to study the crystallization behavior of extruded cast films of neat PTT and PTT/titanate clay based nanocomposites. Neat PTT films were also prepared by pressing injection molded blocks and both are compared. As per DSC results there was no significant increase in crystallinity in PTT/ titanate modified clay based nanocomposites extruded cast films. The % crystallinity was calculated by the formula

$$(\Delta H/ \Delta H_{100})^* 100 = \% \text{ crystallinity}$$

Where ΔH is enthalpy of crystallization of PTT sample

And ΔH_{100} is the enthalpy of crystallization of 100% crystalline PTT

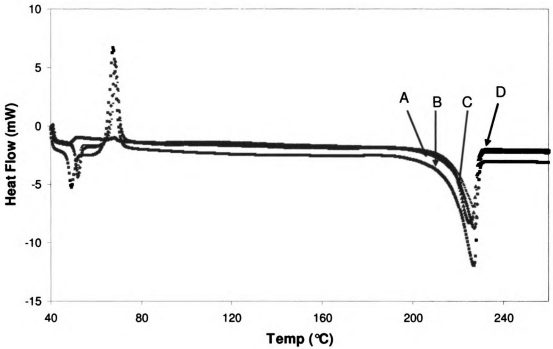

Figure 4.15 *DSC curves for extruded cast films of PTT and its nanocomposites*
A: Neat PTT B: NC-3 (Unstretched area),C: NC-3 (Stretched area) D: NC-4

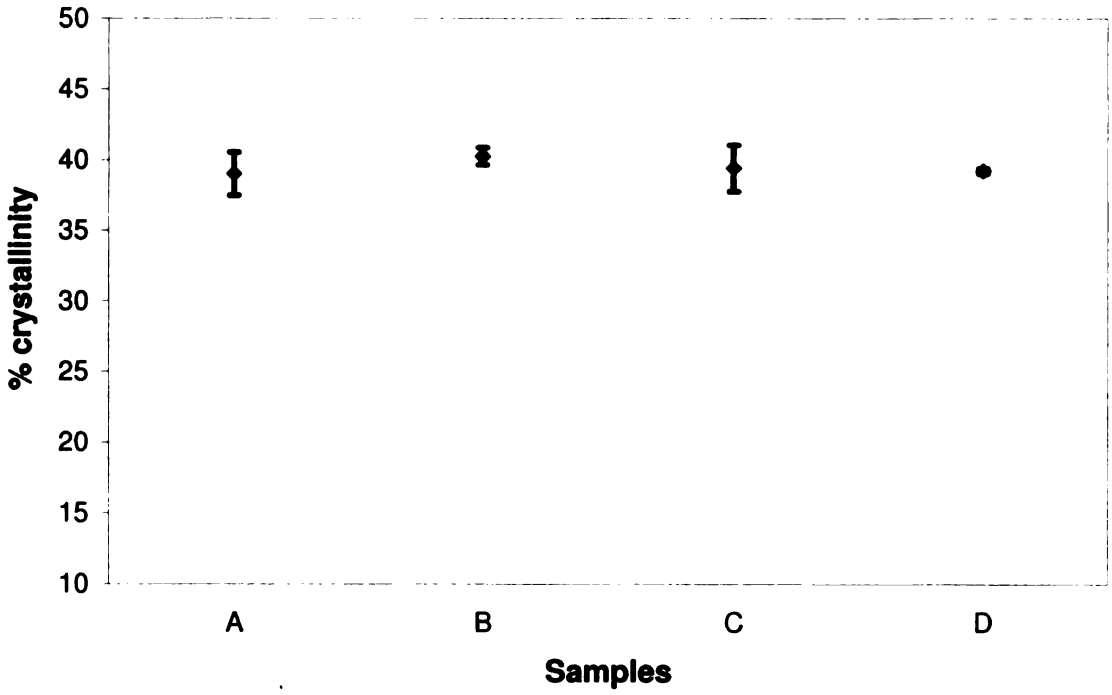

Figure 4.16 *Crystallinity of extruded cast films of PTT and its nanocomposites*
A: Neat PTT B: NC-3 (Unstretched area) C: NC-3 (Stretched area) D:NC-4

4.3.4 Barrier Properties

The barrier properties of neat PTT and its nanocomposites formed as extruded cast films containing 3 and 5 wt.% of titanate modified clay were measured. Table 4.8 lists permeabilities of oxygen and water vapor through extruded cast films of neat PTT and its nanocomposites for 50 cm^2 area films.

Morphological studies of these films showed the presence of voids and agglomeration of clay platelets in nanocomposites which may be due to incompatibility between PTT matrix and organically modified clays. This may be reason for unexpected barrier behavior of nanocomposites extruded cast films.

Table 4.8 *Barrier properties of PTT/organoclay nanocomposites extruded cast films (Value given in parentheses is Standard Deviation)*

Material	O_2 Permeability (cc.mil/100in^2.day.atm)	Water Vapor Permeation (gm.mil/100in^2.day.atm)
Neat PTT	5.8 (0.7)	3.5 (0.1)
NC-4	6.7 (0.3)	4.1 (0.2)

4.3.5 Structural Analysis (XRD)

X-ray diffraction studies of PTT-titanate clay and silane clay based nanocomposites extruded films were conducted to measure the extent of exfoliation/intercalation of clay platelets in the nanocomposites. To measure the d-spacing in films, film sample was mounted on a slit where film sample is exposed to X-ray directly. Table 4.9 shows the basal spacing of PTT based nanocomposites. NC-4 shows maximum increase in d-spacing of 31% versus MMT clay.

Table 4.9 *Basal spacings of raw montmorillonite and modified clays (Value given in parentheses is Standard Deviation)*

Material	2θ°	d spacing(Å)
MMT	7.90	9.71
NC-3	7.00	12.63
NC-4	6.90	12.81
NC-5	7.35	12.02
NC-6	7.10	12.45

4.3.6 Morphological Analysis (TEM & PLOM)

Transmission electron microscopy (TEM) was used to examine the morphology of extruded cast films nanocomposites. The TEM micrographs of NC-1 (Figure 4.17 and 4.18) show intercalation and agglomeration of clay platelets in PTT matrix. The exfoliation of clay is not the only criteria to get enhanced properties of polymer. The polymer/clay interfacial adhesion plays a vital role in properties of polymer, which needs to be further studied.

Polarized light optical microscopy (PLOM) was also used to study the morphological properties of PTT based nanocomposites extruded cast films. Film prepared at US Army Natick Soldier Center labs are shown here. Films prepared at School of Packaging were similar to US Army lab films. PLOM shows that there were voids and clay agglomeration in PTT based nanocomposites extruded cast films, Figure 4.20, whereas in neat PTT films, Figure 4.19, there were less structural and morphological defects which can be a reason for poor barrier properties of PTT-titanate clay based nanocomposites.

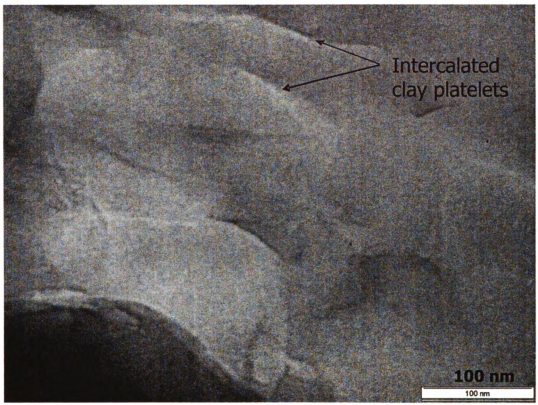

Figure 4.17 *TEM micrograph of NC-1 extruded cast films*

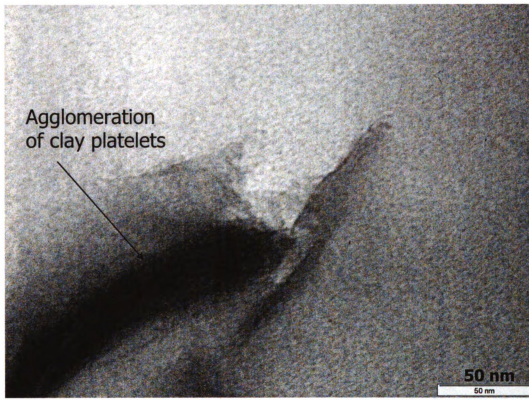

Figure 4.18 *TEM micrograph of NC-1 extruded cast films at 50nm scale*

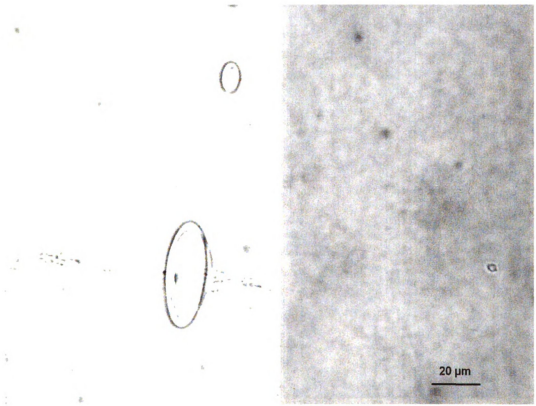

Figure 4.19 *PLOM micrograph of Neat PTT films prepared at US Army Natick Soldier Centre Lab @ 50X*

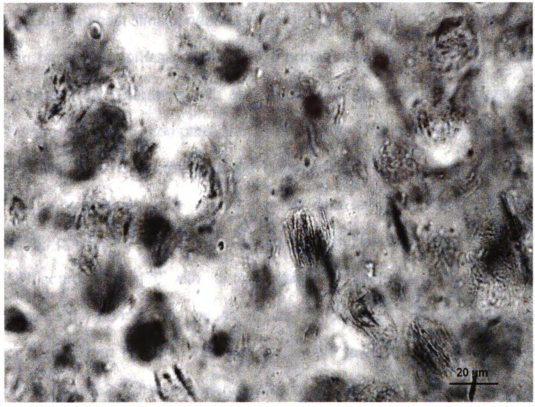

Figure 4.20 *PLOM micrograph of NC-4 films prepared at US Army Natick Soldier Center Lab @ 50X*

4.4 Comparison of Water vapor and Oxygen barrier properties of Sorona® with conventional thermoplastics and poly lactide (PLA)

Extruded cast films of neat PTT (Sorona®) were tested for water vapor and oxygen barrier properties on MOCON® Permatran-W® 3/33 MG and Ox-Tran® 2/21 respectively. Literature data of commercially available thermoplastics and PLA were taken to compare the water vapor transmission and oxygen permeability. We have compared the barrier data of low density polyethylene (LDPE), polypropylene (PP), nylon-6, poly(ethylene terephthalate) (PET) sourced from [68], poly(lactic acid) (PLA) sourced from [69] and ethylene vinyl alcohol (EVOH) sourced from [70] with our fabricated PTT cast films. Units are converted to compare the permeability values. It was found that PTT exhibits better water vapor barrier than Nylon-6, PLA and EVOH but lower than LDPE and PP as shown in Figure 2.2. It was observed that oxygen barrier of PTT is higher than LDPE, PP and PLA but lower than Nylon-6 and EVOH as shown in Figure 2.3. The oxygen barrier and water vapor barrier of PTT films are comparable to PET.

From oxygen permeability and water vapor transmission data, it is clearly evident that PTT (Sorona®) is much better barrier to oxygen and water vapor than PLA, which is 100% renewable based polymer. It can be inferred that Sorona® which is partially bio-based is a better option in cost-performance attribute than 100% bio-based polymers.

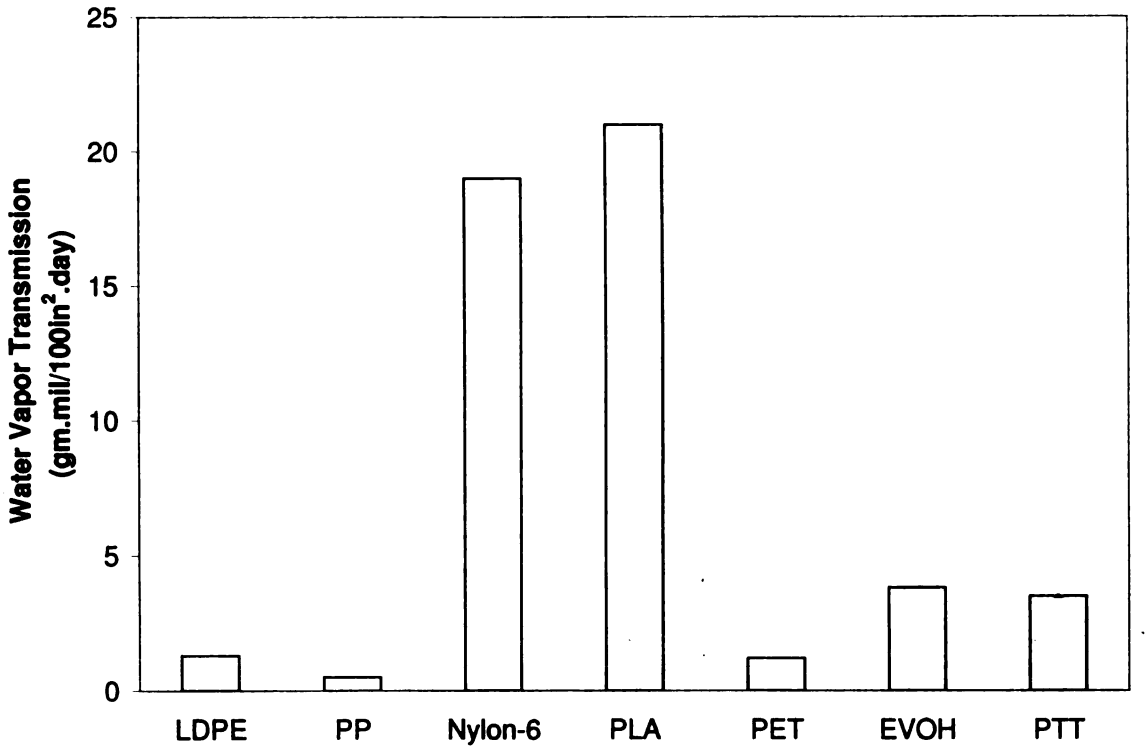

Figure 4.21 *Water Vapor Transmission of polymers at 37.8°C and 50-100%RH (LDPE, PP, Nylon-6 , EVOH and PLA), PTT at 100% RH*

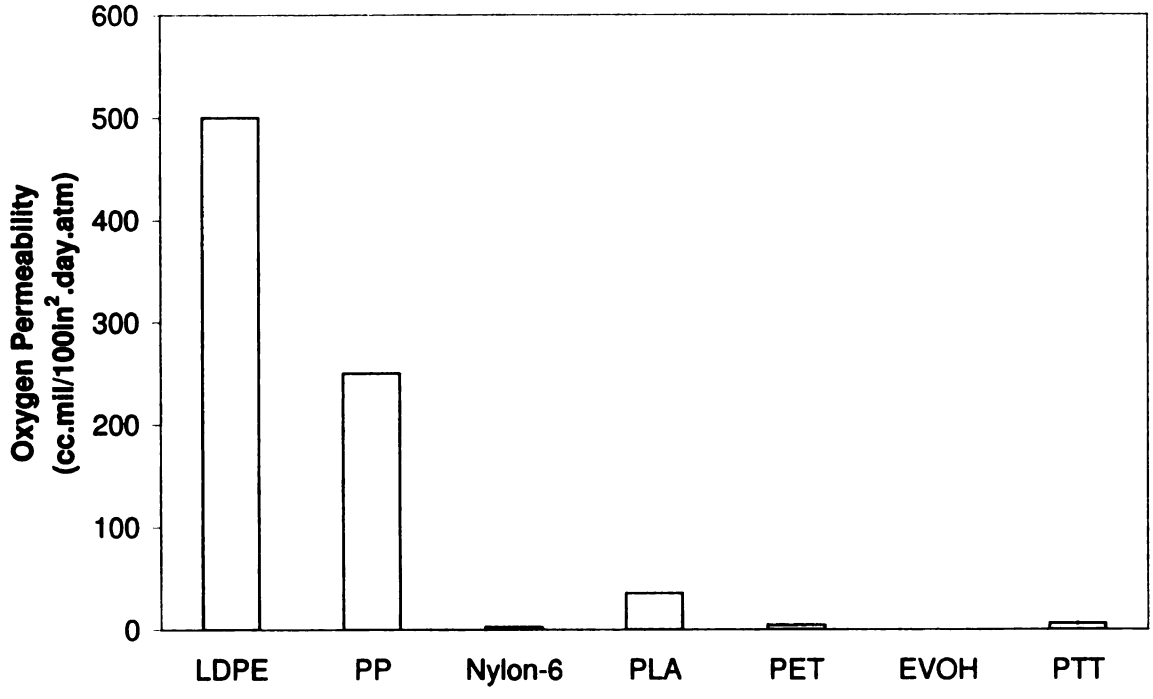

Figure 4.22 *Oxygen permeabilities of polymers at 23°C and 0% RH*

Chapter 5

Conclusions and Recommendations

Poly (trimethylene terephthalate), PTT (Sorona®) is an emerging biobased polymer from DuPont™ that can be made from bio-derived 1, 3 propanediol and petroleum-based terephthalic acid. In this piece of research work, PTT/titanate modified clay (organoclay) nanocomposites were successfully fabricated through melt processing technique. MMT clay was modified with different levels of titanate based organic modifier and silane coupling agent with the target to optimize the titanate modifier loading in clay. XPS, XRD and hydrophilic-hydrophobic balance data validated the successful modification of MMT clay with titanate modifier. Injection molded nanocomposites and cast film nanocomposites were fabricated and characterized. Neat PTT cast film showed gauge bands while PTT/organoclay nanocomposites films were quite even in width and thickness. The tensile modulus and storage modulus of PTT improved by 18% and 28% respectively upon reinforcement with 5 wt% of titanate modified organoclay. Similarly, the heat deflection temperature of PTT improved by 21% with 5 wt% loading of organoclay. Neat PTT and PTT with 5 wt% organoclay nanocomposites film showed brittle failure at a percent elongation value of 5.75 and 3.25%, whilst 3 wt% organoclay nanocomposites films showed quite ductile behavior with no breakage. The transmission electron microscopy (TEM) analysis of PTT/titanate modified clay nanocomposite film revealed intercalated and agglomeration type morphology of the nanocomposites. Polarized light optical microscopy (PLOM) studies showed that there were voids and clay

agglomeration in PTT organoclay nanocomposites films which can be responsible for increasing the permeability of these films. The voids present in 3 wt.% nanocomposites films can allow a larger volume of the matrix in the deformation zone and thereby increasing the elongation to break.

As for future recommendations, the following options can be utilized for optimum properties of PTT and organically modified nanoclays based nanocomposites:

- Use of twice functionalized clay might be a good option to improve compatibility between PTT and clay.
- Use of PTT and tough polymer based blends for improvement of properties.
- Extensive studies on rheology
- Processing optimization

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