Structure-property Relationship of Polylactide/Organoclay Nanocomposites

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Norazura Ibrahim
March 2013
DEDICATION

I dedicate this thesis to my loving family, who ultimately inspired and supported me, each step of the way...
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ABSTRACT

Numerous studies of polylactide (PLA) nanocomposites have been reported. However, the role and importance of processing conditions in preparing the nanocomposites is the subject of very few papers. The effect of filler loadings on nanocomposites also has been widely reported but previous studies either use a narrow range of filler or report a limited range of properties.

In this study, PLA/organoclay nanocomposites with concentrations of 2-10 wt % of montmorillonite (MMT) were prepared by melt intercalation technique and tested for a wide range of properties. One novel contribution of this study is the optimisation of processing conditions by using statistical analysis. A Box-Behnken Design (BBD) of experiments was applied to investigate three variables; processing temperature, rotor speed and mixing time. Results showed that the optimum processing conditions were found to be at 175 °C, 100 rpm and 7 min. These nanocomposites exhibit significant improvement of practical materials properties, such as Young’s modulus and thermal stability, as compared to the neat PLA.

Mixing of the PLA with Cloisite® 30B (the MMT modified with a quaternary ammonium salt) resulted in formation of a nanocomposite material (PLA-30B), with characteristic intercalated peaks seen in small-angle x-ray scattering (SAXS) results and high aspect ratio tactoids or exfoliated layers in transmission electron microscopy (TEM). Rheological behaviour of the PLA nanocomposites showed effective interaction between polymer and organoclay. The rheological properties correlated with the nanostructure evolution and material property enhancement observed in other tests. The percolation threshold was reached around 4.2 wt % filler. Measurement of thermal properties showed that increasing clay content did not influence the glass transition temperature ($T_g$) significantly compared to the pure matrix. However, the melt temperature ($T_m$) and degree of crystallinity ($\chi_c$) increased significantly in the presence of organoclays, indicating the filler acts as a nucleator. An increase in thermal stability with the increase in clay loading level was also observed for PLA nanocomposites. The Young’s modulus of the PLA nanocomposites improved very significantly. At 10 wt % of filler, the increase in Young’s modulus compared with the unfilled PLA was around 54 %. Tensile strength and elongation at break decreased, attributed
to presence of agglomerates. Overall the properties of the nanocomposite PLA-30B were consistent with an exfoliated/intercalated morphology, with good dispersion and interfacial adhesion.

A further novel contribution of this work is the comparison of these nanocomposites to microcomposites made with natural MMT. Microcomposites were made with two types of natural MMT, Cloisite® Na⁺ and Cloisite® Ca²⁺ DEV, to produce samples PLA-Na and PLA-Ca. The main difference between these two types of MMT is that the Na⁺ grade is water dispersible whereas the Ca²⁺ grade is not. Results observed by SAXS shows the composite has a morphology that is neither exfoliated nor intercalated. Scanning electron microscopy (SEM) suggested the morphology has a predominance of agglomerates and aggregates while agglomerates were also observed in TEM. This confirmed that the morphology of these samples was that of a micro- rather than a nanocomposite.

In contrast to PLA-30B, both PLA-Na and PLA-Ca show a decrease in \( G' \), \( G'' \), and \( \eta^* \) in the terminal region (low frequency) compared to neat PLA. This suggested poor dispersion and/or interfacial adhesion between polymer and filler. For the microcomposite samples, the percolation threshold was much higher, around 9 wt %. This is consistent with the lower aspect ratio of filler in these samples compared to a nanocomposite. TGA curves recorded for PLA filled with Cloisite® Na⁺ and Cloisite® Ca²⁺ show that increasing the filler content triggered a substantial decrease in thermal stability, also suggesting poor dispersion. The addition of unmodified clay provided only a modest improvement to the Young’s modulus of PLA. At the same 10 wt % filler loading, PLA-Na and PLA-Ca improved modulus by 18 % and 17 %, respectively. The inferior performance of the micro filler was attributed to the low interaction between the low aspect ratio microparticles and surrounding polymer matrix, as well as the creation of aggregates and/or agglomerates as shown by SEM and TEM. Overall the properties of the microcomposite were consistent with an agglomerated morphology, poor dispersion and interfacial adhesion.

Finally, the composite theory of Halpin–Tsai was applied to predict the Young’s modulus of the nano and microcomposite as a function of the organoclay concentration and aspect ratio. The higher the filler concentration and aspect ratio, the higher the modulus. The objective was to evaluate whether the Young’s modulus of PLA composites (both nano and micro) can be modelled using the Halpin-Tsai micromechanical model. A comparison of the experimental
The data of Young’s modulus with values predicted from a model suggested that the aspect ratio of the clay layer is about 4 for Cloisite® 30B, and about 2 for Cloisite® Na⁺ and Cloisite® Ca²⁺. The model predicted the behaviour of PLA composites satisfactorily with the appropriate material parameters obtained from the literature. However, a more accurate estimate of aspect ratio by quantitative examination of multiple TEM micrographs is recommended.

Other areas suggested for further work include evaluation of barrier properties and biodegradability, whether mixing could be optimised better with a statistical analysis based on a different design of experiments, as well as comparison of properties with other micromechanical models.
Chapter 1: Introduction

1.1 Background

Most plastics are derived from non-renewable crude oil and natural gas resources. They are largely non-biodegradable and caused extensive environmental problems associated with their disposal. Although recycling is an environmentally attractive solution, and most polymers are recyclable, only a small percentage of plastics are actually recycled. On the other hand, recycling processes require considerable expenditure of labour and energy (Ray and Bousmina, 2005). Some widely used plastic materials, notably polystyrene and poly (vinyl chloride), are made from noxious or toxic monomers (Dorgan et al., 2001) that may be released to the atmosphere during their manufacture. Considering the depletion of petroleum reserves in the future, it is desirable to develop materials that use resources other than petroleum, such as renewable resources, to develop commodity plastics that don’t use petroleum or toxic compounds in their manufacture. In addition, such materials also offer the potential of being biodegradable, a property that has value with the growing number of environmentally aware consumers.

Polylactide (PLA) is one of the most important biodegradable and biocompatible polymers in a group of degradable plastics (Mohanty et al., 2002). It can be derived from renewable resources, it is environmentally friendly, and it exhibits interesting physical properties (Drumright et al., 2000, Dorgan et al., 2001, Sinha Ray et al., 2002). Its properties can be further enhanced by filling with selected additives by simple blending in the molten state (Pluta et al., 2007). All these features make PLA an attractive alternative for synthetic plastic materials of petrochemical origin which degrade very slowly (up to several hundred years) (Sinclair, 1996).

The disadvantages with PLA include its relatively high price (Madhavan Nampoothiri et al., 2010, Bhatia et al., 2007), its inherent brittleness, and its tendency to degrade in the presence of water. Hence PLA also poses considerable scientific challenges and limits its large-scale applications (Madhavan Nampoothiri et al., 2010, Nyambo et al., 2010, Wu, 2005). Other main limitations of PLA towards its wider industrial application are its poor thermal resistance and limited gas barrier properties which prevent its complete access to industrial
sectors such as packaging (Singh et al., 2003). Some of the drawbacks can be overcome by the addition of nanoparticles (Kiernowski et al., 2004, Ray and Bousmina, 2005).

In the last few decades, inorganic clay minerals, such as montmorillonite, have been widely used as reinforcement materials for polymers due to their nanoscale size and intercalation/exfoliation properties (Tseng et al., 2001, Vaia et al., 1993, Okamoto et al., 2001b). Nanoclays are less expensive than other nanomaterials, partly because they are produced in existing, full-scale production facilities and because the basic materials come from readily available natural sources (Markarian, 2005). Clay and layered silicate fillers have been most widely investigated for this reason, and now there is a wide body of knowledge on their use in polymer composites (Lan et al., 1995, Ogawa and Kuroda, 1997, Theng, 1974).

It is well known that the combination of polymer and clays, at the nanoscale, can result in remarkably improved mechanical and functional properties with respect to pure polymers or conventional composites (either micro- or macrocomposites) (Okamoto, 2004). Such nanocomposites exhibit improved physical properties, compared to those of the unfilled polymer matrix, as follows: mechanical strength, barrier properties, thermal resistance and dimensional stability. These improvements are seen even at low filler concentration (1-5 wt %) (Sinha Ray et al., 2003c, Ahmadi et al., 2004, Krishnamachari et al., 2009a, Alexandre and Dubois, 2000). The improvement in properties has motivated the academic and industrial communities to develop nanocomposites, looking particularly at the composition and the preparation method (Pluta et al., 2006).

Recently, several studies have focused on the preparation, characterisation, and materials properties of PLA/clay nanocomposites. PLA/clay nanocomposites have special importance because of the promising properties of the polymer matrix and the possibility of high property enhancements by filling with nanoparticles (Pluta et al., 2007). Sinha Ray and co-workers (Ray et al., 2003, Sinha Ray and Okamoto, 2003, Sinha Ray et al., 2002, Sinha Ray et al., 2003b, Sinha Ray et al., 2003a, Maiti et al., 2002b, Sinha Ray et al., 2003c) have undertaken extensive studies on the characterisation, material properties and biodegradability of various PLA/organoclay nanocomposites prepared by melt compounding with a twin screw extruder. Pluta and cowokers (Pluta, 2006, Pluta et al., 2006, Pluta et al., 2002) concentrated on optimisation of the preparation of the nanocomposites (nanoclay delamination) in a counter rotating internal mixer, and characterised the mechanical properties and morphology. Ogata et
al. (1997), Maiti et al. (2002b) and Chang et al. (2003b) have also reported on property enhancement of PLA through the addition of nanoclay.

Despite the recent progress in PLA/clay nanocomposites technology, there are many fundamental questions that have not been answered. Knowledge on the influence of processing conditions on the properties of PLA/organoclay nanocomposites is still lacking. Indeed, understanding the structure–processing–property relationships remains a serious scientific challenge. For example, how do process parameters and fabrication affect composite properties? Although clay has many attractive properties, its application are limited largely because the clay dispersion cannot be easily achieved (Muzny et al., 1996). How efficient is statistical analysis in determining the optimum processing condition to produce composites with better properties? Whether a nanocomposite can be produced for a given polymer and filler, and if formed, will it be intercalated or exfoliated? These issues depend on a variety of factors. These include the type of polymer, layered silicate and organic modifier, the preparation technique and processing conditions (Pavlidou and Papaspyrides, 2008, Liu et al., 2006). It has also been reported that clay aspect ratio and orientation play an important role in determining the properties of polymer nanocomposites (Weon and Sue, 2005).

PLA nanocomposites formed by melt blending have been described previously (Pluta et al., 2002, Sinha Ray et al., 2003a, Di et al., 2005, Pluta et al., 2006); however, these studies have not reported how the conditions were chosen. The role and importance of processing conditions in preparing the nanocomposites is the subject of very few papers. The effect of clay loadings on nanocomposites also has been widely reported (Pluta, 2006, Pluta et al., 2002, Fukushima et al., 2009b) but previous studies either used a narrow range of filler levels or reported on a limited range of properties. Further research is needed to optimise melt blending for PLA nanocomposite preparation.

1.2 Research objectives

The main objectives of the present work can be summarised as follows.

- To find optimum processing conditions of PLA/organoclay nanocomposites made by melt intercalation by using statistical analysis.
To prepare PLA nanocomposites and microcomposites at various concentrations of organoclay and natural clay, respectively.

To investigate the role of structure on the structure-property relationship of PLA/clay nano- and microcomposites by examining the morphology, rheological, thermal and mechanical properties.

To identify the differences in structure and properties between nano- and microcomposites.

To evaluate whether the modulus of PLA/organoclay nanocomposites can be modelled using composite theories such as Halpin-Tsai.

1.3 Research questions
The gap in current knowledge on the structure–property relationships of PLA/organoclay nanocomposites is addressed with the following research questions.

1. What is the morphology of PLA nanocomposites samples produced with various organoclay contents?
2. What is the morphology of PLA microcomposite samples produced with various natural clay contents?
3. What are the thermal, mechanical and rheological properties of the samples?
4. What are the impacts that nanofiller has on thermal, mechanical and rheological behaviour of the PLA composites compare to micro filler?
5. How can the mechanical properties be predicted from knowledge of the structure?

1.4 Research novelty
The novel contributions of this study are:

- The optimisation of processing conditions.
- Broad property assessment (i.e. at various filler content).
- Modelling properties of nanocomposites and microcomposites.
1.5 Research contributions

The outcomes from this project contribute to the field of knowledge of PLA/clay nanocomposites as well as benefiting industry, the community and the environment as below:

*Contribution to the field of knowledge*

- To extend our understanding of the effectiveness and efficiency of organoclay fillers in biopolymers to achieve better properties.
- To promote research into biodegradable polymer and organoclay nanocomposites.

*Benefits to industry*

- To establish an efficient process to optimise processing conditions for melt blending of PLA nanocomposites.
- To identify PLA/organoclay composites that can replace other less environmentally friendly polymer composites in commercial uses.

*Benefits to community and environment*

- To reduce dependence on petroleum based polymers, and hence to reduce pollution caused by synthetic polymer waste.
- To create knowledge that will be useful in the design of more environmentally friendly degradable polymeric materials.
Chapter 2: Literature Review

2.1 Introduction

Plastic packaging materials for example, consist of a large number of different types of polymers; each of them may contain different processing additives such as fillers, colorants, antioxidants and plasticisers. A plastic packaging material may be coated or a multi-layer composite of different polymers for better performance (Davis and Song, 2006). This poses great difficulties in sorting the materials for recycling purposes although there is a crude polymer coding systems already in place. A recycling process requires considerable expenditure of labour and energy: removal of plastic wastes, separation according to the types of plastics, washing, drying, grinding and, only then, reprocessing to final product (Ray and Bousmina, 2005). This process makes the packaging more expensive and makes disposal to landfill a more convenient alternative. Furthermore, the quality of the recycled plastic is lower than that of the material produced directly by the primary manufacturer. Each time polymers are reprocessed there is a loss in physical and mechanical properties due to peroxidation (Gerald, 2000).

The environmental impact of persistent plastic wastes is an increasing global concern. Because of very fast development of society, satisfactory landfill sites are also limited. Incineration of the plastic wastes always produces a large amount of carbon dioxide and creates global warming, and sometimes produces toxic gases, which again contribute to global pollution. Plastics containing chlorinated compounds, such as polyvinyl chloride (PVC), if burnt at low temperatures can produce toxic chlorine compounds with a risk of their additives leaching out (Davis and Song, 2006). Further, since petroleum resources are finite and demand increases year by year, the petroleum price is predicted to surge in future (Anderson, 2000). Hence there are constraints in using raw materials derived from petroleum resources. Consequently, considering the future limits in supply of petroleum, it is necessary to develop materials based on resources other than petroleum such as renewable resources environmental materials (Mohanty et al., 2002, Bogaert and Coszach, 2000).

In the 1970s, it became evident that the very technical advantages which made polymers so useful were disadvantages when polymer-based products were discarded at the end of their
useful life and in particularly when they appeared as litter in the environment (Gerald, 2000). Recycling appeared to be a viable way to reduce pollution and environmental damage when it was first introduced as a waste reduction technique. However, as time has passed, the limitations of recycling have become apparent. It is now obvious that the use of plastics based on renewable feedstocks, which are biodegradable, is a more sensible choice than conventional plastics recycling, as the end products are organic matter, and toxic emissions are avoided. Therefore, the use of plastics which are compostable or easily degraded has been encouraged and developed more intensively (Song et al., 2009, Gross and Kalra, 2002, Kolybaba et al., 2003).

There is a paradigm shift imposed by society’s growing environmental awareness for a safe eco-friendly atmosphere to look for materials and processes that are biodegradable and compatible with the environment. So, as a result of this and decreasing oil reserves, biodegradable materials have been developed. The ever increasing used of plastic films nowadays, results in biodegradability becoming a highly desirable characteristic for plastics, as film has particularly low rates of recycling. In Australia, despite the National Covenant, film recycling is only about 3% (Ark, 2013). Attempts have been made to solve these problems by including biodegradability into polymers in everyday use. This has stimulated research interests in biodegradable polymers.

2.2 Biodegradable polymers

Biodegradable plastics and polymers were first introduced in the 1980s. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources (Vroman and Tighzert, 2009). Biodegradable polymers have attracted significant attention in the last decade in general and, more specifically, they have become the polymer matrix of choice for many researchers in the field of nanocomposites (Marras et al., 2007). Innovations in the development of materials from biodegradable polymers, as well as the possible application of agriculture resources for the production of green materials are some of the reasons why such materials have attracted academic and industrial interest (Lorcks, 1998).
Biodegradable polymers may be defined (Mohanty et al., 2000) as those that undergo microbially induced chain scission, leading to mineralization, photodegradation, oxidation, and hydrolysis, which can alter the polymer during the degradation process. Another definition states that biodegradable polymers are capable of undergoing decomposition, primarily through enzymatic action of microorganisms in to CO\textsubscript{2}, methane, inorganic compounds, or biomass, in a specified period of time.

2.2.1 Biodegradable polymers properties

Most biodegradable polymers have excellent properties comparable to many petroleum-based plastics, and are readily biodegradable, so are competitive with commodity plastics. However, some of the properties, such as brittleness, low heat distortion temperature, high gas permeability, and low melt viscosity, restrict their use in a wide-range of applications. Therefore, modification of biodegradable polymers through innovative technology to is a pressing challenge for materials scientists. On the other hand, nanoreinforcement of pristine polymers to prepare nanocomposite has already proven to be an effective way to improve these properties concurrently (Ray and Okamoto, 2003b). Improvements can include a high storage modulus, both in solid and melt states, increased tensile and flexural properties, a decrease in gas permeability and flammability, increased heat distortion temperature, an increase in the biodegradability rate of biodegradable polymers, and so forth.

2.2.2 Biodegradable polymers applications

Biodegradable polymers can be processed by most conventional plastics processing techniques, with some adjustments of processing conditions and modifications of machinery. Products may be formed by film extrusion, injection moulding, blow moulding, thermoforming etc. (Vroman and Tighzert, 2009). Industry sectors where applications for biodegradable polymers have introduced include (but are not limited to) medicine, packaging, agriculture and the automotive industry (Kolybaba et al., 2003).

According to Gerald (2000), biodegradable polymers are used in two distinct applications. The first is where biodegradability is an essential part of the function of the product. Degradation is important in many applications for various reasons. For examples, in a biomedical application temporary sutures are used in the body during surgery. Degradation of
the polymeric implant means surgical intervention may not be required in order to remove the implant at the end of its functional life, eliminating the need for a second surgery (Gilding and Reed, 1979). Similarly, in agriculture, very thin films of photo-biodegradable polyolefins (mulching films) are used to increase soil temperature, ensuring an earlier harvest. An important requirement is that no significant quantity of plastics residue persist in the soil after the harvest (Gerald, 2000).

The second application for biodegradable polymers is in packaging. Use of biopolymers in packaging continues to receive more attention than in any other application. It is estimated that 41% of plastics are used in packaging, and that almost half of that volume is used to package food products (Kolybaba et al., 2003).

2.2.3 Biodegradable polymers from renewable resources

Over the past decade, there has been a sustained research interest in development of biodegradable polymers from renewable sources as one of the solutions to alleviate solid waste disposal problems and to lessen the dependence on petroleum-based plastics. Biodegradable polymers derived from renewable sources have been a great research challenge to the community of materials scientists and engineers. Interest in short-term packaging and disposable applications has been especially high. (Palade et al., 2001, Ray and Bousmina, 2005).

Biodegradable polymers from renewable resources have been attracting ever-increasing attention predominantly for two reasons: the first being environmental concerns and the second being realization that our petroleum resources are finite. In addition, this kind of material will provide additional income to those involved in agriculture (Yu, 2009). Ray and Okamoto (2003b) reported that nano reinforcement of pristine polymers to prepare nanocomposite has already proven to be an effective way to improve these properties concurrently.

Renewable sources-based biodegradable polymers so far used for the preparation of nanocomposites are PLA (Ogata et al., 1997, Ray and Okamoto, 2003a, Sinha Ray et al., 2002), Poly(3-hydroxybutyrate) (Maiti and Batt, 2003, Bruno et al., 2008, Lim et al., 2003), and thermoplastic starch (Park et al., 2002, Marques et al., 2002) etc. Among these,
polylactides (PLA) are attracting much more attention because of the eco-friendliness of their origin in contrast to petroleum-based biodegradable polymers. (Ray and Bousmina, 2005).

2.3  Polylactide acid (PLA)

PLA is a biodegradable polymer derived from lactic acid. It is a highly versatile material and is made from 100 % renewable resources like corn, sugar beets, wheat and other starch-rich products. PLA exhibits many properties that are equivalent to or better than many petroleum-based plastics, which makes it suitable for a variety of applications (Balkcom et al., 2002).

PLA is not a new polymer. It was first discovered in 1780 by the Swedish chemist Scheele (Datta and Henry, 2006). Historically, due to its high costs resulting from expensive polymerization and purification techniques, low availability and limited molecular weight (Lim et al., 2008, Jacobsen et al., 1999), the main uses of PLA have been limited to medical applications such as medical grade sutures, implants devices and controlled drug release applications. However, recent developments include the discovery of new polymerization routes that allow the economical production of high molecular weight PLA, along with the elevated environmental awareness of the general public, have resulted in an expanded use of PLA for consumer goods and packaging applications (Lim et al., 2008).

2.3.1  PLA productions

PLA belongs to the family of aliphatic polyesters. The molecular structure of PLA is schematically presented in Figure 2.1. PLA is an inherently polar material due to the basic repeat unit of lactic acid (Gruber and O'Brien, 2005). The basic building block of PLA, lactic acid, can be produced by carbohydrate fermentation or chemical synthesis from non-renewable oil-based resources but the former route has received considerable interest recently, due to environmental concerns and the depletion of petrochemical feedstocks.
Three stereoisomers of lactide exist: L-lactide, D-lactide, and meso-lactide (Figure 2.2) (Madhavan Nampoothiri et al., 2010). A polymer made from pure L, or D lactide will be of a semi-crystalline nature, while mixtures of both or a small content of meso-lactide together with L, or D, lactide as a main component will result in amorphous polymers (Jacobsen et al., 1999). Depending on the polymer architecture (i.e., proportion of the L-lactide, D-lactide, and meso-lactide), PLA of variable material properties, such as melting point, mechanical strength, and crystallinity, can be derived. The glass transition temperature ($T_g$) of PLA ranges from 50 °C to 80 °C while the melting temperature ($T_m$) ranges from 130 °C to 180 °C (Auras et al., 2005). This allows the production of a wide spectrum of PLA polymers to match performance requirements (Lim et al., 2008).

![Figure 2.1 Basic structure of PLA](image1)

![Figure 2.2 Stereoforms of lactides](image2)
PLA can be prepared by both direct condensation of lactic acid and ring opening polymerization of the cyclic lactide. Steps of PLA synthesis and can be found in a recent review by Bajpai et al. (2012) and life cycle of its materials is shown in Figure 2.3. The products can be recycled after use either by remelting and processing the material a second time or they can be hydrolysed into lactic acid, the basic chemical. This lactic acid can be re-introduced into the production process of PLA. The last possibility is to compost the PLA to introduce it into the natural life cycle of all biomass, where it degrades into CO$_2$ and water. Here the diversity of PLA becomes obvious. It can be recycled following the traditional ways, composted like all other organic matter, and it will do no harm if burned in an incineration plant or introduced into a classical waste management system (Jacobsen et al., 1999).
2.3.2 PLA advantages

1) *Eco-friendly* - PLA is biodegradable, recyclable and compostable (Drumright et al., 2000, Auras et al., 2004). Its raw material, lactic acid can be efficiently produced by fermentation from renewable resources such as corn, wheat or rice (Lim et al., 2008, Rasal et al., 2010). This can help improve farm economies (Auras et al., 2004). Its production also consumes carbon dioxide (Dorgan et al., 2001). These sustainability and eco-friendly characteristics make PLA an attractive biopolymer.
2) **Biocompatibility** - The most attractive aspect of PLA, especially with respect to biomedical applications, is its biocompatibility. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. Also, the degradation products should not interfere with tissue healing. PLA degradation products are non-toxic (at a lower composition) making it a natural choice for biomedical applications (Athanasiou et al., 1996). PLA is a non-volatile, odourless polymer and is classified as GRAS (generally recognized as safe) by the Food and Drug Administration in the United States (Datta et al., 1995).

3) **Processability** – PLA has thermoplastic processability. PLA resin can be processed like all other thermoplastic polymers with extrusion, injection moulding, blow moulding, or fibre spinning processes into various products (Auras et al., 2004, Auras et al., 2003).

4) **Energy savings** - PLA requires 25-55% less energy to produce than petroleum-based polymers and estimations show that this can be further reduced to less than 10% in the future (Vink et al., 2003). Lower energy use makes PLA production potentially advantageous with respect to cost as well.

PLA has reasonably good optical, physical, mechanical, and barrier properties compared to existing petroleum-based polymers (Auras et al., 2003, Fang and Hanna, 1999). Although PLA is an eco-friendly bioplastic with excellent biocompatibility, processability and less energy dependence, it has drawbacks as well, which limit its use in certain applications.

### 2.3.3 PLA limitations

1) **Poor toughness** - While PLA has modulus and tensile strength comparable to petroleum-based polymers such as poly(ethylene terephthalate) (PET) (Auras et al., 2004). PLA is brittle and has relatively low thermal and impact resistance properties (Lim et al., 2008). The brittleness of PLA may also prevent its use in applications where toughness and impact resistance are critical.

2) **Slow degradation rate** - PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on the PLA crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content (Janorkar et al., 2004, Park and Xanthos, 2009). The degradation rate is often
considered to be an important selection criterion for biomedical applications (Tokiwa and Calabia, 2006). The slow degradation rate leads to a long in vivo life time, which could be up to years in some cases (Bergsma et al., 1995). There have been reports of a second surgery almost 3 years after implantation to remove a PLA-based implant (Bergsma et al., 1995, Incardona et al., 1996). However the slow degradation rate is a serious problem with respect to disposal of consumer commodities.

3) *Lack of reactive side-chain groups* - PLA is chemically inert with no reactive side-chain groups making its surface and bulk modification a challenging task (Rasal et al., 2010).

### 2.3.4 PLA applications

The unique physical characteristics that PLA possesses make it suitable for many different applications. PLA is widely used in the food, cosmetic, medical and pharmaceutical industry. Recently, because of the degradation mechanism, PLA is ideally suited for many applications in the environment where recovery of the product is not practical such as agricultural mulch films and bags (Baek, 2010).

Polylactic acid also has many potential uses in fibres and non-wovens. Major applications for PLA fibres and non-wovens include, but are not limited to, clothing and furnishings such as drapes, upholstery and covers. Some exciting potential applications include household and industrial wipes, diapers, feminine hygiene products, disposable garments, and UV resistant fabrics for exterior use (awnings, ground cover, etc.) among others (Lunt and Shafer, 2000).

### 2.4 Clays

The commonly used clays for the preparation of polymer/clay nanocomposites belong to the same general family of 2:1 layered or phyllosilicates (see Table 2.1). Clays have layered structure. The layers are built from tetrahedral sheets in which a silicon atom is surrounded by four oxygen atoms and octahedral sheets in which a metal like aluminium or magnesium is surrounded by eight oxygen atoms. The tetrahedral (T) and octahedral (O) sheets are fused together by sharing the oxygen atoms (Olad, 2011). The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 30 nm to several microns and even larger depending on the particular layered silicate. This type of layered silicate is characterised by a
A moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 g. This charge is not locally constant, but varies from layer to layer, and must be considered as an average value over the whole crystal (Okamoto, 2004, Alexandre and Dubois, 2000). Details regarding the structure and chemistry for these layered silicates are provided in Figure 2.4.

### Table 2.1 Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates

<table>
<thead>
<tr>
<th>2:1 phyllosilicates</th>
<th>Chemical formula</th>
<th>CEC (mequiv/100 g)</th>
<th>Particle length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$</td>
<td>110</td>
<td>100–150</td>
</tr>
<tr>
<td>Hectorite</td>
<td>$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$</td>
<td>120</td>
<td>200–300</td>
</tr>
<tr>
<td>Saponite</td>
<td>$M_xMg_6(Si_8-xAl_x)Si_8O_{20}(OH)_4$</td>
<td>86.6</td>
<td>50–60</td>
</tr>
</tbody>
</table>

$M$, monovalent cation; $x$, degree of isomorphous substitution (between 0.5 and 1.3).

![Figure 2.4 Scheme of the 2:1 clay structure (Olad, 2011)](image-url)
Among these clays, montmorillonite (MMT) has the widest acceptability for use in polymer nanocomposites. The main advantages of MMT are low cost, ready availability, great potential surface area (750 m²/g), well known intercalation/exfoliation chemistry, high aspect ratio and good swelling properties. Their rich intercalation chemistry allows them to be chemically modified and made compatible with organic polymers for dispersal on a nanometer scale (Krishnamoorti and Silva, 2000). The MMT layer aspect ratio can be in the range 1000 in a well dispersed state without breaking of layers. The clay layers break into smaller plates during preparation process of nanocomposite, so the aspect ratio decreases to about 300-500 (Olad, 2011). When dispersed homogeneously in a polymer matrix, even at a very low weight ratio, the nanolayers can greatly enhance the thermal stability, mechanical and barrier properties, as reported in the literature (Kojima et al., 1993, Alexandre and Dubois, 2000, Maiti et al., 2002a, Ray and Okamoto, 2003b).

2.4.1 Organoclay

Surface modifications of clay minerals have received attention because it allows the creation of new materials and new applications. Organoclays are the most dominant commercial nanomaterial to prepare polymer nanocomposites, accounting for nearly 70 % of the volume used (Markarian, 2005).

The preparation of polymer/clay nanocomposites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles (Olad, 2011). Being only 1 nm thick, the smaller the reinforcing elements are, the larger is their internal surface and hence their tendency to agglomerate due to the high face to face stacking of layers. It is not easy to disperse nanolayers in most polymers due to their tendency to agglomerate rather than to disperse homogeneously in a matrix and their intrinsic hydrophilicity which make them incompatible with hydrophobic polymers (Fischer, 2003, Olad, 2011, Muzny et al., 1996). Only a few hydrophilic polymers, such as poly (ethylene oxide) and poly (vinyl alcohol), can be miscible with clay nanolayers (Pavlidou and Papaspyrides, 2008).

To improve miscibility with other polymer matrices, one must convert the normally hydrophilic silicate surface to organophilic, which makes intercalation possible with many engineering polymers. Generally, this can be done by ion-exchange reactions with cationic
surfactants including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations. The role of alkylammonium or alkylphosphonium cations in the organosilicates is to lower the surface energy of the inorganic host and improve the wetting characteristics with the polymer matrix. This results in a larger interlayer spacing (Okamoto, 2004). Additionally, the alkylammonium or alkylphosphonium (onium) cations could provide functional groups that can react with the polymer matrix or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and the polymer matrix (Krishnamoorti et al., 1996, Blumstein, 1965).

2.5 Polymer nanocomposites
Polymer nanocomposites are commonly defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range (<100 nm). The additives can be one-dimensional (examples include nanotubes and fibres), two-dimensional (which include layered minerals like clay), or three-dimensional (including spherical particles) (Ray and Bousmina, 2006).

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer sizes, nanocomposites with good filler dispersion exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability. Due to nanometer length scale which minimizes scattering of light, nanocomposites are usually transparent (Lagashetty and Venkataraman, 2005). The main reason for these improved properties in nanocomposites is the nanometer scale of the dispersed fillers and the interfacial interaction between matrix and organoclay as opposed to conventional composites (Chen et al., 2002).

2.6 Composites structures
Any physical mixture of a polymer and silicate (or inorganic material in general) does not necessarily form a nanocomposite (Pavlidou and Papaspyrides, 2008). Three main types of composites may be obtained when a layered clay is associated with a polymer, depending on the nature of the components used (layered silicate, organic cation and polymer matrix) and
the method of preparation (Alexandre and Dubois, 2000, Olad, 2011). These are illustrated schematically in Figure 2.5.

Figure 2.5 Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite (Alexandre and Dubois, 2000)

a. *Phase separated structure*: The organic polymer fails to interact with inorganic clay (unmodified clay), so the polymer is unable to intercalate within the clay layers and the clay is dispersed as aggregates or particles, with layers stacked together within the polymer matrix. Unseparated clay layers, after introduction into the polymer, are often referred to as tactoids (Lan et al., 1995, Lan and Pinnavaia, 1996). The composite structure that is obtained is considered to be “phase separated”. The properties of phase separated polymer/clay composites are in the range of traditional micro composites (Olad, 2011). In this systems, the poor physical attraction between the organic and the inorganic components leads to relatively
poor mechanical properties. Furthermore, particle agglomeration tends to reduce strength and produce weaker materials (Giannelis, 1996).

b. *Intercalated structure:* The term intercalation describes the case where a small amount of polymer moves into the gallery spacing between the clay platelets, but causes less than 20–30 Å separation between the platelets (Dennis et al., 2001b). The result is a well ordered multilayer structure of alternating polymeric and inorganic layers, with a repeat distance between them (Pavlidou and Papaspyrides, 2008).

c. *Exfoliated structure:* In exfoliated structures, the silicate layers are completely and uniformly dispersed in a continuous polymer matrix. Exfoliation or delamination occurs when polymer further separates the clay platelets, e.g. by 80–100 Å or more (Dennis et al., 2001b). Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite. For completely exfoliated organoclay, no wide angle x-ray peak is expected for the nanocomposite since there is no regular spacing of the platelets. The distances between platelets is, in any case, too large to be detected by wide angle x-ray scattering (D.R. Paul, 2008).

The early literature seemed to suggest that “intercalation” would be useful and perhaps a precursor to exfoliation (Pavlidou and Papaspyrides, 2008). The exfoliation configuration is of particular interest and more desirable because it maximizes the polymer–clay interactions making the entire surface of layers available for the polymer. This should lead to the most significant changes in mechanical and physical properties. It is generally accepted that exfoliated systems give better mechanical properties than intercalated ones (Varlot et al., 2001, Chin et al., 2001). This good dispersion of the clay platelets gives rise to a bigger property enhancement, since the nanostructure effect can be more pronounced in the exfoliated nanocomposite than in the intercalated one (Marras et al., 2007). However, it is not easy to achieve complete exfoliation of clays and, indeed with few exceptions, the majority of the polymer nanocomposites reported in the literature were found to have intercalated nanostructures or mixed intercalated-exfoliated nanostructures (Chin et al., 2001).
2.7 Preparation of nanocomposite

There are several techniques for preparing polymer-layered silicate nanocomposites. They include four main processes:

Intercalation of polymer and pre-polymer from solution: This is based on a solvent system in which the polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent such as water, chloroform, or toluene (Ray and Bousmina, 2005). It is well known that such layered silicates, owing to the weak forces that stack the layers together can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. This process also includes nanocomposites obtained through emulsion polymerization, where the layered silicate is dispersed in the aqueous phase (Oriakhi, 1998). The first attempts by Ogata et al. (1997), involved dissolving the polymer in hot chloroform in the presence of organomodified MMT. However, TEM and WAXD analyses revealed that only microcomposites were formed and that an intercalated morphology was not achieved. In a later study, Krikorian and Pochan (2003) prepared PLA nanocomposites using dichloromethane as the polymer solvent and as the organoclay dispersion medium. They obtained intercalated or exfoliated nanocomposites, depending on the type of organoclay used.

In situ intercalative polymerization: In this technique, the layered silicate is swollen within the liquid monomer (or a monomer solution) so as the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cationic exchange inside the interlayer before the swelling step by the monomer (Oriakhi, 1998). In Paul et al. (2003a), PLA in the presence of Cloisite® 30B by in situ polymerization lead to an exfoliated morphology. Moreover, intercalated nanocomposites were found to appear even for natural unmodified MMT (Cloisite® Na⁺) (Paul et al., 2003a, Paul et al., 2005a). This technique has also been largely studied for producing poly(styrene)-based nanocomposites (Alexandre and Dubois, 2000). The major disadvantage of this approach is that a suitable solvent is not always available (Stackhouse et al., 2001).
Melt intercalation: The layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. In this technique, no solvent is required (Oriakhi, 1998). As with in situ intercalative polymerization, direct polymer melt intercalation usually requires some pretreatment of the clay mineral, again via exchange of the natural cations with an organic salt. However, in this case the purpose of the treatment is not to aid delamination of the clay mineral. Rather, the presence of the alkylammonium cations within the interlayer renders the hydrophilic clay mineral layers organophilic and therefore increases the enthalpic interactions with the intercalating polymer (Stackhouse et al., 2001).

Template synthesis: This technique, where the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks has been widely used for the synthesis of double-layer hydroxide-based nanocomposites (Oriakhi et al., 1997, Wilson Jr et al., 1999) but is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow (Oriakhi, 1998).

Among these techniques, melt intercalation and in situ intercalative polymerization are the two most commonly used to prepare polymer/clay nanocomposites (Paul et al., 2005a). The first method is effective whenever the thermodynamics of the molten polymer/organoclay pair allows the chains to crawl within the clay interlayer spaces, so pushing the individual sheets apart one from each other. The second method relies on the swelling of the organoclay by the liquid monomer (or by the molten monomer if solid) followed by the in situ polymerization initiated by a suitable compound (Paul et al., 2005a).

Knowing that the best improvement of the matrix properties is most often achieved by the complete delamination of the aluminosilicate layers, there is therefore much interest in preparing exfoliated nanocomposites on an industrial scale. The in situ polymerization approach has several major disadvantage, it employs organometallic catalysts, a degradation-sensitive monomer, and in some cases solvent(s). This limits its (industrial) exploitation. In the case of the solution intercalation technique, its disadvantage is that a relatively large number of solvent molecules must be desorbed from the host in order to accommodate the
incoming polymer chains (Ray and Okamoto, 2003b). Hence the technique of melt intercalation is preferred (Paul et al., 2005a).

The melt intercalation technique has become the method of choice because it is the most industrially viable approach that can lead to commercialized processes using existing infrastructure in the plastics industry such as extrusion and injection moulding (Ray and Bousmina, 2005, Krishnamachari et al., 2009a). The melt intercalation method has great advantages over either polymerization intercalation or polymer solution intercalation. For example, direct melt intercalation is highly specific for the polymer, leading to new hybrids that were previously inaccessible (Vaia et al., 1993). In addition, the absence of a solvent makes direct melt intercalation an environmentally sound and an economically favourable method for industries from a waste perspective. (Krishnamachari et al., 2009a, Shen et al., 2002, Ray and Bousmina, 2005, Vaia et al., 1993). Finally, the new intercalated hybrids represent ideal systems to study polymers in a restricted, two-dimensional geometry produced by conventional techniques such as extrusion and injection moulding. This new approach provides a simple alternative for studying materials properties at interfaces by eliminating the need for specialized analytical techniques with enhanced sensitivity (Vaia et al., 1993). The melt intercalation method allows the use of polymers which were previously not suitable for polymerization or solution intercalation. (Shen et al., 2002).

Quite a number of polymers, including PLA (Krishnamachari et al., 2009a, Ray and Okamoto, 2003a, Fukushima et al., 2009a, Kontou et al., 2011, Pluta, 2006, Sinha Ray et al., 2002, Pogodina et al., 2008) have been blended using melt intercalated with clays, predominantly with layered silicates that have been organomodified.

The work that has already been done on PLA nanocomposites to understand the complex structure–property relationships of the nanocomposites is outlined in the next sections.

2.8 Techniques used for morphology characterisation

Two complementary techniques are generally used to characterise the state of dispersion and exfoliation of nanoparticles: x-ray diffraction (XRD) and transmission electron microscopy (TEM) (Alexandre and Dubois, 2000, Ray and Okamoto, 2003b, Morgan and Gilman, 2003, Giannelis, 1996). Due to its ease of use and availability, wide-angle x-ray diffraction
(WAXD) is the most commonly used technique to characterise the degree of nanodispersion of MMT organoclay in a specific polymer. A second similar technique that is used to characterised high degree of nano dispersion is small angle x-ray scattering (SAXS). WAXD is non-destructive and does not require elaborate sample preparation, which partly explains the wide usage of this technique in material characterisation. Both techniques allow the determination of the spaces between structural layers of the silicate utilizing Bragg’s law: \( \sin \theta = n\lambda/2d \), where \( \lambda \) corresponds to the wave length of the x-ray radiation used in the diffraction experiment, \( d \) is the spacing between atomic planes in the crystalline phase and \( \theta \) is the measured diffraction angle. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (exfoliated or intercalated) may be identified.

With XRD, **immiscible** materials have no change in \( d \)-spacing, meaning that no polymer has entered the gallery and that the spacing between clay layers is unchanged (basal reflections do not change). **Intercalated** nanocomposites have an increased \( d \)-spacing, indicating that polymer has entered the interlayer gallery, expanding the layers, leading to a shift of the diffraction peak towards lower angle, according to Bragg’s law. On the other hand, **exfoliated** nanocomposite show no peak by XRD, suggesting that a great amount of polymer has entered the gallery space, expanding the clay layers so far apart that diffraction cannot be observed with wide-angle XRD techniques or because the nanocomposite does not present ordering (Alexandre and Dubois, 2000, Vaia and Giannelis, 1997).

XRD can be affected by many parameters:

- Sampling (powder vs. solids, alignment of clay platelets)
- Experimental parameters (slit width, count time, angle step rate)
- Layered silicate order (disordered/amorphous materials exhibit no pattern by XRD) (Koo, 2006).

WAXD is relatively a simple process but the analysis can be misleading and are not quantitative (Vaia and Liu, 2002, Morgan and Gilman, 2003). A few studies claim that a structure is exfoliated due to absence of a peak (Krishnamachari et al., 2009a, Denault et al., 2006). However the absence of a peak is not conclusive evidence of an exfoliated structure (Morgan and Gilman, 2003); many factors must be considered to interpret WAXD scans. Intercalated structures may exhibit small or no peaks under a variety of circumstances.
including if the sensitivity or counting time of the scan is low, when the tactoids are internally disordered or not well aligned to one another or when the peak falls outside the WAXD range (Paul and Robeson, 2008). This can lead the erroneous assumption that the clay layers are far apart when in reality they may be closely packed together. This suggests that some samples listed in the literature, from studies that have only used XRD to analyse the nanocomposite materials, may be disordered (immiscible or intercalated) rather than exfoliated, for example (Ishida et al., 2000, Lee et al., 1996). Therefore, XRD results by themselves cannot be used to adequately describe the nanoscale dispersion of the layered silicate present in polymer-layered silicate nanocomposites (Morgan and Gilman, 2003).

In layered silicate nanocomposite systems, a fully exfoliated system is characterised by the absence of intensity peaks in WAXD pattern e.g., in the range $1.5 \degree \leq 2\theta \leq 10 \degree$, which corresponds to a $d$-spacing of at least 6 nm (Park and Jana, 2003). XRD is most useful for the measurement of the $d$-spacing of ordered immiscible and ordered intercalated polymer-layered silicate nanocomposites, but it may be insufficient for the measurement of disordered and exfoliated materials that give no peak. XRD however, has some shortcomings in that it cannot differentiate between delaminated and disordered immiscible systems. As disorder increases in the sample, XRD becomes a less definitive technique (Morgan, 2000).

On the other hand, SAXS can be more informative and somewhat quantitative as reported by numerous studies (Lincoln et al., 2001, Vaia et al., 2003, Justice et al., 2005). However, this technique has not been widely used except in a few laboratories possibly because most laboratories do not have SAXS facilities or experience in interpreting the results (Paul and Robeson, 2008). SAXS is typically used to observe structures on the order of 10Å or larger, in the range of $0 \degree$ or $0.5 – 5 \degree$ (Hussain et al., 2006).

While XRD is the conventional method to determine the interlayer spacing of the silicate layers in the original layered silicates and the intercalated nanocomposites (within 1–4 nm) it does not allow the spatial distribution of the silicate layers or any structural inhomogeneities in nanocomposites to be characterised (Sinha Ray et al., 2003a). Additionally, some layered silicates initially do not exhibit well-defined basal reflections (Vaia et al., 1996). Thus, peak broadening and intensity decreases make some polymer nanocomposites difficult to study with XRD (Ray and Bousmina, 2005).
XRD is usually used in combination with a second technique (TEM) to overcome its limitation. The major drawbacks of XRD are that it may not be sensitive enough to be used with dilute clay loadings (<5%), the results depend on order (such as orientation) and it cannot differentiate between types of dispersions (Morgan, 2000, Morgan and Gilman, 2003). TEM has the key advantage in that it can be used to analyse a system regardless of order or disorder in the clay and it can also determine the difference between a delaminated system and a disordered immiscible system (Morgan, 2000). Morgan and Gilman (2003) revealed that the overall nanoscale dispersion of the clay in the polymer is best described by TEM, especially when mixed morphologies are present (regions of both exfoliated and intercalated nanostructures). TEM allows a qualitative understanding of the internal structure, spatial distribution and dispersion of the nanoparticles within the polymer matrix, and views of the defect structure through direct visualization (Monticelli et al., 2007). However, special care must be exercised to guarantee a representative cross section of the sample. TEM can solve some of the shortcomings encountered with XRD, but it has its limitations as well (Table 2.2); mainly the inability to precisely determine the d-spacing between clay layers and very labour intensive sample preparation and analysis.

<table>
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<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>XRD</td>
<td>Ease of analysis (auto sampling).</td>
<td>Technique dependent on extent or order in clay.</td>
</tr>
<tr>
<td>XRD</td>
<td>Can determine d-spacing between clay layers.</td>
<td>Cannot determine difference between disordered immiscible and delaminated systems.</td>
</tr>
<tr>
<td>TEM</td>
<td>Can determine all types of clay nanostructures.</td>
<td>Labour intensive sample preparation, analysis.</td>
</tr>
<tr>
<td>TEM</td>
<td>Analysis not dependent on order of clay.</td>
<td>Cannot determine d-spacing between clay layers precisely.</td>
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Another technique used to assess micro, hybrid, agglomerate and the morphology of fracture surface of the specimen is scanning electron microscope (SEM). Because the electrons in a TEM pass through the sample, it is commonly used to look at the internal structure of the sample, while SEM looks at the surface (or the near-surface) (Zhou and Wang, 2007). Due to the relative narrower electron beam, SEM has a much greater depth of field (that is, the depth over which the object remains in focus) than TEM, thus yielding a characteristic three-dimensional appearance useful for investigating the surface of objects which have a complicated topography (Liu et al., 2010).

Although the SEM technique has developed significantly in the past decades, it also has some shortcomings that limit its application. For example, samples subjected to SEM analysis must be conductive, although nonconductive samples can be coated with a thin layer of conductive materials, it might cause artifacts on the micrographs. Traditional SEM also requires high vacuum test environment. Environmental SEM was developed to work at higher pressure but the resolution of these devices is relatively limited. The damage to sample surfaces caused by the electron beam is another problem that needs to be considered, which could also create artifacts from time to time. When these problem are solved by advances in SEM technology, a great many more opportunities will be open to the material scientists (Liu et al., 2010).

Combining these techniques provides us with a better description and analysis of these polymer nanostructured materials. No single technique provides sufficient analytical information on the structural characteristics of a polymer nanocomposite. More than one technique is recommended to understand the structures and properties of the polymer nanocomposites fully. One needs to be selective in the choice of analytical tools to be used in each study. Each technique has its own advantages and shortcomings.

In conclusion, XRD results when properly interpreted and combined with TEM results give a clear picture of the nanoscale dispersion and overall bulk dispersion of the clay in nanocomposites polymer samples (Morgan and Gilman, 2003). SEM is used to observe the microstructure of a conventional microcomposite. To provide the most accurate analysis of polymer clay nanocomposites of all types, it is sensible to utilize both XRD and TEM as complimentary tools in the characterisation of these materials. To provide the most accurate analysis of polymer clay microcomposites, it is sensible to use both XRD and SEM.
2.9 PLA/Organoclay nanocomposite properties

Many researchers have been involved in working on PLA/organoclay nanocomposites. Various technologies have been used to produce PLA nanocomposites. Sinha Ray et al. (2002, 2003c, 2003, 2003b) carried out extensive studies on the effects of organic clay modifiers on the properties (biodegradability, melt rheology, etc.) of PLA-clay nanocomposites prepared by melt compounding with a twin screw extruder. Pluta et al. (2002) compared the structure and several physical properties of PLA/clay nanocomposite loaded with organoclay and PLA/clay microcomposite containing sodium montmorillonite prepared by melt compounding using a mixer. Ogata et al. (1997) and Maiti et al. (2002b) have also reported on property enhancement of PLA through the addition of nanoclay.

2.9.1 Morphology properties

PLA MMT nanocomposites have been reported with either exfoliated or intercalated morphology. At lower clay loading (e.g., 2 wt %), a disordered and exfoliated clay nanostructure is most commonly reported, whereas at higher clay concentration (> 5 wt %), a typical ordered intercalated nanoclay morphology is most commonly seen (Singh et al., 2012, Balakrishnan et al., 2010). This indicates that at lower nanoclay content, the clay layers can disperse better and as a result more PLA chains can enter into the clay galleries.

The increase in interlayer spacing of MMT is attributed to the organic modification of MMT which provides the possibility for PLA chains to diffuse between the layers during processing (Shyang and Kuen, 2008). As reported in literature, Cloisite® 30B organoclay has favourable enthalpic interaction between diols present in the organic modifier with the C=O bonds present in the PLA backbone, which is expected to play a significant role in observing exfoliated morphology (Krikorian and Pochan, 2003). It appears that PLA is a polymer that readily interacts during melt blending with a montmorillonite organomodified with dimethyl 2-ethylhexyl (hydrogenated tallow alkyl) ammonium cation, leading to the formation of at least an intercalated structure (Pluta et al., 2002).

Most studies of polymers melt blended with unmodified Cloisite® Na⁺ report formation of a microcomposite, attributed to most polymers being too highly hydrophobic to migrate into the hydrated Na⁺ interlayer space (Paul et al., 2003b).
2.9.2 Rheology properties

The measurement of rheological properties of a polymeric material in the molten state is crucial to gain fundamental understanding of the processability of that material (Sinha Ray and Okamoto, 2003). Polymeric materials, unlike other materials, exhibit liquid-solid (viscoelasticity) behaviour in the melt phase and this leads to added complications in processing. The rheology of polymeric materials often provides an additional insight into the molecular structure of the polymer under varied conditions and thus helps in controlling the desired properties of the final materials (Doyle et al., 1997, Bar-Chaput and Carrot, 2006, Krishnamoorti and Yurekli, 2001). In the case of polymer/layered silicate nanocomposites, the measurements of rheological properties are not only important to understand the knowledge of the processability of these materials, but is also helpful to find out the strength of polymer-layered silicate interactions and the structure-property relationship in nanocomposites (Sinha Ray and Okamoto, 2003).

The rheology of polymer micro and nanocomposites is affected by the level of interaction between the polymer and the filler (Huang and Han, 2006). For nanocomposites, the level of interaction is a function of the shape, size, concentration, and functionality of the filler (Gupta et al., 2010). The clay particles have functional groups that readily interacted with the polymer chains. The clay particles also have very large surface areas due to the high aspect ratio. As discussed previously, the clay particles are normally 1 nm thick and around 100 nm in length. Sometimes, the lateral dimensions go up to few microns as well. It was noted that for polymer-clay nanocomposites, a small amount of clay loading provides significant improvement in rheological response as compared to conventional filled polymeric systems (Gupta et al., 2010).

The investigated rheological properties of PLA/clay nanocomposite are important to understand the effect of organically modified layered silicates (OMLS) (organoclay) on processing as well as the change in viscoelastic properties due to polymer filler interaction (Singh et al., 2012). Many studies have reported the detailed melt rheological properties of a series of organoclay-based nanocomposites of polylactide (Sinha Ray and Okamoto, 2003, Singh et al., 2012, Di et al., 2005, Gu et al., 2007, Wu et al., 2006). The frequency sweep data showed a monotonic increase in storage modulus (G’), loss modulus (G’’), and dynamic viscosities (η*) with organoclay content. The G’ and G’’ of PLA nanocomposites were higher than those of pure PLA at all frequencies and their values increased with increasing clay
content especially at low frequencies. At low frequencies, both dynamic moduli exhibited weak frequency dependence with increasing organoclay content, attributed to gradual changes of behaviour from liquid like to solid like with increasing organoclay content. This behaviour was attributed to the formation of mesoscopic structure of randomly oriented intercalated and stacked silicate layers in the PLA matrix (Sinha Ray and Okamoto, 2003).

2.9.3 Thermal properties

Thermal analysis is an analytical experimental technique which is used to investigate the physical properties of a sample as a function of temperature or time under controlled conditions (Hatakeyama and Hatakeyama, 2004). Instruments used to measure these properties include the differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), differential thermal analysis (DTA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA). Among these, DSC is most popular thermal analysis technique. TGA provides complimentary and supplementary characterisation information to the DSC. Since DSC and TGA were carried out for thermal analysis of the nanocomposites, it is briefly described in the following section.

2.9.3.1 Modulated differential scanning calorimetry (MDSC)

The T_g depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction and steric effects, etc. (Clegg and Collyer, 1986, J.M.G, 1991). Some studies have found that the clay filler does not influence the T_g and T_m of the PLA matrix (Paul et al., 2003b, Chow and Lok, 2009).

One study reported an increase in the T_g of 6 °C with the addition of low levels of filler (1 % Cloisite® 30B). The increase in T_g that comes with the lower loading levels of the Cloisite® 30B could be attributed to the decrease in free volume in the polymer nanocomposite due to cross-linking caused by the intermolecular attraction between the diols of the organic modifier (Cloisite® 30B) with the C=O bonds present in the PLA (Krishnamachari et al., 2009b).

This and other studies also reported a decrease in T_g with the addition of higher levels of filler (Lee et al., 2003, Krishnamachari et al., 2009b). At higher loading levels the nanoclay
particles may provide steric factors that play a role in increasing the chain flexibility of the PLA resin system. This increased flexibility and mobility of the PLA backbones would lead to a decrease in $T_g$. It is possible that the plasticizing effects of clay surfactants are more pronounced at higher loading levels (Krishnamachari et al., 2009a, Krishnamachari et al., 2009b).

One study found that the crystallisation temperature ($T_c$) decreased with the addition of clay when compared to neat PLA (Lee et al., 2003). This was attributed to the large surface areas of nanoclay facilitate the PLA crystallisation process. The nanosized organo-montmorillonite (OMMT) plates provide large surface area due to their small size and thus it is reasonable to consider that the clay particles could act as effective nucleating sites of PLA crystallisation (Lee et al., 2003).

Insufficient DSC data on PLA nanocomposites has been reported to fully understand the influence of morphology on thermal properties (Pluta, 2004).

### 2.9.3.2 Thermogravimetric Analysis

The thermal stability of polymeric materials is usually studied by thermogravimetric analysis (TGA).

Several studies have shown that thermal stability increases with nanoclay loading (Krishnamachari et al., 2009a). This was attributed to an ablative reassembling of the silicate layers, which may occur on the surface of the nanocomposites, creating a protective physical barrier (Krishnamachari et al., 2009a). The increase in thermal stability was also attributed to the high thermal stability of clay and to the favourable interactions between the surface of nanoclay particles and the polymer matrix (Fischer et al., 1999, Petrović et al., 2000).

One study also showed an improvement in the nanocomposite thermal stability under oxidative conditions, reduced flammability, together with char formation, for PLA/MMT nanocomposites, compared to the microcomposites and pure PLA (Pluta et al., 2002, Pluta, 2006). Addition of Na$^+$ montmorillonite (unmodified) to PLA did not significantly affect the thermal degradation. By varying the blending time, Pluta and coworkers also showed that the increase in decomposition temperature was related to the increase of dispersion of the silicate...
nanoplatelets, confirmed by TEM and XRD analysis. This was attributed to higher dispersion of silicate nanoplatelets making a more efficient obstacle in the progress of degradation process.

Some studies observed a decrease in thermal stability at high levels of MMT loading (Balakrishnan et al., 2010), Wu and Wu (2006) attributed to agglomeration and poor dispersion of MMT. Agglomeration reduces MMT’s surface area available for char formation thus, reducing the degradation temperature of PLA nanocomposites.

2.9.4 Mechanical properties

Most studies of PLA/organoclay nanocomposites report dramatic improvements in mechanical and various materials properties compared with those of pure PLA. Many studies have shown increases in modulus and strength. Krishnamachari et al (2009a) reported there was a 12 % increase in tensile strength and 16 % increase in Young’s modulus with addition of just 1 % (w/w) of Cloisite® 30B. The addition of 4 phr of MMT to PLA increased the Young’s modulus of the nanocomposites by 10 % (Balakrishnan et al., 2010). Jiang et al. (2007) also reported an increase in Young’s modulus from 3500 to 5000 MPa in PLA/MMT nanocomposites with 7.5 wt % concentration of MMT. The improvement in stiffness was attributed to the reinforcement effect of the rigid inorganic MMT, which constrains the molecular motion of PLA chains as well to, the existence of hydrogen–bondings interactions between PLA hydroxyl end groups and the MMT platelets surfaces and/or the hydroxyl groups of the ammonium surfactant in the organically modifies clay. The PLA’s chain movement was also suppressed by MMT tethering and gallery confinement (Jiang et al., 2007).

The improvement in the modulus of PLA/MMT nanocomposites may also be caused by the intercalation and exfoliation of MMT layers in PLA (refer to morphological analysis). When the clay particles are dispersed in intercalated and/or exfoliated form, it leads to a higher aspect ratio of the silicate layer, and a larger interfacial area. Both the higher aspect ratio and interfacial area will make stress transfer to the silicate layers more effective, and subsequently improve the mechanical properties of the formed nanocomposites. A dramatic improvement in modulus attributed to the exfoliated morphology has also been reported for PLA/MMT nanocomposites by other researchers (Chang et al., 2003a, Wu and Wu, 2006).
Although the addition of MMT improves the Young’s modulus of nanocomposites, some studies report it comes with a sacrifice of tensile and flexural strength which is important for certain applications such as packaging. Balakrishnan (2010) reported that the addition of 4 phr of MMT had decreased the tensile strength and flexural strength by 10 % and 25 %, respectively.

Most studies on the mechanical properties of nanocomposites were limited to using dynamic mechanical analysis (Ray and Okamoto, 2003b). Little data has been reported using tensile (tension) tests. These mechanical properties of PLA nanocomposites have not been studied in detail.

2.10 Modelling of mechanical properties

Quite a few theoretical frameworks have been developed for predicting properties of composite materials based on the properties of the pure components and the morphology of the composite. An assumption inherent in all of these theories is that each component of the composite acts independently of the other. While the general objective of such theories is to predict performance of the composite for given set of components, these theories enable a simple route for evaluation of the individual contribution of component properties such as matrix and filler modulus, volume fraction, filler aspect ratio, filler orientation, and so forth. Aspect ratio is an important factor in polymer nanocomposites and drives an interest in achieving a high level of platelet exfoliation. (Fornes and Paul, 2003).

In general, it is held that the same approaches used for conventional composites could be applied to nanocomposites. Ideally experimental-based research is used to determine structure-property relationships of nanostructured composites. However, experimental synthesis and characterisation of nanostructured composites demands the use of sophisticated processing methods and testing equipment; which could result in excessive costs. To this end, modelling techniques for the determination of mechanical properties of nanocomposites are in reasonable agreement (Fornes and Paul, 2003, Valavala and Odegard, 2005, Odegard et al., 2005).

Micromechanical-based models have been used in the case of composites to analyse the effect of filler's structural parameters, such as shape, aspect ratio, and orientation, on the mechanical
properties of a neat matrix. Although these micromechanical models cannot be used to fully account for the exact mechanical behaviour of polymer nanocomposites, they generally give satisfactory correlations.

Numerous attempts have been made to study the mechanical behaviour of polymer nanocomposites using modelling techniques. Among of these, Halpin–Tsai and Mori–Tanaka (Fornes and Paul, 2003; Valavala and Odegard, 2005; Weon, 2009; Yung et al., 2006) are commonly used in polymer nanocomposites. According to Weon (2009), mechanic-based model prediction, such as Mori-Tanaka, Halpin-Tsai and shear lag, provides a better understanding regarding the dependence of the nanocomposites’ reinforcement efficiency on conventional filler structural parameters such as filler aspect ratio ($\alpha$), filler orientation ($S$), filler weight fraction ($\psi_f$), and filler/matrix stiffness ratio ($E_f/E_m$).

It is well known that Halpin-Tsai and Mori-Tanaka theories are wildly applied to predict the stiffness of discontinuous fibre-reinforced composites. Mori-Tanaka theory (1973) offered the best prediction for the properties of composites with relatively large aspect ratio of fillers. The models based on Halpin-Tsai theory (Ashton et al., 1969, Halpin, 1969, Affdl and Kardos, 1976) provided reasonable estimations for reinforcement efficiency of composite materials.

### 2.10.1 Halpin–Tsai model

The Halpin–Tsai theory is adaptable for a variety of reinforcement geometries, especially discontinuous filler reinforcements. A detailed review and derivation is provided by Halpin and Kardos (1976). In the Halpin–Tsai theory, the longitudinal and transverse Young’s moduli are expressed by $E_{11}$ and $E_{22}$, respectively (Sperling, 2005). Halpin and Tsai developed a well-known composite theory for predicting the stiffness of unidirectional composites as a function of aspect ratio (Affdl and Kardos, 1976, Halpin, 1969, Ashton et al., 1969). This theory is based on the early micromechanical works of Hermans (1967) and Hill (1964). Hermans generalized the form of Hill’s self-consistent theory by considering a single fibre encased in a cylindrical shell of the matrix that is embedded in an infinite medium assumed to possess the average properties of the composite.
Halpin and Tsai reduced Herman’s results into a simpler analytical form adapted for a variety of reinforcement geometries, including discontinuous filler reinforcement. The overall composite moduli $E_c$ can predicated by Halpin and Kardos (1976):

$$\frac{E_c}{E_m} = \frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f}$$

Equation 2.1

where constant, $\eta$ is given by

$$\eta = \frac{E_f / E_m - 1}{E_f / E_m + \zeta}$$

Equation 2.2

where $E_c$, $E_f$, and $E_m$ represent the overall Young’s modulus of the composite, filler, and matrix, respectively, $\phi_f$ is the volume fraction of the filler, $\zeta$ is a shape parameter dependent upon filler geometry, orientation and loading direction, which is a function of aspect ratio.

For $E_{11}$, $\zeta$ equals $2(l/t)$, where $l$ and $t$ represent the length and thickness of the fibre. The transverse modulus, $E_{22}$, perpendicular to the fibre direction, remains relatively insensitive to the fibre aspect ratio, and is approximated by $\zeta = 2$.

Furthermore, the Halpin–Tsai equations retain the same form for both discontinuous cylindrical fibres and lamellar shape reinforcements such as rectangular platelets. For rectangular platelets, however, the quantity $\zeta$ equals $l/t$ and $w/t$ for calculating $E_{11}$ and $E_{22}$, respectively, where $l$ represents the length, $w$ the width, and $t$ the thickness of the dispersed platelets Halpin and Kardos (1976).

Figure 2.6 (Fornes and Paul, 2003) summarises the results of the Halpin–Tsai equations, and also those of the Mori–Tanaka theory, to be discussed later. It is apparent from their geometry, that disk-like platelets can provide equal reinforcement in two directions. Also, note the symbolism where $E_\parallel$ and $E_\perp$ represent the composite modulus parallel and perpendicular to the major axis of the filler.
Tucker and Liang (1999) have reported the application of several models for fibre-reinforced composites demonstrating that the Halpin–Tsai theory (Affdl and Kardos, 1976) gives reasonable predictions in the case of the modulus. However, at high filler concentration, Nielsen (1970) reported that the predicted value of Equation 2.1 is lower than the experimental data, which can be assigned to the fact that Equation 2.1 omits several important factors. Fornes and Paul (2003) show that in the case of completely random orientation in all three orthogonal directions, platelets will inherently provide more effective reinforcement than fibres. The equivalent equation for randomly placed platelets is given by

$$E_{\text{ran-3D}}^\text{platelets} = 0.49E_{\parallel} + 0.51E_{\perp}$$

Equation 2.3
Fiber Disk-like Platelet

Direction of Applied Load | Halpin-Tsai Composite Modulus | Shape Parameter, $\zeta^{(a)}$  
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibers</td>
<td>Platelets</td>
</tr>
<tr>
<td>1</td>
<td>$E_{11} = E_\parallel$</td>
<td>$E_{11} = E_\parallel$</td>
</tr>
<tr>
<td>2</td>
<td>$E_{22} = E_\perp$</td>
<td>$E_{22} = E_\parallel$</td>
</tr>
<tr>
<td>3</td>
<td>$E_{33} = E_\perp$</td>
<td>$E_{33} = E_\parallel$</td>
</tr>
</tbody>
</table>

(a)The symbol $l$ represents the length of the fiber or diameter of the disk, $d$ represents the fiber diameter, and $t$ is thickness of the disk.

(b)

Fiber Disk-like Platelet

<table>
<thead>
<tr>
<th>Direction of Applied Load</th>
<th>Mori-Tanaka Composite Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fibers</td>
</tr>
<tr>
<td>1</td>
<td>$E_{11} = E_\parallel$ (Eq 2.4)</td>
</tr>
<tr>
<td>2</td>
<td>$E_{22} = E_\perp$ (Eq 2.5)</td>
</tr>
<tr>
<td>3</td>
<td>$E_{33} = E_\perp$ (Eq 2.5)</td>
</tr>
</tbody>
</table>

Figure 2.6 Physical representations, coordinate systems, and corresponding (a) Halpin–Tsai and (b) Mori–Tanaka equations used for the calculation of composite stiffness based on fibre and disk-like platelet reinforcement.
2.10.2 Mori–Tanaka model

In the Mori–Tanaka method, it is assumed that there are only two phases (matrix and reinforcement), and they are perfectly bonded to each other. Through a multitude of publications, the Mori–Tanaka approach (Benveniste, 1987, Mori and Tanaka, 1973) has been used to accurately predict overall properties of composites when the reinforcements are on the micrometer-scale level, or higher. At these higher length scales, the assumption of the existence of two phases is apparently acceptable. However, for nanometer-sized reinforcement, it has been shown that the molecular structure of the polymer matrix is significantly perturbed at the reinforcement/polymer interface, and this perturbed region is on a length scale that is the same at that of the nanometer-sized reinforcement (Odegard et al., 2003). Therefore, at the nanometer level, the reinforcement and adjacent polymer region is not accurately described as consisting of just two phases, thus the Mori–Tanaka model is not expected to perform well for nanostructured reinforcements (Odegard et al., 2005). The Mori-Tanaka models are expressed (Tandon and Weng, 1984):

\[
\frac{E_{11}}{E_m} = \frac{A}{A + \phi_f (A_1 + 2\nu_m A_2)}
\]

\text{Equation 2.4}

\[
\frac{E_{22}}{E_m} = \frac{2A}{2A + \phi_f [-2\nu_m A_3 + (1 - \nu_m)A_4 + (1 + \nu_m)A_5 A]}
\]

\text{Equation 2.5}

Where \( \phi_f \) is the volume fraction of filler, \( \nu_m \) is the Poisson’s ratio of the matrix, and \( A_1; A_2; A_3; A_4; A_5; \) and \( A \) are functions of the Eshelby’s tensor and the properties of the filler and the matrix, specifically Young’s modulus, Poisson’s ratio, filler concentration and filler aspect ratio; complete details of these equations are given elsewhere (Tandon and Weng, 1984). It is important to note that the composite moduli in Equation 2.4 and Equation 2.5 are dependent upon the shape of the filler. Figure 2.6 (b) shows the Mori–Tanaka physical representation of glass fibres and disk-like platelets and tabularizes the different equations used to calculate composite moduli along the three principle orthogonal directions (Fornes and Paul, 2003).
A number of assumptions are inherent to both approaches. It must be noted that the Mori-Tanaka theory treats fibres and disks as ellipsoidal particles, whereas the Halpin-Tsai theory treats a fibre directly, but assumes that a disk is a rectangular platelet (Fornes and Paul, 2003). Using micromechanics-based composite models, a few of the more recent studies (Sheng et al., 2004, Fornes and Paul, 2003) have attempted to examine how the nanofiller structural parameters (e.g. shape, aspect ratio and orientation) affect the mechanical properties. Although these micro-mechanical models cannot be used to fully account for the exact mechanical behaviour of polymer nanocomposites, they generally give satisfactory correlations.

Last, it is important to emphasize that numerous complexities arise when comparing composite theory to experimental composite data, particularly for polymer layered silicate nanocomposites. Fornes and Paul (2003) summarises some of the issues involved in Table 2.3.
Table 2.3 Some important issues that limit the ability to model the stiffness properties of polymer-layered silicate nanocomposites (Fornes and Paul, 2003)

<table>
<thead>
<tr>
<th>Issue</th>
<th>Theory</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler shape and size</td>
<td>▪ Uniform shape</td>
<td>▪ Non-uniform shape</td>
</tr>
<tr>
<td></td>
<td>▪ Constant dimensions</td>
<td>▪ Distribution of lengths and thickness</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Imperfect exfoliation of layered silicates</td>
</tr>
<tr>
<td>Filler orientation</td>
<td>▪ Unidirectional</td>
<td>▪ Some degree of misalignment</td>
</tr>
<tr>
<td>Filler interface</td>
<td>▪ The filler and matrix are well bonded</td>
<td>▪ Imperfect bonding between the filler and matrix</td>
</tr>
<tr>
<td>Filler modulus</td>
<td>▪ Assumes filler modulus is the same in all directions</td>
<td>▪ Filler is anisotropic</td>
</tr>
<tr>
<td>Matrix considerations</td>
<td>▪ Assumes matrix is isotropic</td>
<td>▪ Polymer chain orientation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Presence of polymer crystallites</td>
</tr>
<tr>
<td>Filler concentration effects</td>
<td>▪ No particles-particle interactions</td>
<td>▪ Particle-particles interactions and agglomerations</td>
</tr>
<tr>
<td></td>
<td>▪ Ignores changes in viscosity</td>
<td>▪ Changes in viscosity can alter morphology during injection moulding</td>
</tr>
<tr>
<td></td>
<td>▪ No particle agglomeration</td>
<td>▪ Changes in crystalline morphology (e.g type, crystallite size and amount)</td>
</tr>
</tbody>
</table>
Chapter 3 : Experimental

3.1 Introduction

This chapter describes the materials, equipment and the methodologies used in the study and characterisation of PLA nanocomposites. The techniques include mechanical measurements by Instron, rheology measurement by an advanced rheometric expansion system (ARES), thermal measurement by modulated differential scanning calorimeter (MDSC) and thermogravimetric analysis (TGA), and morphology measurements by small-angle x-ray scattering (SAXS), environmental scanning electron microscopy (ESEM) and transmission electron microscopy (TEM). In addition molecular weight measurement of polymer using gel permeation chromatography (GPC) and filler size using dynamic light scattering (DLS) are covered. The inherent errors that exist in the experiments carried out in this study and the steps taken to minimise them are also briefly discussed.

3.2 Materials

NatureWorks® PLA polymer 7000D used in this study is a commercial product of NatureWorks LLC. This resin was obtained from Dr. Katherine Dean, CSIRO. It is a bottles grade resin designed for injection stretch blow moulded applications. PLA polymer 7000D typically processes at lower temperatures than PET and can retain a greater level of detail on conventional equipment. The PLA7000D® contains 6.4 % of D-lactic units (Julien et al., Bergeret and Benezet, 2011). Table 3.1 shows the properties of PLA 7000D.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>PLA 7000D</th>
<th>ASTM Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.25-1.28</td>
<td>D792</td>
</tr>
<tr>
<td>Melt Density (230 °C)</td>
<td>1.08-1.12</td>
<td>D1238</td>
</tr>
<tr>
<td>$T_g$ (°C)</td>
<td>55-60</td>
<td>D3417</td>
</tr>
<tr>
<td>$T_c$ (°C)</td>
<td>145-155</td>
<td>D3418</td>
</tr>
</tbody>
</table>

(1) Typical properties; not to be construed as specifications.
The organoclay used to form the nanocomposites here are produced by Southern Clay Products, Inc. marketed under the trademark Cloisite® 30B. It is a natural MMT modified with a quaternary ammonium salt. Cloisite® 30B is an additive for plastics to improve various plastic physical properties such as modulus, heat deflection temperature (HDT), coefficient of linear thermal expansion (CLTE) and barrier. This organoclay has a surfactant (see Figure 3.1) having two hydroxyl groups.

Two types of natural MMT, Cloisite® Na⁺ and Cloisite® Ca⁺⁺DEV were also used in this study. The difference between these two types of MMT is that the Na⁺ grade is water dispersible whereas the Ca⁺⁺ grade is not. Both can be used for plastics to improve physical properties. Table 3.2 shows the properties of Cloisite® 30B, Cloisite® Na⁺ and Cloisite® Ca⁺⁺DEV (as stated by the manufacturer).

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OH} & \\
| & \\
\text{CH}_3 - \text{N}^+ - \text{T} & \\
| & \\
\text{CH}_2\text{CH}_2\text{OH} & 
\end{align*}
\]

Where T is Tallow (~65 % C18; ~30 % C16; ~5 % C14)

MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

**Figure 3.1 Chemical structure of surfactant**

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Cloisite® 30B</th>
<th>Cloisite® Na⁺</th>
<th>Cloisite® Ca⁺⁺DEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Off-white</td>
<td>Off-white</td>
<td>Off-white</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.98</td>
<td>2.86</td>
<td>2.80</td>
</tr>
<tr>
<td>d-spacing (d_{001}) (Å)</td>
<td>18.5</td>
<td>11.7</td>
<td>15.5</td>
</tr>
<tr>
<td>Organic modifier</td>
<td>MT2EtOH</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Modifier concentration</td>
<td>90 meq/100g clay</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Solubility (Water)</td>
<td>Insoluble</td>
<td>Negligible</td>
<td>Insoluble in water and organic solvent</td>
</tr>
</tbody>
</table>
In this study, PLA-clay compositions were prepared by melt blending the components at optimum processing conditions. Through this method, PLA-based nanocomposites were loaded with various loading of organomodified MMT (Cloisite® 30B) and PLA-based microcomposites were loaded with various loading of natural MMT (Cloisite® Na⁺ and Cloisite® Ca⁺⁺DEV). For the sake of comparison, unfilled PLA was processed under the same conditions.

### 3.3 Drying

PLA is a hygroscopic thermoplastic. That is, it readily absorbs moisture from the atmosphere. The presence of even small amounts of moisture will hydrolyze PLA in the melt phase, reducing the molecular weight. As a result, the mechanical properties of PLA decrease and the end-product quality is compromised. Therefore, PLA must be thoroughly dry just prior to melt processing. NatureWorks® (2005) recommends PLA to be dried less than 0.025 % or 250 parts per million (ppm) moisture and maintained at this moisture level to minimize hydrolysis during melt processing and to prevent viscosity degradation. This is not just advisable with PLA; it is absolutely essential. It is important to note that inadequate drying, (on a ppm level) causes a large portion of all quality problems in PLA processing. Dryness of the PLA must be maintained until it enters processing equipment. It is best to use dried material right away so it does not absorb ambient moisture. Depending on ambient conditions, dried PLA that is not kept in a sealed enclosure can pick up enough moisture in five minutes to defeat most of the benefits of drying. To remove water and other volatile components in this research work, PLA pellets and clays were dried in a vacuum oven at 90 °C for 24 hours prior to processing.

### 3.4 Preparations of nanocomposites

PLA pellets and various amount of clay were melt-blended in a counter rotating Haake Rheomix 600 (Figure 3.2). In order to minimise moisture gain, the PLA and organoclay should not be exposed to atmospheric conditions after drying. For determining optimum processing condition of the nanocomposites, experimental design was carried out. Three levels of processing temperature, rotor speed and mixing time with a constant amount (2 wt %) of organoclay Cloisite® 30B was chosen. The detail of this experimental design is explained in detail in Chapter 4. With this optimum processing condition, nanocomposites
with various organoclay loading were prepared. The clay loadings were 2, 3.25, 4.50, 5.75, 7, 8.25 and 10 wt %. For better comparison, the pure PLA sample was also processed in the Rheomix to ensure similar thermal histories for all samples.

While processing temperature, rotor speed and mixing time are considered important factors to be optimised during process development, the fill factor of the mixer is considered a fixed parameter and frequently neglected. The fill factor, however, is known to be a critical parameter for compounding by a batch mixer (Wiedmann and Schmid, 1982, Dierkes, 2005). Fill factor was calculated by the percent of fill of the mixing chamber of a Haake Rheomix 600 following melting of the polymer. The net chamber volume of Haake Rheomix 600 is 69 cm³ and the density of PLA used was 1.24 g/cc. To ensure that Haake Rheomix produces an effective mixing process, fill factor of 0.8 was selected. Predetermined amounts of PLA pellets and nanoparticles were prepared to provide 80 vol % filling of the mixer chamber as in Table 3.3 -Table 3.5. The PLA and organoclay were carefully weighed out using an electronic set of scales that were accurate to ±0.01 grams. However since adding nanoparticles do not
change the density of the polymer itself, the amount of nanoparticles required to be added into the mixture can be calculated using the desired weight percentage content of each sample. Thus, the batch weight equation is given as:

\[
\text{Batch weight} = \text{net chamber volume} \times \text{density of compound} \times \text{fill factor}
\]

**Equation 3.1**

### Table 3.3 PLA/Cloisite® 30B composite formulations

<table>
<thead>
<tr>
<th>Wt % of clay</th>
<th>Label</th>
<th>Weight (g)</th>
<th>PLA</th>
<th>Cloisite® 30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PLA-30B-0</td>
<td>68.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.00</td>
<td>PLA-30B-2.00</td>
<td>67.08</td>
<td>1.37</td>
<td>2.22</td>
</tr>
<tr>
<td>3.25</td>
<td>PLA-30B-3.25</td>
<td>66.23</td>
<td>3.08</td>
<td>3.94</td>
</tr>
<tr>
<td>4.50</td>
<td>PLA-30B-4.50</td>
<td>65.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.75</td>
<td>PLA-30B-5.75</td>
<td>64.51</td>
<td>3.94</td>
<td>6.85</td>
</tr>
<tr>
<td>7.00</td>
<td>PLA-30B-7.00</td>
<td>63.66</td>
<td>4.79</td>
<td></td>
</tr>
<tr>
<td>8.25</td>
<td>PLA-30B-8.25</td>
<td>62.80</td>
<td>5.65</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>PLA-30B-10.00</td>
<td>61.60</td>
<td>6.85</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3.4 PLA/ Cloisite® Na<sup>+</sup> composite formulations

<table>
<thead>
<tr>
<th>Wt % of clay</th>
<th>Label</th>
<th>Weight (g)</th>
<th>PLA</th>
<th>Cloisite® Na&lt;sup&gt;+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PLA-Na-0</td>
<td>68.45</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3.25</td>
<td>PLA-Na-3.25</td>
<td>66.23</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>5.75</td>
<td>PLA-Na-5.75</td>
<td>64.51</td>
<td>3.94</td>
<td></td>
</tr>
<tr>
<td>10.00</td>
<td>PLA-Na-10.00</td>
<td>61.60</td>
<td>6.85</td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>PLA-Na-20.00</td>
<td>54.76</td>
<td>13.69</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.5 PLA/Cloisite® Ca** composite formulations

<table>
<thead>
<tr>
<th>Wt % of clay</th>
<th>Label</th>
<th>Weight (g)</th>
<th>PLA</th>
<th>Cloisite® Ca**</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PLA-Ca-0</td>
<td>68.45</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.25</td>
<td>PLA-Ca-3.25</td>
<td>66.23</td>
<td>2.22</td>
<td>3.94</td>
</tr>
<tr>
<td>5.75</td>
<td>PLA-Ca-5.75</td>
<td>64.51</td>
<td>0</td>
<td>3.94</td>
</tr>
<tr>
<td>10.00</td>
<td>PLA-Ca-10.00</td>
<td>61.60</td>
<td>6.85</td>
<td></td>
</tr>
<tr>
<td>20.00</td>
<td>PLA-Ca-20.00</td>
<td>54.76</td>
<td>13.69</td>
<td></td>
</tr>
</tbody>
</table>

Once the sample was mixed, the batch was extracted from the mixing chamber manually and transfer into the moulding plate. The samples were moulded by compression moulding for various characterisations at 190 °C for 3 minutes and allowed to cool to ambient temperature under pressure (10 kN). Cooling water was used to cool the mould temperature, then the specimens were taken out from the mould. Care must be taken to ensure that all the samples had no air bubbles or free voids and had a uniform cross-section all through.

Melt mixing is one of the widely used methods for the preparation of nanocomposites as it is a more efficient and cost effective process (Reddy et al., 2007, Wiedmann and Schmid, 1982). Also, it is known that nanocomposite preparation requires delamination of clay and strong polymer filler interaction. PLA is polar (Auras et al., 2003) i.e. it has polar groups in its back bone; thus, the homogenous dispersion of the hydrophilic silicate layers in its matrix is possible. In general, layered silicate is modified with alkylammonium to facilitate its interaction with a polymer because alkylammonium makes the hydrophilic silicate surface organophilic (Wang et al., 2001).

3.5 Experimental design
Polymer layered silicate nanocomposites have been studied for nearly 50 years (Dennis et al., 2001b, Cho and Paul, 2001), but few references deal with the importance of how the organoclay was processed into the plastic of choice. Many articles focus on the importance of the chemistry used to modify the surface of the clay, usually montmorillonite, without including the role of processing (Dennis et al., 2001b). It is well known that mixing is a key
step in almost every polymer processing operation, affecting material properties, processability and cost (Manas-Zloczower and Cheng, 1996). Processing conditions are important variables that must be optimised to achieve a high degree of exfoliation and dispersion. Degree of exfoliation depends on the properties of the components, competitive interactions and preparation conditions (Kutz, 2011). For this purpose, statistical approach can be used to understand the impact of variables on the process.

The classical approach of changing one factor at a time (OFAT) to study the effect of a variable on the response is very widespread in experimental research. In a simple system with one variable, it is efficient and effective. However, Hockmain and Jenkins (1994) reported that this approach depends upon guesswork, luck, experience and intuition for its success. This type of experimentation requires large resources to obtain a limited amount of information about the process. OFAT experiments often are unreliable, time consuming, inefficient and may yield false optimum conditions for the process (Logothetis, 1992). By contrast, OFAT plans are generally discouraged for any use primarily because they: 1) require more runs for the same precision in effect estimation; 2) cannot estimate interactions, 3) can miss optimal settings of factors. These cautions are valid, but it does not logically follow that OFAT should be discouraged in all cases (Frey et al., 2008).

The main reason for designing an experiment statistically is to obtain unambiguous answers to questions of major interest at a minimum cost. The need to quantify effects, learn about interactions among variables, model relationships and measure experimental error are some added reasons for designing an experiment statistically (Anderson and Whitcomb, 2000). DOE are statistical techniques which can be used for optimizing such multivariable systems. Using DOE based on response surface methodology, the aggregate mix proportions having least void content can be identified with a minimum number of experiments: DOE avoids the need to study all possible combinations experimentally. Further the input levels of the different variables for a particular level of response can also be determined (Muthukumar et al., 2003).

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It usually contains three stages (Myers and Montgomery, 1995): (1) design of experiments, (2) response surface modelling through regression, and (3) optimisation. The main advantage of RSM is the
The reduced number of experimental trials needed to evaluate multiple parameters and their interactions (Lee et al., 2000, Porretta et al., 1995). The experimental data were utilized to build mathematical models using regression methods. Once an appropriate approximating model is obtained, this model can then be analyzed using various optimisation techniques to determine the optimum conditions for the process. The optimisation process involves measuring the response when statistically designed combinations are used. The coefficients for a mathematical model that best fits the experimental conditions are then estimated. This model can then be used to predict the optimum conditions to produce a maximum or minimum response (as desired). These conditions can then be run, to check the adequacy of the mode.

The principal response surface methodologies are the Central Composite Design (CCD) and Box-Behnken Design (BBD). These have been widely used (Box et al., 1978, Dean and Voss, 1999). Box-Behnken is a spherical and revolving design, which has been applied to optimisation of chemical and physical processes (Bae and Shoda, 2005, Dong et al., 2009, Ferreira et al., 2007, Muthukumar et al., 2003). A comparison between the BBD and other response surface designs has demonstrated that the BBD is slightly more efficient than the CCD but much more efficient than the three-level full factorial designs (Ferreira et al., 2007).

3.5.1 Benefits of DOE

DOE allows experimenters to identify the critical variables affecting a process, optimise the process variables (or parameters) and thereby substantially improve product and process performance (Antony and Antony, 1998). Experimental design methods have great potential for applications in engineering design and development including (Antony and Antony, 1998, Antony and Capon, 1998):

- studying product or process behaviour over a wide range of operating conditions;
- improving the yield, stability and reliability of an continuous manufacturing process;
- determining the optimal parameter settings of a process;
- reducing product and process design and development time;
- increasing process productivity by reducing scrap, rework etc.;
- studying the relationship between a set of independent process variables (i.e., process parameters) and the output (i.e., response);
- understanding the process under study and thereby improving its performance;
Experiments are often conducted to determine if changing the values of certain variables leads to worthwhile improvements in the mean yield of a process or system. DOE assists experimenters to determine at what levels these variables should be set to optimise performance. The advantage of experimental design is that it allows interactions between the parameters to be evaluated with the minimum of time, material and labour effort. In this study a DOE technique was used to identify how the processing conditions affected the Young’s modulus (the response).

DOE are particularly good at identifying the interaction between several factors. Interactions cannot be determined by OFAT (Czitrom, 1999). If interactions are important, factors and their interactions can be modelled, and the optimum operating condition can be predicted.

3.5.2 DOE in this study

The objective of the use of DOE in this study was to determine the optimum settings of the processing conditions that would maximise the modulus of the nanocomposites. This study used a BBD. As BBD does not contain combinations for which all factors are simultaneously at their highest or lowest levels, it is particularly suited in polymer processing when otherwise unsatisfactory results are likely to occur (Ferreira et al., 2007).

Flow process of experimental work is shown in Figure 3.3. Further details of the experimental set-up, procedures, interpretation of data analysis and the optimisation study are given in Chapter 4.
Figure 3.3 Flow process of experimental work

Identify the optimum processing conditions

PLA + Cloisite® 30B (Nanocomposites) + Cloisite® Na⁺ Cloisite® Ca⁺⁺ Dev (Microcomposites)

Produce PLA nanocomposites/microcomposites with varies clay loading at the optimum mixing conditions – 175 °C/ 100 rpm/ 7 min.

Characterisation

- Mechanical Test - Instron
- Morphology - SAXS, ESEM, TEM
- Rheology Test - ARES
- Molecular weight - GPC

Nanocomposites vs Microcomposites

DOE

Internal Mixer

Thermal Test - MDSC, TGA

Micromechanical model
3.6 Characterisation

3.6.1 Gel permeation chromatography (GPC) measurements

Polymer molecular weight is important because it determines many physical properties. If molecular weight is too low, the transition temperatures and the mechanical properties will generally be too low for the polymer material to have any useful commercial applications. For a polymer to be useful it must have transition temperatures to waxes or liquids that are above room temperatures and it must have mechanical properties sufficient to bear design loads (Nairn, 2007).

Polymers can be characterised by a variety of definitions for molecular weight including the number average molecular weight ($M_n$), the weight average molecular weight ($M_w$), the size average molecular weight ($M_z$), or the viscosity molecular weight ($M_v$). GPC measures the molecular weight and molecular weight distribution of a polymer with comparing to a known standard. In the procedure, a polymer is dissolved in a solvent and injected through a series of columns consisting of tightly packed porous polymer beads. As the polymer molecules travel down the column, the smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. All columns have a range of molecular weights that can be separated. In a typical distribution curve, the average values are related to each other as follows: $M_n < M_v < M_w < M_z$. Polydispersity index (PDI) of a sample is defined as $M_w$ divided by $M_n$ and gives an indication just how narrow a distribution is (Young and Lovell, 1991). The distribution as given by PDI can provide a rough indication of the breadth of the distribution. The PDI approaches 1.0 (the lower limit) for special polymers with very narrow molecular weight distribution, but, for typical commercial polymers, is typically greater than 2 (occasionally much greater) (Robello, 2002).

Molecular weights determination before and after processing of the selected PLA composites were measured by GPC (Waters e2695 separation modules). Samples were dissolved in eluent (0.2 % w/v) and then filtered using nylon membrane (pore size 0.45 µm) before injection. Tetrahydrofuran (THF) was used as effluent, and the analysis was done at 35 ºC and a flow rate of 1 ml/minute. The molecular weight of polymer was based on the calibration using polystyrene standards. The determination of molecular weight was used to study the effect of
processing conditions and filler loading on the molecular characteristics of the PLA composites in this study. GPC measurements are accurate to ±10 % (Scholte et al., 1984).

3.6.2 Morphology measurements

The morphology properties of the PLA/MMT composites were studied using SAXS, ESEM and TEM.

3.6.2.1 Small-angle x-ray scattering (SAXS)

The quantitative assessment of the morphology of the PLA/MMT nanocomposites was studied using SAXS. The interlayer spacing $d_{001}$ was examined using a Bruker AXS Nanostar x-ray diffractometer (Figure 3.4) operating at 40kV and 35mA with CuKα radiation ($\lambda = 1.54$ Å). The d-spacing of clay in nanocomposites was calculated from Bragg’s equation using the XRD results, which is the common procedure for polymer layered silicate nanocomposites (Utracki, 2004). Measurements were carried out in the range from $2\theta = 0.6$ to $14^\circ$. 
3.6.2.2 Environmental scanning electron microscopy (ESEM)

The morphology of fracture surfaces from the tensile tests of the nanocomposites were studied at room temperature. A FEI Quanta 200 Environmental scanning electron microscopy (ESEM) (Figure 3.5) with an accelerating voltage of 30 kV was used to collect SEM images for the nanocomposites specimens. The sample surfaces were mounted on aluminium stubs and gold-coated with a sputter coater to avoid charging. The samples were viewed perpendicular to the fractured surface.
3.6.2.3  Transmission electron microscopy (TEM)

TEM images were obtained using a JEOL 2100 electron microscope (Figure 3.6), with a Gatan ORIUS™ SC1000 digital camera. Most of the measurements were carried out using an accelerating voltage of 200 kV, while the exposure times were varied from 1 to 6 seconds. Samples were cut using a Diatome diamond knife on a Leica UC6 at room temperature to give sections with a nominal thickness of 75 nm. Sections were collected onto formvar and carbon coated copper grids. Due to some limitations, only a few samples were taken for measurements. The materials were sampled by taking several images of various magnifications to ensure that analysis was based on a representative region of the sample.
3.6.3 Rheology measurements

Oscillatory measurement is the most common dynamic method to study the viscoelastic behaviour of any material. Dynamic oscillatory shear measurements were performed using an advanced rheometric expansion system (ARES; Rheometrics Scientific) (Figure 3.7) testing machine. A 25 mm diameter parallel plate measuring geometry, with a gap of about 1-2 mm was used for the measurements. Samples were prepared by compression moulding to the thickness of 2.0 mm at 190 °C for 3 min. All tests were performed under a nitrogen atmosphere to prevent polymer degradation. Common reference temperature ($T_{ref}$) of 175° was chosen as the most representative of a typical processing temperature of PLA (Gu et al.,
2007, Singh et al., 2012, Gu et al., 2008, Sinha Ray and Okamoto, 2003, Sinha Ray et al., 2003c). The linear viscoelastic regions of the PLA and PLA nanocomposites were initially determined by a dynamic oscillatory strain sweep followed by frequency sweep measurement. Rheological parameters (elastic modulus, $G'$; viscous modulus, $G''$; and complex viscosity, $\eta^*$) were directly obtained using the manufacturer supplied computer software (RSI Orchestrator software package). At least two trials were run for each experimental condition to check for reproducibility of the results.

The following tests were performed:

(i) Dynamic Strain Sweep  
(ii) Dynamic Time Sweep  
(iii) Dynamic Frequency Sweep
3.6.4 Thermal measurements

The thermal properties of the PLA/MMT composites were studied using MDSC and TGA.

3.6.4.1 Modulated differential scanning calorimeter (MDSC)

The thermal properties of PLA and PLA nanocomposites were determined by a modulated differential scanning calorimeter (MDSC TA2920, TA Instruments) (Figure 3.8). In all the experiments, an encapsulated sample of 5-10 mg in an aluminium pan was used. An empty aluminium pan was used as an inert reference when the sample pan was loaded into the cell. It
was first heated from -20 to 220 °C at a heating rate of 2 °C/min with a heating/cooling cycle of modulation period of 40 s and amplitude ±0.5 °C. After heating up to 220 °C, the samples were isothermally held for 5 min to eliminate the previous heat history and subsequently cooled down to -20 °C at a cooling rate of 2 °C/min. A second heating scan at 2 °C/min was also performed. Only measurements from the second heating cycle were used in analysis. N₂ and He gases were used as carrier (purge) gas to heat and cool the samples. A flow rate for purge gas was set as 100 ml/min with nitrogen and 35 ml/min with helium. All the data were recorded in TA Instrument Control software installed with the equipment.

Figure 3.8 MDSC TA2920, TA Instruments

The degree of crystallinity ($\chi_c$) of all samples was calculated by Equation 3.2.

$$\frac{\Delta H_{cc}}{(1 - \phi) \Delta H_m} \times 100\%$$

Equation 3.2
Most commonly, an enthalpy of fusion of 93.6 J/g is used for a 100 % crystalline PLA (Fischer et al., 1973). $\Delta H_m$ is the measured heat of fusion and $\Delta H_{cc}$ is the heat of cold crystallisation. $\phi_{\text{PLA}}$ is the PLA content in the component.

3.6.4.2 Thermogravimetric analysis (TGA)

The thermal stability of layered nanocomposites was investigated by using a TGA (Perkin Elmer STA6000) (Figure 3.9). Samples of about 10 - 20 mg were heated with a heating rate of 10 °C/min from room temperature to 600 °C both in oxidizing (air) and inert (nitrogen) atmosphere. The resulting thermograms were processed using Pyris version 11. The experiments were repeated to maximize the accuracy of the results.

Figure 3.9 Thermogravimetric analyzer (Perkin Elmer STA6000)
3.6.5 Mechanical measurements

Tensile tests were performed on dumbbell-shaped specimens, according to ASTM D638, by using an Instron Universal Testing Machine, Model 4465 (Figure 3.10) at room temperature (measurement region: 50 mm initial gauge length, 10 mm width, 3 mm thickness) and a crosshead speed of 5 mm/min. Samples were dried in a vacuum oven at 50 °C for 24 hours prior before testing. Property values reported here represent an average of the results for tests run on four specimens for each samples.

The processing conditions always have a strong influence on the properties of a semicrystalline polymer (as well as other polymers), particularly its mechanical and long-term behaviour (Banik and Mennig, 2005). When a polymer is deformed, the stress increases with strain. The properties of these polymers can be related to the characteristics of their stress-strain curves.
Tests may be performed in tensile, shear, flexure, compression, or torsion. Tensile properties are the most important single indication of strength in a material. The force needed to pull the specimen apart is determined, along with how much the material stretches before it breaks. The tensile modulus is the ratio of stress to strain below the proportional limit of the material.

Determination of these properties helps to derive relationships between the mechanical behaviour and the chemical or molecular structure of polymers, which can, in turn help to predict and improve the performance of materials.

Tensile strength is defined as a stress, which is measured as force (amount force applied as measured by the load cell in the testing machine) per unit area. Typically, the cross-sectional area of the specimen that is used is the original cross section of the gauge length area of the specimen, and this is commonly referred to as the engineering stress.

In the SI system, the unit is the pascal (Pa), often megapascals (MPa), or equivalently to pascals, newtons per square metre (N/m²).

Stress, $\sigma$ is defined as:

\[
\sigma = \frac{F}{A}
\]

**Equation 3.3**

Modulus of elasticity or Young's modulus, $E$ is defined as the ratio of a simple tensile stress, $\sigma$ to the corresponding tensile strain, $\varepsilon$.

\[
E = \frac{\sigma}{\varepsilon}
\]

**Equation 3.4**

The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. If a specimen is loaded within this linear region, the material will return to its exact same condition if the load is removed. At the point that the curve is no longer linear and deviates from the straight-line relationship, Hooke's Law no longer applies and some permanent deformation occurs in the specimen. This point is called the "elastic or
proportional limit”. From this point on in the tensile test, the material reacts plastically to any further increase in load or stress. It will not return to its original, unstressed condition if the load were removed.

3.7 Error analysis

All measurements are subject to some uncertainty as a wide range of errors and inaccuracies can and do happen. Measurements should be made with great care and with careful thought to reduce the possibility of error as much as possible. Errors can be human, systematic or random. So it is an essential requirement to minimise the inherent errors in the experimental data to minimise their effects on conclusions. This section will briefly discuss the inherent errors that exist in the experiments carried out in this study and the steps taken to minimise them.

3.7.1 Nanocomposite preparation

Drying prior to processing is essential to process PLA 7000D, which is supplied with a moisture content of less than 0.025 % (250 ppm). The recommended moisture content to prevent viscosity degradation and possible lactide reformation is less than 0.010 % (100 ppm). The PLA and clay were dried at 90 ºC for 24 h to eliminate moisture content and stored in a desiccator prior to compounding. The resin should not be exposed to atmospheric conditions after drying. The resin package was kept sealed until it's ready to be used and promptly reseal packages of unused material.

3.7.2 Error analysis of morphology measurement

XRD’s potential, however, does not extend to the provision of information concerning the spatial distribution of the silicate in the polymer matrix, nor the shape of the hybrid, since all its data are “averaged” over the whole of the sample. Furthermore, some layered silicates do not display well defined basal reflections and it is difficult to determine the intensity pattern and the shape of the relative peaks. Conclusions regarding the formation mechanisms and nanostructure of hybrids based solely on XRD data, therefore, cannot be other than approximations (Zanetti et al., 2000).
TEM is known as complimentary technique which is used simultaneously together with XRD. TEM provides direct visual information of the morphology, atom arrangement, spatial distribution of the phases and structural defects of a selected area of the sample. Its only limitations are operational, since great care is needed in preparation of the sample in such a way as to enable a representative section to be examined (Zanetti et al., 2000). TEM sample preparation is of utmost importance in obtaining a TEM with good resolution. The basic requirements are that the specimen has to be thin enough to be transparent to the electron beam, must be clean, without much damage or contamination (Koo, 2006).

3.7.3 Error analysis of MDSC measurement

Samples amount and weight used in experiments were very small of the range 5 - 10 mg. Therefore, sample was chosen carefully so that it should represent the whole sample. Since the sample size is so small in MDSC study, the actual amount of crystalline PLA in the mixture could deviate from the theoretical amount due to errors in sampling. Such deviation could be substantial and lead to a large variation in quantifying the crystallinity of PLA among samples. This error is estimated by averaging several repeat measurements. Repeatability of this study was found to be ±1.9 °C (melting) and ±2.3 °C (crystallisation) (Figure 3.11).

![Figure 3.11 MDSC thermograms of PLA-30B-10 nanocomposites](image)
3.7.4 Error analysis of mechanical measurement

Since PLA are highly hydrophilic, all tests were performed in the same way to minimize the effect of temperature and humidity on the sample results. All the specimens were kept in a desiccator prior to testing to avoid moisture absorption. The tests were conducted at room temperature (23 ±2 °C), thus atmospheric conditions were same for all the tests. The thickness and width of the specimens were measured by Vernier caliper; with a precision to 0.01 mm. Each set of samples and the mean values as well as the standard deviations (SD) were calculated by the Instron software (Series IX version 8.34.00). Other parameters like crosshead speed and specimen dimensions were also constant for all the samples. All specimens were inspected to ensure they were bubble free. The modulus SD of set of four specimen range from 1.2 to 3.0 %. The repeatability of sample PLA-30B-2.00 was 1240 ±32 MPa.
Chapter 4 : Design of Experiments

4.1 Introduction

According to Pluta (2006) improvement of nanocomposites properties should be dependent not only on the organoclay concentration but also on the degree of its dispersion. Degree of dispersion is very important because failure can be induced by agglomerates. In general, many of the properties associated with polymer clay nanocomposites are a function of the extent of exfoliation of the individual clay sheets. The greatest benefits come with exfoliation. This is controlled by the processing conditions as well as by matching the interaction of organomodified clay to the polymer matrix. The latter is well documented (Denault et al., 2006, Paul et al., 2003b, Pluta, 2006, Krishnamachari et al., 2009a). However, which processing factor imparts the better level of dispersion is still under discussion (Pogodina et al., 2008, Dennis et al., 2001b, Modesti et al., 2005, Jollands and Gupta, 2010, Davis et al., 2002, Zhao et al., 2008).

It is well known that mixing is a key step in almost every polymer processing operation, affecting material properties, processability and cost (Manas-Zloczower and Cheng, 1996). PLA nanocomposites formed by melt blending have been described previously (Pluta et al., 2002, Sinha Ray et al., 2003a, Di et al., 2005, Pluta et al., 2006); however, these studies have not reported how the conditions were chosen. Some studies have looked at different processing conditions in PLA (Denault et al., 2006, Hasook et al., 2008) and other polymer, such as polyamides (Dennis et al., 2001b, Zhao et al., 2008, Chavarria et al., 2007, Dennis et al., 2001a), but they failed to show that the conditions were optimum. Very few studies optimised processing conditions for PLA nanocomposites (Jollands and Gupta, 2010, Bourbigot et al., 2008). Process conditions must be optimised to achieve a high degree of exfoliation and dispersion. Developing a better understanding of the mixing process and its effect on dispersion is critical to optimising morphology.

DOE is a powerful technique for studying a process, to understand the impact of variables on the process, and thereby provide an insight into continuous quality improvement possibilities. DOE has been used to improve process yield, capability, performance and to reduce process variability (Antony and Capon, 1998). DOE is widely used in research and development to
solve optimisation problems (Dong et al., 2009, Ibrahim et al., 2010, Bae and Shoda, 2005, Ferreira et al., 2007, Garrote et al., 1993). However, application of DOE techniques by the engineering fraternity is limited, and they are often applied incorrectly (Antony and Kaye, 1995) due to lack of skills in manufacturing and lack of statistical knowledge.

A DOE technique was used in this study to find the optimum processing conditions for preparing the nanocomposites. The following sections describe the experimental set-up and procedures for this study.

4.2 Experimental set-up

In this study three variables were selected: processing temperature, rotor speed and mixing time. These were chosen because they are considered to have the most significant effects on processing of nanocomposites (Hasook et al., 2008, Jollands and Gupta, 2010, Modesti et al., 2006, Pluta, 2006). Three levels of temperature, speed and time were selected as high, centrepoint and low (shown in Table 4.1). These ranges were chosen after taking into consideration processing temperature suggested by manufacturer and also based on a few studies on PLA (Hasook et al., 2008, Denault et al., 2006, Jollands and Gupta, 2010, Pluta, 2006). Also, it can be expected that very long compounding time and high compounding temperature can lead to organoclay degradation (Denault et al., 2006).

All samples were made with a constant amount (2 wt %) of organoclay Cloisite® 30B. This level of clay was chosen because Ray (2003c), Di (2005) and Jollands and Gupta (2010) identified 4, 5 and 3.7 wt % filler as an optimum loading, respectively, as other mechanical properties decreased above this level. Therefore we shall only be considering concentrations below this optimum level where almost complete exfoliation of the nanoplatelets is expected. The assumption was made that samples made with higher levels of clay would have similar optimum processing conditions because the processing window was found to be very broad at 2 %. In addition, higher loading of clay samples appeared to have similar heat history as the sample had similar colour and odour.

The chosen response was Young’s modulus. Young’s modulus is commonly used because it is readily measured and is the mechanical property most sensitive to changes in microstructure of the nanocomposites (Liu et al., 1999).
The DOE were designed and analysed using Minitab Statistical software. The 15 runs design included 12 combinations of the factors plus three centre points (in which all factors are at their central values). The three centre point runs measure process stability and inherent variability. A significance level of 0.05 was used for all statistical analyses. Traditionally, experimenters have used either the 0.05 level (sometimes called the 5 % level) or the 0.01 level (1 % level). Although the choice of levels is largely subjective, but for many applications, a level of 5 % is only a convention, but reasonable and accepted in the scientific community (Kohlmann and Moock, 2009). Table 4.1 presents the process parameters and levels identified for the experiment.

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Parameter labels</th>
<th>Units</th>
<th>Low levels (-1)</th>
<th>High levels (+1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>$x_1$</td>
<td>°C</td>
<td>175</td>
<td>195</td>
</tr>
<tr>
<td>Speed</td>
<td>$x_2$</td>
<td>rpm</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Time</td>
<td>$x_3$</td>
<td>min</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

The data were fitted with a second-order polynomial to model the relationship between independent variables and response (Young’s modulus). For a three factors model, the equation used is of the form

$$Y = \beta_o + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j$$

**Equation 4.1**

where $Y$ is the predicted response; $\beta_o$ is a model constant; $\beta_i$ is the coefficient of $i$th individual factor, $\beta_{ii}$ is the coefficient of $i$th factor squared, $\beta_{ij}$ is the coefficient of interaction between the $i$th and $j$th factors, and $x_n \ (n = i, j)$ is the variable or factor value. The quality of fit of the polynomial model equation is expressed by the coefficient of determination $R^2$. 

67
Table 4.2 shows the experimental conditions or settings for each of the factors at each design point. The settings with ‘-’ represents for the low factor setting, ‘0’ for the middle setting, and ‘+’ for the high setting. The experiment was performed in a random order as shown in Table 4.2. Randomization is one of the methods experimenter often rely on to reduce the effects of experimental bias. The purpose of randomization is to reduce the systematic bias that is induced into the experiment. The bias may be due to the effect of uncontrolled factors or noise such as machine ageing, changes in raw material, tool wear, change of relative humidity, power surges, change of ambient temperature and so on. These changes, which often are time related, can significantly influence the response (Antony, 2003). Otherwise, the DOE may indicate factor effects that are really due to uncontrolled variables that just happened to change at the same time.

<table>
<thead>
<tr>
<th>Run</th>
<th>Blk</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
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<td>0</td>
</tr>
<tr>
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<td>1</td>
<td>-</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>+</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
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<td>-</td>
<td>0</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
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<td>+</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
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<td>+</td>
<td>+</td>
<td>0</td>
</tr>
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<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>0</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>13</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>0</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
4.3 Experimental procedure

The DOE and results are given in Table 4.3, the reported Young’s modulus is the average of results from testing four specimens for each sample, as described in 3.6.5. Selected optimisation plots are shown to illustrate the relationship between parameters and mechanical properties.

<table>
<thead>
<tr>
<th>Run</th>
<th>( x_1 ) °C</th>
<th>( x_2 ) rpm</th>
<th>( x_3 ) min</th>
<th>Young’s Modulus (MPa)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
<td>Predicted</td>
</tr>
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<tr>
<td></td>
<td>Average</td>
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</tr>
<tr>
<td></td>
<td>sd</td>
<td></td>
<td></td>
<td>33.3</td>
<td>30.0</td>
</tr>
</tbody>
</table>

The average modulus for all samples is 1150 MPa. The SD of the mid-points (runs 1, 5 and 14) was 21 MPa (1.7 %). The difference from one run to another is not significant at the 95 % confidence limit. This suggests that the processing window for these nanocomposites is quite broad.
4.4 Data analysis and interpretation

The first step in the analysis involves finding the significant parameters. The analysis in this study was done using coded units. Use of coded units helps to eliminate any spurious statistical results due to different measurement scales of the factors and makes them easier to interpret (Malik et al., 2011).

From the analysis as shown in Table 4.4, the p-values for the estimated coefficients of quadratic terms (Time*Time) and interaction (Temp*Speed) are 0.006 and 0.048, indicating that they are significantly related to modulus at an α-level of 0.05. Interestingly, other coefficients are higher than 0.05, so are not considered to have a significant effect for the range of conditions studied in this DOE. This is consistent with the low range of values of modulus for individual runs shown in Table 4.3.

<table>
<thead>
<tr>
<th>Term</th>
<th>Coef</th>
<th>SE Coef</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>1173.75</td>
<td>11.637</td>
<td>100.866</td>
<td>0.000</td>
</tr>
<tr>
<td>Temperature</td>
<td>-4.24</td>
<td>7.126</td>
<td>-0.594</td>
<td>0.578</td>
</tr>
<tr>
<td>Speed</td>
<td>4.36</td>
<td>7.126</td>
<td>0.612</td>
<td>0.567</td>
</tr>
<tr>
<td>Time</td>
<td>-2.08</td>
<td>7.126</td>
<td>-0.291</td>
<td>0.783</td>
</tr>
<tr>
<td>Temperature*Temperature</td>
<td>3.96</td>
<td>10.489</td>
<td>0.378</td>
<td>0.721</td>
</tr>
<tr>
<td>Speed*Speed</td>
<td>0.11</td>
<td>10.489</td>
<td>0.010</td>
<td>0.992</td>
</tr>
<tr>
<td>Time*Time</td>
<td>-48.66</td>
<td>10.489</td>
<td>-4.639</td>
<td>0.006</td>
</tr>
<tr>
<td>Temperature*Speed</td>
<td>-26.17</td>
<td>10.078</td>
<td>-2.597</td>
<td>0.048</td>
</tr>
<tr>
<td>Temperature*Time</td>
<td>19.10</td>
<td>10.078</td>
<td>1.895</td>
<td>0.117</td>
</tr>
<tr>
<td>Speed*Time</td>
<td>-12.90</td>
<td>10.078</td>
<td>-1.280</td>
<td>0.257</td>
</tr>
</tbody>
</table>

The adequacy of the model can be checked with $R^2$ and $R^2_{\text{adjusted}}$. $R^2_{\text{adjusted}}$ is considered rather than solely relying on $R^2$ value because $R^2$ value can be easily increased by adding more variables, regardless of whether these factors are statistically significant or not (Montgomery, 2009). The $R^2$ and $R^2_{\text{adjusted}}$ values for the above regression model are 88 % and 65 %, respectively. For general rule of thumb, the R-squared or adjusted R-squared should be higher than 0.80 to produce a good linear model. If R-squared is less than 0.5, it is recommended to consider other type of model rather than linear model (Teknomo, 2006). These values indicating that the model fits the data reasonably well. In general, the higher the $R^2$, the better
the model fits our data. The polynomial model for Young’s modulus (Y) was regressed by considering only the significant terms and shown as below:

\[ Y = -1291.8 + 10.0445x_1 + 24.4253x_2 + 170.290x_3 - 12.2377x_3^2 - 0.130850x_{12} \]

**Equation 4.2**

### 4.5 Determination of the optimal conditions

The optimum conditions are determined using the Minitab Response Optimiser. Response optimisation is useful to determine optimum operating conditions. It helps to identify the combination of input variable settings that jointly optimise a single response or a set of responses. This is useful when we need to evaluate the impact of multiple inputs on a response.

Once an optimisation plot has been created, the input variable settings can be changed. For response surface designs, the factor levels can be adjusted. Input variable settings on the optimisation plot can be change for many reasons (Minitab Inc, 2007), including:

- To search for input variable settings with a higher composite desirability
- To search for lower-cost input variable settings with near optimal properties
- To explore the sensitivity of response variables to changes in the design variables
- To “calculate” the predicted responses for an input variable setting of interest
- To explore input variable settings in the neighbourhood of a local solution

Figure 4.1 shows an optimisation plot: each factor (column) is plotted against the response and composite desirability (rows). The vertical red lines on the graph and the red numbers displayed at the top of a column show the current factor level settings. The horizontal blue lines and numbers represent the responses for the current factor level. The optimal solution serves as the starting point for the plot. This optimisation plot allows us to interactively change the input variable settings to perform sensitivity analyses and attempt to improve on the initial solution. For each new set of input variables, the optimisation plot is redrawn and the predicted response and desirability are recalculated. The optimisation plot allows us to shows how the factors affect the predicted responses.
Temperature: Decreasing temperature moved Young’s modulus towards its maximum. This effect is attributed to PLA were found to be highly sensitive to heat, especially at temperatures higher than 190 °C (Jamshidi et al., 1988, Garlotta, 2001).

For the effect of temperature on nanocomposites, the results reported in the literature are relatively controversial. Kwak et al. (2002) reported a better dispersion of organoclay in polyethylene at higher temperature (230 °C instead of 170 °C). Modesti et al. (2005, 2006) obtained better results at lower temperature (170 °C instead of 200 °C), but for polypropylene. In fact, it seems that, beside the nature of the nanocomposite considered, the temperature cannot be considered independently of the other parameters such as screw speed (Tillekeartne et al., 2003). As temperature increases, viscosity decreases, and thus the stress necessary to break the clay aggregates decreases. At the same time, diffusion is improved, which can help to intercalate and exfoliate the platelets. In addition, a temperature too high could cause a degradation of the organoclay intercalants, leading to a collapse of the interlayer galleries and decreased intercalation (Mederic et al., 2006).
**Speed:** Increasing speed moved Young’s modulus towards its maximum. Generally speaking, it is well admitted in the literature that an increase in screw speed leads to a better dispersion. This effect has been observed on different systems, including nanocomposites based on polyamide (Cho and Paul, 2001, Incarnato et al., 2003), polyethylene (Kwak et al., 2002), and polypropylene (Modesti et al., 2005, Modesti et al., 2006, Lertwimolnun and Vergnes, 2005). It can be explained by the fact that a higher shear rate allows to break the agglomerates in smaller aggregates, enhancing polymer–clay interactions by making the entire surface of layers available for the polymer (Beyer, 2002, Lertwimolnun and Vergnes, 2007). This suggests that the optimum speed at these factor conditions is above the range trialled in this study.

**Time:** Increasing time first increased then decreased Young’s modulus. It reached a maximum within the range of times trialled, so the optimum is around 7 minutes for these factor conditions. Figure 4.1 show that Young’s modulus has a high coefficient for Time*Time, that is, it increases quadratically with time.

Denault and coworkers (2006) reported that long compounding time and high compounding temperature can lead to organoclay degradation in a polymer nanocomposite. Bourbigot et al. (2008) also reported that longer times accompanied by higher shear lead to the reagglomeration of the platelets.

**Optimum conditions:** The Minitab Response Optimiser calculated that modulus is maximized when temperature is at the lowest setting, speed is at the highest setting and time is at a mid-point (Temperature =175 °C, Speed =100 rpm and Time =7 min).

However the optimum conditions to maximise Young’s modulus appear to be beyond the range of factors trialled in this study. The optimum temperature may be lower than 175 °C and the optimum speed may be higher than 100 rpm while the optimum time is clearly around 7 min (Figure 4.1). Hence the Response Optimiser is not the best approach when the optimum is outside the experimental range. An empirical model based on the best fit to the data can be used to predict an optimum point beyond the measured range. Once the optimum is found, the accuracy of the model can be improved if desired, by repeating the experiments at a wider range of conditions.
According to the best fit model to the data, the maximum Young’s modulus was predicted to be 1210 MPa at a temperature, speed and time of 175 °C, 100 rpm and 7 min. The model was tested for robustness by making samples at the predicted optimum mixing conditions, then the measured modulus was compared with the prediction. The modulus of a sample made at the optimum conditions was 1240 MPa, which is higher 2.4 % than predicted by the best fit model. This difference is not significant at a 95 % confidence level. Hence the agreement between the measured and predicted response is considered to be reasonable, and the model is considered robust.

The optimum modulus (1240 MPa) is also 7.8 % higher than the average modulus for the BBD runs (1150 MPa), so it is significant at the 99 % confidence level. Hence making samples at optimised conditions improved the modulus significantly.

This is in reasonable agreement with other studies of optimum process conditions for polymer nanocomposites. Jollands and Gupta (2010) reported the optimum mixing conditions 185 °C, 80 rpm and 7 min. The small differences may be attributed to different mixer and/or material grade. Bourbigot et al. (2008) reported a mixing study for PLA/clay nanocomposites with 3 % Closite® 30B using a DSM twin screw micro extruder at various speeds and residence times. A DSM micro extruder has a recirculating channel so that residence time can be controlled. They produced samples at 25, 50, and 100 rpm at 185 °C and residence time of 1 – 15 min under a nitrogen blanket. They reported the optimum conditions were “high shear stress” (100 rpm) for 1 min, then low shear stress (25 rpm) for an additional 5 min. The differences to this study may also be attributed to different equipment and PLA material grade and that temperature was not varied. Hasook and coworkers (2008) reported a mixing study for intercalated PLA/clay nanocomposites with 5 % and 10 % organoclay using a TSE co-rotating twin screw extruder at two speeds. They produced samples at 180 °C and 65 and 150 rpm, and found better properties at the higher speed. The differences to this study may also be attributed to different equipment and PLA material grade and residence time was not controlled.

Although numerical optimisation along with graphical analysis can provide useful information, it is not a substitute for subject matter expertise. Relevant background information, theoretical principles, and knowledge gained through observation or previous experimentation needs to be considered when applying these methods (Minitab Inc, 2007).
It should be noted that determination of the optimum conditions is specific for this one nanocomposite material in this one mixing configuration. When different materials or mixers are used then the optimum conditions will also change.

4.6 Summary

In order to optimise processing conditions for preparing the polylactide nanocomposites in this study, a BBD of experiments was applied to investigate three variables; processing temperature, rotor speed and mixing time. The interaction effect with most influence on the Young’s modulus of these PLA/organoclay nanocomposites is temperature and speed. Young’s modulus also increases quadratically with time.

The data were fitted with a simple mathematical model that was used to predict the conditions to maximise Young’s modulus. The model was found to be robust. Samples produced at the predicted optimum temperature, speed and time had a significant increase in modulus of 7.8 % compared to the average for all the runs.

Statistical data analysis can help researchers predict better processing conditions or better properties, leading to better outcomes of studies of materials such as nanocomposites. DOE can assist experimenters to determine at what levels variables should be set to optimise performance. The advantage of experimental design is that it allows interactions between the parameters to be evaluated without consuming time, material and labour effort. It is the strategy of the management in today's competitive world market to develop products and processes insensitive to various sources of variation using experimental design (Antony and Capon, 1998).

In the next chapter work on the molecular weight, morphology, rheology, thermal and mechanical properties of these samples will be presented and discussed.
Chapter 5: Properties of Polylactide Nanocomposites

5.1 Introduction

In this chapter, the properties of the PLA and PLA nanocomposites with various Cloisite® 30B loadings (2 - 10 wt %) are presented. These were prepared at optimum processing condition, as described in Chapter 4. The measured properties are molecular weight, morphology, rheology, thermal and mechanical properties.

5.2 Gel permeation chromatography (GPC)

PLA is very sensitive to hydrolysis during processing (Garlotta, 2001, Södergård and Stolt, 2002) leading to decreases in molecular weight that can be detrimental to final product properties such as strength, fracture resistance and colour (Södergård and Stolt, 2002). Hence PLA must be thoroughly dried before processing (Carrasco et al., 2011). Measurement of PLA molecular weight before and after processing shows whether degradation has occurred. The polydispersity index (PI) of polymer indicates the molecular weight distribution in the polymer chain. Changes in PI after degradation give a quantitative idea on the structural changes in the polymer chain after processing (Reddy et al., 2008). GPC measurements are accurate to ±10 % (Scholte et al., 1984). GPC has a precision comparable to other molecular weight measuring systems, i.e., light scattering, osmometry and ultracentrifugation (Ouano, 1972).

The number ($M_n$) and weight ($M_w$) average molecular weights and polydispersity index (PI) of PLA before and after processing were determined by GPC as described in section 3.6.1. Two samples were tested for each data point. The changes in $M_w$, $M_n$ and PI for PLA nanocomposites samples are shown in Table 5.1.

Table 5.1 shows that the melt processing of unfilled PLA led to a significant decrease of $M_w$ and $M_n$ by 14 % and 17 %, respectively. The chromatographs showed that the molecular weight distribution was unimodal (see Appendix A and B). The PI did not change significantly. These results suggest that some limited degradation occurred during the mixing
process, attributed to presence of small amounts of moisture and shearing forces (Pluta, 2006, Sinha Ray et al., 2003b). Filled samples were not tested due to lack of availability of suitable testing facilities. It was assumed that melt processing of PLA with or without the organoclay would lead to a similar small decrease in $M_w$ as reported by a few other studies (Sinha Ray et al., 2002, Pluta, 2006, Sinha Ray et al., 2003b).

<table>
<thead>
<tr>
<th>Materials</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>Polydispersity (PI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA unprocessed</td>
<td>$1.2 \times 10^5$</td>
<td>$2.2 \times 10^5$</td>
<td>1.8</td>
</tr>
<tr>
<td>PLA processed (175 °C/100 rpm/7 min)</td>
<td>$1.0 \times 10^5$</td>
<td>$1.9 \times 10^5$</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Pluta and co-workers (Pluta, 2006, Pluta et al., 2007) reported the $M_n$ of the unfilled PLA decreased by 25% compared to the neat PLA. Evidence from a number of previous studies by Pluta and co-workes (Pluta et al., 2002, Pluta et al., 2006) also indicated that the behaviour of PLA during melt processing depends on many factors including the grade of PLA used, processing conditions applied (temperature, rotation speed, residence time, atmosphere, drying efficiency of the components), the presence of additives and their chemical nature.

### 5.3 Morphology properties

Morphology of nanocomposites is of interest for several reasons. Morphological details, such as intercalation or exfoliation, have a significant effect on the properties of nanocomposites. The degree of intercalation/exfoliation of the nanocomposites was investigated by SAXS, SEM and TEM. XRD studies provide a quantitative understanding of the global morphology in reciprocal space, whereas TEM quantitatively visualizes the complimentary local structure in real space (Krikorian and Pochan, 2003). In XRD equipment, there is an angle below which results are not recorded, which defines the lower limit. SAXS has a lower limit than WAXS, and can be used to examine lower angles (equivalent to larger d-spacings of the gallery space) (Hussain et al., 2006, Zhu and Wilkie, 2007). To overcome the limitations of XRD and further differentiate between the intercalated and exfoliated morphologies, TEM is used to give a
clearer picture of the nanoscale dispersion and overall bulk dispersion of the clay in the polymer.

5.3.1 Small-angle x-ray scattering (SAXS)

In Figure 5.1, the SAXS diffractograms of PLA, Cloisite® 30B and the corresponding PLA-30B nanocomposites are presented for the range of 2θ between 0.6° and 10°. According to Zhu and Wilkie (2007), both the position at which peak is found and its width are important. If the position is at a lower value of 2θ, this indicates that the d-spacing has increased and is indicative of nanocomposite formation. If the peak is broad, this may be interpreted as indicating disorder while if the peak is sharp intercalation is likely. On the other hand, the absence of a peak could mean either that a delaminated structure has been produced, which has lost registry and thus shows no peak, or the tactoids are internally disordered (disordered immiscible or intercalated) or not well aligned to one another (Zhu and Wilkie, 2007, Morgan and Gilman, 2003, Paul and Robeson, 2008).

It can be seen from Figure 5.1 that Cloisite® 30B is characterised by a single diffraction peak at 2θ = 4.9°, which corresponds to the d-spacing of d_{001} = 1.8 nm. In the nanocomposites the diffraction peak is shifted to lower angles and the intensity is lower. The unfilled PLA (but subjected to the same mixing process) did not show any diffraction peak (below 2θ = 10.0°) as expected. For the PLA-30B nanocomposites of different nanoclay loading levels, the diffraction patterns also showed shifting of the characteristic peak towards lower 2θ value ranges between 1.7 - 2.2° in all cases. The d-spacing is inversely proportional to the angle, so it can be deduced that all the nanocomposites have d-spacings greater than the nanoclay. As the nanocomposite peaks are lower and broader than the organoclay, the accuracy of the d-spacing calculation is lower and suggests the formation of a disordered intercalated structure. The d-spacing estimates are given in Table 5.2.

This is consistent with the expected compatibility between PLA polymer and the hydroxyl groups of the intercalant (bis-2-hydroxyethyl, quaternary ammonium) of the Cloisite® 30B. Similar findings were reported by other research groups (Denault et al., 2006, Singh et al., 2012). The Cloisite® 30B organoclay interaction with PLA is attributed to favourable enthalpic interactions between diols present in the organic modifier with the C=O bonds present in the PLA backbone (Krikorian and Pochan, 2003).
Figure 5.1 SAXS Diffractograms: Cloisite® 30B and PLA-30B nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>$2\theta$ (°)</th>
<th>$d_{001}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite® 30B</td>
<td>4.9</td>
<td>1.8</td>
</tr>
<tr>
<td>PLA-30B-2.00</td>
<td>2.0</td>
<td>4.4</td>
</tr>
<tr>
<td>PLA-30B-3.25</td>
<td>1.7</td>
<td>5.2</td>
</tr>
<tr>
<td>PLA-30B-4.50</td>
<td>1.9</td>
<td>4.6</td>
</tr>
<tr>
<td>PLA-30B-5.75</td>
<td>1.8</td>
<td>4.9</td>
</tr>
<tr>
<td>PLA-30B-7.00</td>
<td>2.1</td>
<td>4.2</td>
</tr>
<tr>
<td>PLA-30B-8.25</td>
<td>1.9</td>
<td>4.6</td>
</tr>
<tr>
<td>PLA-30B-10.00</td>
<td>2.2</td>
<td>4.0</td>
</tr>
</tbody>
</table>

In the literature, some studies reported XRD results showed morphology was exfoliated while TEM showed it contained intercalated particles or agglomerates. Krishnamachari et al. (2009a) reported there were no noticeable XRD peaks of PLA-30B nanocomposite of different nanoclay loading levels, observed at low-angle range, concluding that the silicate
layers of Cloisite® 30B were exfoliated in the PLA matrix. The study also reports TEM observations, where regions of tactoids of nanoclay are visible, indicating that the exfoliation was not complete. The authors commented on the discrepancy between the XRD and TEM results may be due to the disorderly and random distribution of the clay platelets within the PLA matrix. Similar results were also reported by Paul and Robeson (2008). As disorder increases in the sample, XRD becomes a less definitive technique (Morgan, 2000).

In another study, Lee et al. (2002) reported unusual observations of aliphatic polyester (APES)/organoclay nanocomposites. The XRD patterns of APES/Cloisite® 30B hybrids showed no peaks at high filler contents (15 - 30 wt %) of Cloisite® 30B, indicating an exfoliated structure, while there were peaks at lower filler contents, indicating an intercalated nanostructure. The TEM images of samples with both high and low filler content showed intercalated nanostructures with an expanded layer gap, regardless of the clay contents. However, the authors do not comment on the discrepancy between the XRD and TEM results. This calls for consideration of an accurate and quantitative SAXS analysis to complement and enrich the traditional morphological investigation of nanocomposites made by TEM and WAXD (Causin et al., 2005).

These studies emphasize the importance of using complementary techniques like TEM and SEM to fully characterise the composite morphology. XRD gives a large volume but intensity-proportional characterisation limited to d-spacing determination below 10 nm (Perrin-Sarazin et al., 2005). TEM is commonly used to look at the internal structure of the sample, while SEM looks at the surface (or the near-surface) (Zhou and Wang, 2007). TEM is capable of displaying magnified images of a thin specimen, typically with a magnification in the range $10^3$ to $10^6$ (resolution ~ 0.2 nm). A modern SEM provides an image resolution typically between 1 nm and 10 nm (Egerton, 2005).

The results for SEM and TEM are presented in the next sections.
5.3.2 Scanning electron microscopy (SEM)

To investigate the fracture surface of the samples for signs of large tactoids, such as agglomerates, samples were imaged using SEM. Selected SEM images of the PLA-30B nanocomposite (2, 5.75, and 10 wt % of nanoclay 30B) are shown in Figure 5.2 at 800x magnification, respectively. The unfilled sample exhibited characteristically smooth surfaces representative of brittle failure in a homogenous material. Samples of low clay concentration (2 wt %) evidenced minimal surface roughness isolated to small regions. Unlike the unfilled PLA (sample PLA-30B-0), the fracture surfaces of all the hybrid samples showed some voids and clay agglomeration. The clay spots can be seen clearly compared to that in unfilled PLA. SEM micrographs show that as the clay concentration in the nanocomposites increases, larger agglomerates of particles are observed and the average distance between the agglomerates decreases. At high clay loadings, owing to the difference in the scattering density between the clay and PLA, large clay aggregates can be easily observed. Also, some large deformed portions were seen, giving the fracture surface a coarse appearance. This might be due to pull-out of large aggregates of clay particles. Agglomerates give rise to lower clay-polymer surface interactions and higher stress concentrations. In general, both of these factors lead to lower mechanical properties of the nanocomposites. On the other hand, smaller agglomerate size and exfoliation of the clay result in highly improved mechanical properties (Basara et al., 2005). These morphological observations are consistent with tensile results in section 5.6.
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5.3.3 Transmission electron microscopy (TEM)

Generally, it is hard to achieve complete exfoliation of clays directly by melt mixing due to the physical and chemical environment between the organic and inorganic component. Moreover, some of the silicate layers flocculate easily owing to hydroxylated edge–edge interaction among themselves (Okamoto et al., 2001a). The majority of the polymer nanocomposites reported in the literature were found to have intercalated or mixed intercalated-exfoliated nanostructures (Chin et al., 2001). This is because the silicate layers are highly anisotropic, with lateral dimensions ranging from 100 to 1000 nm, and even when
separated by large distances (i.e. when delaminated) cannot be placed completely randomly in
the polymer matrix (Pavlidou and Papaspyrides, 2008). Hence an intercalated structure or
mixed intercalated-exfoliated structure is expected for this type of melt-mixed nanocomposite.

TEM is used to assess the nanostructure, in particular, the level of exfoliation, in a
nanocomposite. It can confirm the dispersion state of the clay in the matrix. Figure 5.3
presents the TEM image of PLA-30B-3.25 at a magnification of 10,000x and 80,000x. The
micrographs show there are many exfoliated and a few intercalated structures. For PLA-30B-
4.50 nanocomposite (see Figure 5.4 (a)), a mixed morphology of exfoliated and intercalated
nanostructure was observed at a magnification of 15,000x. A few stacked and flocculated
silicate layers randomly distributed in the PLA matrix can be seen with increasing clay
content. For 10 wt % clay loading (see Figure 5.4 (b)), the tactoids are composed of several
tens to hundreds of silicate layers, some are bent or broken into fragments due to the high
shear during melt processing. Some single layers are also apparent. Thus the PLA-30B is a
typical intercalated nanocomposite, with some exfoliated layers, and some agglomerates. This
is consistent with the results from SEM and SAXS. SAXS showed a weakly intercalated
structure, while SEM showed the structure contained some agglomerates.

The results are in good agreement with other studies. Krishnamachari et al. (2009a) and Zaidi
et al. (2010) studied the morphological properties of the PLA-30B nanocomposite prepared
by melt intercalation technique. They found that PLA and Cloisite 30B formed at least an
intercalated structure.
Figure 5.3 TEM micrographs of PLA-30B-3.25 at (a) 10,000x and (b) 80,000x magnification
Figure 5.4 TEM micrographs of (a) PLA-30B-4.50 at 15,000x magnification and b) PLA-30B-10.00 at 10,000x magnification
5.4 Rheology properties

The measurements of rheological properties are important to understand the processability of nanocomposites, as well as indicating the strength of polymer-layered silicate interactions and the structure-property relationship in nanocomposites. This is because the rheological behaviour is strongly influenced by nanoscale structure and interfacial characteristics (Sinha Ray and Okamoto, 2003). Under certain conditions, the rheological behaviour of the nanocomposites can vary, controlled by the dispersion degree (at constant loading), organoclay content, or the procedure of preparation. This indicates that optimisation of the fabrication conditions of the nanocomposites is essential (Pluta, 2006).

Determination of the linear viscoelastic region is essential before commencing tests for frequency sweep. Dynamic strain sweep was used to determine the linear viscoelastic region (LVR) of pure PLA and its nanocomposites. The plateau region, where storage modulus is independent of strain amplitude is the LVR. In this region the internal structure of the polymer is not affected by shear forces, so storage modulus ($G'$), loss modulus ($G''$) and complex viscosity ($\eta^*$) are independent of imposed strain. The configuration of the macromolecules is unperturbed by the flow history (Carreau et al., 1997). It means that the microstructure of the material is not affected by shear alignment during the experiment. $G'$ has been used here because it is the rheological function most sensitive to changes in the mesoscopic structure of the nanocomposite (Krishnamoorti et al., 2001, Prasad et al., 2006).

Dynamic strain sweep measurements to determine the LVR were performed at 175 °C and a frequency of 1 rad/sec. These showed that the LVR is very sensitive to the presence of the organoclay. Similar findings were also reported by other research groups (Pluta, 2006, Singh et al., 2012). As shown in Figure 5.5 the plateau region was found to decrease with the addition of MMT. The linear region for PLA was up to 100 % strain, whereas it decreased to about 5 % strain for PLA nanocomposites with 10 wt % of clay loading (see Figure 5.5). Hence the strain amplitude was taken as 1 % for all subsequent linear viscoelastic tests, which is well within the LVR for all samples.
In addition, dynamic time sweep tests (see Figure 5.6) were employed to check thermal stability of the melt samples for any changes with time. $G'$ was measured over time at a constant frequency (1 rad/sec) and strain (1%). As it can be seen in Figure 5.6, all melt samples had nearly constant $G'$ up to 100 sec and thus thermal stability for up to that time. A similar finding was recently reported by (Singh et al., 2012) for a similar PLA system.

Dynamic frequency sweeps are useful to assess the microstructure and dynamics of the materials (Prasad et al., 2006). In particular, the $G'$, $G''$, and $\eta^*$, estimates at very low frequencies are useful to compare the linear viscoelastic characteristics of the PLA nanocomposites with neat PLA. $G'$ and $G''$ are interesting as they represent the elastic and viscous responses of the studied system, respectively.
The master curves for $G'$ and $G''$ as a function of frequency of pure PLA and various PLA nanocomposites with different weight percentages of MMT loading are presented in Figure 5.7 and Figure 5.8. $G'$ and $G''$ increase with frequency for all samples, especially in the low frequency region. At low frequencies (<10 rad/s), both moduli exhibit weak frequency dependence with increasing MMT content, such that there are gradual changes of behaviour from liquid-like to solid-like with increasing MMT content. At high frequencies (>10 rad/s), the viscoelastic behaviours of all PLA nanocomposites converge. Other researchers also reported similar observation in polymer clay nanocomposites (Krishnamoorti et al., 1996, Gu et al., 2007, Ph, 2008, Singh et al., 2012)
Figure 5.7 Storage modulus ($G'$) of PLA nanocomposites ($T_{\text{ref}}: 175 \degree \text{C}$)

Figure 5.8 Loss modulus ($G''$) of PLA nanocomposites ($T_{\text{ref}}: 175 \degree \text{C}$)
Figure 5.9 shows the frequency dependency of the complex viscosity ($\eta^*$) for PLA and PLA nanocomposites. The $\eta^*$ of the unfilled PLA does not change at low frequencies, indicating behaviour is Newtonian, which is then followed by a shear thinning response in the higher frequency region. At low frequencies the polymer chains are fully relaxed and exhibit characteristic homopolymer-like terminal flow behaviour. A Newtonian plateau was also observed for the nanocomposites with low filler loading, up to 3.25 wt %. However, at higher clay loadings, from 4.50 wt % onwards, no Newtonian plateau was observed within the studied frequency range and the viscosity continued to increase with decreasing frequency, indicating a pseudo-yield-stress behaviour at low frequencies. Such pseudo-yield-stress behaviour was most prominent for the nanocomposite with the highest clay loading, 10 wt %. The frequency range and the viscosity continued to increase with decreasing frequency indicating more pseudo-yield-stress behaviour at lower frequencies. The pseudo-yield-stress behaviour was more prominent for the nanocomposites with higher MMT content, attributed to the formation of shear induced alignment of the dispersed clay particles (Gu et al., 2004, Sinha Ray and Okamoto, 2003). The increases in $G'$, $G''$ and $\eta^*$ with higher MMT loading suggest increasing confinement of polymer chains within and between the MMT layers. Indeed, it has been reported that the viscosities of confined polymer melts are greater than those of bulk chains (Luengo et al., 1997).
As shown in Figure 5.7 - Figure 5.9, the rheological behaviour of the nanocomposites investigated reveals clear dependence on the organoclay loading. The higher the organoclay loading in the PLA matrix the larger the interface area between the components (the aspect ratio of the silicate nanoplatelets is high). This makes a higher fraction of polymer chains confined by the organoclay surrounding; therefore, its mobility is restricted. Some contribution from direct interactions between individual silicate nanoplatelets and their tactoids is also possible (Pluta, 2006). At higher frequencies, the filler plays a smaller role in modifying the rheological behaviour of the polymer: both $G'$ and $\eta^*$ are similar for the nanocomposites and unfilled PLA. This implies that at higher frequencies the properties of the polymer matrix dominate the rheological behaviour of the nanocomposite system (Pluta, 2006).

The influence of organoclay loading on the melt rheology of the PLA matrix is similar qualitatively to several other studies of PLA/MMT nanocomposites with similar ranges of filler loadings up to 7 wt % (Sinha Ray et al., 2002, Sinha Ray et al., 2003c), and 10 wt % (Di et al., 2005), (Lee et al., 2006). Similar behaviour was also observed for nanocomposites
based on other polymer matrices, e.g., polypropylene (Solomon et al., 2001) and poly(butylenes terephthalate) (Wagener and Reisinger, 2003).

The percolation threshold corresponds to the formation of a three-dimensional network structure whereby clay layers act as physical cross linkers hence forming a mesostructure with enhanced clay-clay interactions (Reddy et al., 2007). It can be estimated for a system from the transition from viscous (liquid like) to more elastic (solid like) dynamic behaviour. The slopes of the terminal regions of the master curves for $G'$ and $G''$ are presented in Table 5.3. For pure PLA, the slope of $G'$ and $G''$, in the terminal region of the master curves is 1.72 and 1, respectively. These values are within the range expected for polydisperse polymers (Hoffmann et al., 2000). Polymer samples with similar molar mass had slopes of 2 and 1 for $G'$ and $G''$, respectively (Hoffmann et al., 2000).

For nanocomposite samples, the slopes of $G'$ and $G''$ are considerably lower than for pure PLA. For PLA nanocomposites with high MMT content, $G'$ becomes nearly independent at low frequency and exceeds $G''$, which is characteristic of materials exhibiting a pseudo-solid-like behaviour (Pluta et al., 2007, Ren et al., 2000).

According to Hoffmann et al. (2000), the slopes and the absolute values of the dynamic moduli indicate a supermolecular structure formation in the nanocomposites. The higher the $G'$ moduli and the smaller the slope, the more pronounced the interaction between the silicate platelets and their tendency to form a three-dimensional superstructure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G'$(ω)</th>
<th>$G''$(ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-30B-0</td>
<td>1.72</td>
<td>1.00</td>
</tr>
<tr>
<td>PLA-30B-2.00</td>
<td>0.93</td>
<td>0.92</td>
</tr>
<tr>
<td>PLA-30B-3.25</td>
<td>0.48</td>
<td>0.74</td>
</tr>
<tr>
<td>PLA-30B-4.50</td>
<td>0.28</td>
<td>0.64</td>
</tr>
<tr>
<td>PLA-30B-5.75</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>PLA-30B-7.00</td>
<td>0.17</td>
<td>0.41</td>
</tr>
<tr>
<td>PLA-30B-8.25</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td>PLA-30B-10.00</td>
<td>0.20</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 5.3 Terminal regions slopes of $G'(ω)$ and $G''(ω)$
Percolation threshold gives an indication where the three-dimensional network structural build up starts. The percolation threshold is the filler loading above which no further exfoliation is possible even if the shear rate applied to the sample is increased (Bhattacharya et al. 2009). When filler loading exceeds the percolation threshold, an exfoliated nanocomposite cannot form. The percolation threshold in PLA nanocomposites varies widely, attributed to intensity of the filler-filler and filler-polymer interactions and the degree of intercalation and exfoliation achieved within the nanocomposites. The value of percolation threshold is also very sensitive to the polymer type and aspect ratio of the reinforcement (Karippal et al., 2010).

The percolation threshold is estimated from the change in behaviour of the slopes of the terminal region from the dynamic frequency plot (as shown in Figure 5.10). It indicates that the viscoelastic properties of PLA nanocomposites in lower clay loadings (<4 wt %) are viscous, that is, dominated by the polymer matrix. With an increase in clay loading, there is a transition from liquid-like to solid-like behaviour, and the properties are elastic, that is, dominated by the filler. The figure shows that a distinct change in the slope of the curve takes place at around the 4.2 wt % clay loading region, indicating that the percolation threshold for the samples is between 3.25 to 6.00 wt %. This is consistent with reports of other studies in similar composites of percolation thresholds from 3 wt % to 5 wt % (Bhatia et al., 2009, Wu et al., 2006). The relatively low value of percolation threshold (4.2 wt %) for samples evaluated in this study suggests that they have a small average tactoid size. A range of percolation thresholds are quote in the literature. However, the authors don’t report on the tactoids size. TEM results (section 5.3.3) showed that up to 4.50 wt % of clay, the nanocomposite samples have mixed morphology of exfoliated and intercalated nanostructure. Above the percolation threshold, exfoliation decreases, and the structure becomes predominantly intercalated, with more and more agglomerates as the filler level increases.
Gupta and coworkers (Gupta et al., 2005) suggested that beyond a critical clay loading, the clay layers or tactoids are unable to rotate freely and thus prevent polymer chains from completely relaxing at low frequencies. Obviously, such a linear rheological response of polymer nanocomposites is closely related to polymer–clay and clay–clay interactions. Therefore rheological measurements offer direct information that characterises the behaviour of polymer nanocomposites in the molten state and assists in the elucidation and differentiation of the structure under shear flow.

In summary, the rheological properties of the PLA and its nanocomposites show that the $G'$, $G''$, and $\eta^*$ increased with addition of nanoclay content. This indicates that the PLA filled with Cloisite® 30B has good filler-matrix interactions.
5.5 Thermal properties

Several papers have shown that PLA is a thermally unstable polymer (Garlotta, 2001, Auras et al., 2004, Kopinke et al., 1996). One of the drawbacks of processing PLA in the molten state is its tendency to undergo thermal degradation at processing temperatures over 200 °C (Plackett et al., 2003). Because inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components, such as clay into organic materials, can improve their thermal stabilities (Chang et al., 2003b, Wu et al., 2006). The thermal characteristics of PLA nanocomposites were investigated using MDSC. The thermal stability of PLA nanocomposites was studied by TGA.

5.5.1 Modulated differential scanning calorimeter (MDSC)

The MDSC results of PLA and PLA nanocomposites are shown in Table 5.4 and Figure 5.11. These results reveal the following: glass transition temperature, \( T_g \), cold crystallisation temperature, \( T_{cc} \), enthalpy of crystallisation, \( \Delta H_c \), degree of crystallinity, \( \chi_c \), melting temperature, \( T_m \), enthalpy of fusion, \( \Delta H_m \). \( T_{cc} \) and \( T_m \) are taken at the peak maximum of the crystallisation and melting peaks. All results are from the second cycle of heating or cooling. \( T_g \) was taken as the midpoint of the incremental step change in heat capacity for heating scans. The SD of temperatures were measured as 0.7 °C (\( T_g \)), 2.3 °C (\( T_{cc} \)), 1.9 °C (\( T_m \)) and \( \chi_c \) as 2.2 %. Of these thermal properties, crystallisation is the most important from both a scientific and commercial viewpoint, because many mechanical properties of PLA are significantly influence by its crystallinity (Tsuji and Ikada, 1995, Kulinski and Piorkowska, 2005). Higher crystallinity leads to changes in properties such as higher modulus. The higher modulus of the nanocomposites is generally attributed to reinforcement effect of the filler, but may also indicate that the crystallinity is higher (Tanniru et al., 2006). Although PLA possesses many desirable properties, its crystallisation rate is extremely slow in comparison with commercial thermoplastics. The most viable method to increase the overall crystallisation rate was the blending of nucleating agent (Liao et al., 2007).

Table 5.4 shows that the \( T_g \) of pristine PLA decreased 1 - 2 °C with the addition of the organoclay, which is not significant compared to the measured SD (0.7 °C). The \( T_g \) depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction and steric effects, etc. (Clegg and Collyer, 1986, Cowie and Arrighi, 2007).
drop in $T_g$ could be due to a number of reasons such as clay aggregates, interphase regions, adhesion problems at the clay–matrix interface at elevated temperatures (Yasmin et al., 2006).

### Table 5.4 Thermal properties of PLA nanocomposites at various clay loadings

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\chi_c$ (%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-30B-0</td>
<td>61.9</td>
<td>120.6</td>
<td>25.2</td>
<td>26.9</td>
<td>151.0</td>
<td>21.5</td>
</tr>
<tr>
<td>PLA-30B-2.00</td>
<td>61.2</td>
<td>121.0</td>
<td>27.1</td>
<td>29.5</td>
<td>151.2</td>
<td>23.6</td>
</tr>
<tr>
<td>PLA-30B-3.25</td>
<td>61.0</td>
<td>114.6</td>
<td>28.3</td>
<td>31.3</td>
<td>155.1</td>
<td>23.3</td>
</tr>
<tr>
<td>PLA-30B-4.50</td>
<td>60.6</td>
<td>114.2</td>
<td>28.4</td>
<td>31.8</td>
<td>154.9</td>
<td>23.1</td>
</tr>
<tr>
<td>PLA-30B-5.75</td>
<td>60.8</td>
<td>116.5</td>
<td>28.2</td>
<td>32.0</td>
<td>155.0</td>
<td>23.2</td>
</tr>
<tr>
<td>PLA-30B-7.00</td>
<td>60.2</td>
<td>116.7</td>
<td>28.5</td>
<td>32.7</td>
<td>155.1</td>
<td>23.1</td>
</tr>
<tr>
<td>PLA-30B-8.25</td>
<td>60.0</td>
<td>115.2</td>
<td>28.3</td>
<td>33.0</td>
<td>155.0</td>
<td>23.1</td>
</tr>
<tr>
<td>PLA-30B-10.00</td>
<td>59.9</td>
<td>113.6</td>
<td>26.8</td>
<td>31.8</td>
<td>155.0</td>
<td>22.7</td>
</tr>
</tbody>
</table>

![Figure 5.11 MDSC curves of PLA/Organoclay nanocomposites](image.png)
Similar thermal behaviour has also been reported by several research groups (Kontou et al., 2011, Lee et al., 2003, Pluta et al., 2007). The $T_g$ reduction was attributed to an increase in polymer mobility (Ash et al., 2004, Zax et al., 2000). In such a case, Kontou et al. (2011) claimed that the interphase between matrix and nanofillers must be poor because of the lack of connecting polymer from the nanoparticles to the surrounding polymer matrix. Lee et al. (2003) reported that the MMT nanoclay may provide steric factors that provide more flexibility and mobility to the PLLA backbones, resulting in a decreased $T_g$. Meanwhile, Pluta et al. (2007) claimed this $T_g$ decrease can be explained by a plasticizing effect of the clay surfactant (~30 % in the Cloisite® 30B organoclay). The effect of plasticizers on the crystallisation of PLA is discussed in detail in other papers (Jacobsen and Fritz, 1999, Kulinski and Piorkowska, 2005, Pluta, 2004).

Paul et al. (2003b) reported increasing filler content did not significantly influence the $T_g$ or $T_m$ of PLA Cloisite® 30B nanocomposites. The SEM images of the nanocomposites showed aggregates, and the size of the aggregates increased with the nanofiller content. Because of the creation of aggregates, the increase of the nanofiller content did not lead to an extra increase of the total nanofiller surface area, and hence there was no effect on $T_g$ and $T_m$. MMT nanoparticles have a great tendency to create aggregates because of their larger surface area (Kontou et al., 2011).

In contrast to the above findings, Krishnamachari et al. (2009b) reported an increase of 6 °C in the $T_g$ with the addition of 1 wt % Cloisite® 30B in PLA. A further 2 °C increase was seen when the filler was increased to 2 wt % Cloisite® 30B. Thereafter the $T_g$ decreased by 6 °C as the filler loading was increased to 5 wt % of Cloisite® 30B, but still higher than that of the control sample of PLA. They attributed the initial increase in $T_g$ to a decrease in free volume in the polymer nanocomposite due to cross-linking caused by the intermolecular attraction between the diols of the organic modifier (Cloisite® 30B) with the C=O bonds present in the PLA. Exfoliation was indicated by XRD results. The differences between these studies suggest that changes in thermal properties depend on the degree of dispersion. A high degree of dispersion leads to an increase in $T_g$ and $T_m$.

Table 5.4 shows that the PLA sample had a melting point at about 151 °C and a heat of fusion of 21.5 J/g. The incorporation of MMT clays led to an increase by 4 °C at 3.25 wt % of clay
loading. Thereafter the $T_m$ did not change significantly. Most studies (Zou et al., 2012, Paul et al., 2003b, Di et al., 2005) reported that the incorporation of MMT clays did not significantly change the melting point of the materials. Sinha Ray and co-workers (2002, 2003c) reported a slight increase in $T_m$ (2 °C) with addition of organoclay, however, the authors did not comment on the increase.

Table 5.4 also shows that the cold crystallisation temperature, $T_{cc}$, of the PLA nanocomposites was significantly reduced by addition of organoclay. The $T_{cc}$ of PLA-30B-10 nanocomposites was 7 °C lower than neat PLA. Similar observations were reported by Lee et al. (2003) and Day et al. (2006). Both stated that clay nanoparticles can act as effective nucleating sites for crystallisation in PLA. This was attributed to the nucleating effect of the nanosized clay. The large surface area facilitates the PLA crystallisation process, thus, $T_{cc}$ decreases with the addition of nanoclays (Lee et al., 2003).

From Table 5.4, it can also be seen that the $\chi_c$ of PLA nanocomposites increased significantly (by $\pm 2.2$ SD) in the presence of organoclay up to around 8.25 wt %. Above 8.25 wt %, $\chi_c$ decreased. This indicates that the clay had a nucleation effect at lower clay loadings (Lewitus et al., 2006). The nucleation efficiency will be the highest below the percolation threshold. Thereafter the rate of increase of nucleation due to the presence of fillers reduces, finally becoming very low at very high clay loadings (Bhattacharya et al., 2009). This behaviour is attributed to the creation of larger agglomerates above the percolation threshold, and hence a reduction in the number of available nucleation sites. It can be said that a small amount of nucleating agent helps form polymer crystals while a larger amount hinders the ordered arrangement of molecular chains resulting in low crystallinity (Liao et al., 2007).

In summary, the $T_g$ did not change, the $T_m$ increased significantly, the $T_{cc}$ reduced significantly and the degree of crystallinity increased significantly, particularly at lower filler levels. This suggests the organoclay acts as a nucleator in PLA, especially at lower filler levels when there is a good degree of dispersion.

5.5.2 Thermogravimetric analysis (TGA)

Thermal stability is considered as an important factor from a scientific and industrial point of view, playing an important role in the nanocomposite structure and morphology formation.
(Leszczynska et al., 2007). In general, addition of filler can improve the thermal stability of the filled polymer composite systems. As inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components into organic materials can improve their thermal stabilities. Many studies have reported that polymer/MMT composites have higher thermal stability than that of the neat polymer matrix (Fukushima et al., 2009b, Kontou et al., 2011, Krishnamachari et al., 2009a, Krishnamachari et al., 2009b).

TGA is the method most commonly used to evaluate thermal stability in polymers. An increase in thermal stability with the increase in clay loading level was observed from the TGA traces, shown in Figure 5.12. The SD of the maximum degradation temperature was ±1.2 °C.

Table 5.5 summarises the maximum degradation temperatures. The degradation temperature was higher in all nanocomposites than in PLA. The shift was more pronounced for the nanocomposites with higher filler content. This suggests that the introduction of nanofillers increases the thermal stability of PLA (Krishnamachari et al., 2009b, Chow and Lok, 2009). The increase in thermal stability could be caused by an ablative reassembling of the silicate layers, which may occur on the surface of the nanocomposites, creating a protective barrier. In addition, the decomposition might also be delayed as a result of exfoliated silicate layers in the polymer matrix (Gilnian et al., 1998). The increase in the thermal stability has also been attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix (Fischer et al., 1999, Petrović et al., 2000). This is a common behaviour observed for nanocomposites and is partly responsible for their flame-retardant properties that are usually improved as well as their thermal stability (Alexandre and Dubois, 2000, Alexandre et al., 2001).

Figure 5.12 shows that at high temperatures the nanocomposites leave some residue. The weight of the residue at 600 °C increased linearly for all PLA/organoclay hybrids (see Table 5.5) as expected: the residue consists principally of clay. There are some significant differences between the nominal filler level and the residue level, attributed to small differences in filler level at the mixing stage. The SD of the residual weight % was measured as ±0.2.
Figure 5.12 TA thermograms of PLA-30B nanocomposites

Table 5.5 Thermal degradation behaviour of PLA nanocomposites at various clay loadings (as determined from the Derivate Weight loss curves)

<table>
<thead>
<tr>
<th>System</th>
<th>Onset degradation temperature (°C)</th>
<th>Maximum degradation temperature (°C)</th>
<th>Residue (wt %) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-30B-0</td>
<td>341</td>
<td>357</td>
<td>1.0</td>
</tr>
<tr>
<td>PLA-30B-2.00</td>
<td>342</td>
<td>359</td>
<td>3.4</td>
</tr>
<tr>
<td>PLA-30B-3.25</td>
<td>340</td>
<td>362</td>
<td>3.5</td>
</tr>
<tr>
<td>PLA-30B-4.50</td>
<td>341</td>
<td>363</td>
<td>5.2</td>
</tr>
<tr>
<td>PLA-30B-5.75</td>
<td>343</td>
<td>365</td>
<td>5.7</td>
</tr>
<tr>
<td>PLA-30B-7.00</td>
<td>343</td>
<td>369</td>
<td>7.2</td>
</tr>
<tr>
<td>PLA-30B-8.25</td>
<td>342</td>
<td>368</td>
<td>8.7</td>
</tr>
<tr>
<td>PLA-30B-10.00</td>
<td>342</td>
<td>370</td>
<td>9.1</td>
</tr>
</tbody>
</table>
In particular, two major factors, compatibility between the clay particles and the polymer matrix and thermal stability of clay, must be considered in order to produce nanocomposites by melt blending (Cai et al., 2010). One should set the processing temperature lower than decomposition temperature of the organic component used for montmorillonite modification, in order to avoid decomposition during processing. Xie et al. (2001) reported that at temperatures between 200 and 500 °C, the organic constituent in the organically modified MMT begins to decompose. Therefore, temperatures used in processing of these samples (175 – 195 °C) were set lower than the degradation temperature measured here, and hence it was expected that degradation would be avoided.

In conclusion, the thermal properties of PLA are significantly influenced by the addition of the organoclay Cloisite® 30B. The results suggest the nanocomposites have a degree of dispersion, but the dispersion decreases as the filler level increases. The organoclay acts as a nucleating agent for PLA. PLA nanocomposites containing a few percent of Cloisite® 30B are more thermally stable than neat PLA. The role of the organoclay in the nanocomposite acts as a heat barrier, which enhances the overall thermal stability of the system.

5.6  Mechanical properties

The tensile results of pristine PLA and PLA nanocomposites are presented in Figure 5.13 and summarised in Table 5.6. Values reported here are the averages of four specimens for each sample. The average Young’s modulus for neat PLA (SD) was 1108 MPa (±19 MPa) and average strength (SD) was 57 MPa (±2.2 MPa).

Table 5.6 shows that the modulus of the nanocomposites increased monotonically with increasing clay content. The increase in modulus at 10 wt % clay loading compared with the unfilled control PLA sample is around 54 %, which is a very significant improvement. This significant improvement in modulus is consistent with the nanocomposites having an intercalated structure and a high level of polymer-silicate interaction.
Tensile properties of PLA nanocomposites as a function of clay loading  

Figure 5.13  

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-30B-0</td>
<td>1110</td>
<td>57</td>
<td>7.0</td>
</tr>
<tr>
<td>PLA-30B-2</td>
<td>1240</td>
<td>59</td>
<td>9.6</td>
</tr>
<tr>
<td>PLA-30B-3.25</td>
<td>1250</td>
<td>56</td>
<td>7.0</td>
</tr>
<tr>
<td>PLA-30B-4.50</td>
<td>1360</td>
<td>55</td>
<td>6.3</td>
</tr>
<tr>
<td>PLA-30B-5.75</td>
<td>1430</td>
<td>47</td>
<td>4.5</td>
</tr>
<tr>
<td>PLA-30B-7.00</td>
<td>1560</td>
<td>38</td>
<td>3.5</td>
</tr>
<tr>
<td>PLA-30B-8.25</td>
<td>1710</td>
<td>32</td>
<td>2.5</td>
</tr>
<tr>
<td>PLA-30B-10.00</td>
<td>1710</td>
<td>29</td>
<td>2.3</td>
</tr>
</tbody>
</table>

There are only a few published results on tensile (tension) properties of PLA/organoclay nanocomposites (Thellen et al., 2005). Most studies on the mechanical properties of PLA/organoclay nanocomposites were reported using dynamic mechanical analysis (Sinha Ray et al., 2003c, Sinha Ray et al., 2003b, Krikorian and Pochan, 2003, Pluta et al., 2007).
Nevertheless, two studies did report improved tensile properties of the PLA nanocomposites. Thellen et al. (2005) reported the increase in the modulus of blown film PLA nanocomposites with 5 wt % MMT was 30 to 40 %. Li et al. (2006) also reported that adding 5 wt % MMT, Cloisite® 20A or Cloisite® 30B, to PLA increased the modulus by 15 % and 21 %, respectively. The nanoclay acts as a mechanical reinforcement of the polymer at a nanoscale molecular level and thus gives a higher modulus value (Lee et al., 2003).

The tensile strength and elongation at of the nanocomposite increased slightly at low levels of clay content (between 2 and 4 wt %), and decreased almost linearly with increases in the clay content. Many studies on polymer/organoclay nanocomposites have reported increased Young's modulus but lowered tensile strength and elongation at break (Alexandre and Dubois, 2000). Increased tensile strength was reported only for systems where strong polymer/organoclay interaction occurred (Lan and Pinnavaia, 1994, Fornes et al., 2001, Kojima et al., 1993). This indicates in this study the clay is dispersed uniformly at low concentrations (between 2 and 4 wt %) with a high surface attraction between the clay and the polymer matrix. Above this concentration, the attractive force between the clay and the polymer matrix was disturbed by the tactoid form of the clay (Rhim et al., 2009). This corresponds to passing through the percolation threshold region, estimated at 4.2 wt % clay loading (section 5.4). These results are consistent with presence of agglomerates above the percolation threshold, as seen in the SEM results (section 5.3.2). According to Chang et al. (2003a, 2003b), strength and elongation decrease if agglomerates are present.

PLA is a semicrystalline polymer, so the Young’s modulus partly depends on the crystallinity (Sedighiamiri et al., 2010): the higher the crystallinity, the higher the modulus. The higher modulus at higher clay loadings is consistent with the higher crystallinity (section 5.5.1 and Figure 5.14). This confirms that the nanoclays act as a nucleation agent and mechanical reinforcement of polymer chains in the nanoscale molecular level and thus give higher modulus values (Lee et al., 2003). This may be attributed to the surface modification treatment of Cloisite® 30B with MT2EtOH organic modifier, which allows higher degree of intercalation/exfoliation and better dispersion.
5.7 Summary

The influence of melt compounding conditions on the nanostructure of nanocomposites composed of PLA and Cloisite® 30B (up to 10 wt % fraction) and various properties was investigated. As revealed by GPC, the melt processing of PLA leads to a decrease in molecular weight and polydispersity due to hydrolysis. However, processing of the samples was optimised to minimise degradation: the polymer and clay were dried, the process temperature, mixing time and pressure were carefully controlled during the preparation process. They can be melt processed in a similar way to any commodity plastic composite. The ability to use conventional manufacturing processes is a very important factor for commercialisation of novel materials (Oksman, Skrifvars & Selin 2003).

Evolution of the nanostructure was induced by the intercalation followed by small tactoid formation and exfoliation of organoclay, observed by SAXS and TEM. Some agglomerates formed above the percolation threshold, observed by TEM and SEM. These three techniques complement each other in morphology characterisation of complex composite structures.
morphology studies revealed clearly that disordered intercalated nanocomposites were obtained by melt blending Cloisite® 30B with a PLA matrix.

The rheological behaviour of nanocomposites showed good polymer-silicate interaction and good dispersion. This shows the clay-surface modification was successful and the optimised mixing conditions provided sufficient shearing forces during melt compounding to achieve good dispersion. The rheological behaviour was sensitive to the nanostructure evolution showing pseudosolid-like behaviour as the filler loading increased.

Thermal stability of the nanocomposites improved with increasing Cloisite® 30B content. The crystallinity of the PLA matrix increased with clay loading: the nanoclay acts as a nucleator. It also provides mechanical reinforcement, thus giving higher modulus values.

In the next chapter work on PLA and natural MMT will be presented and discussed.
Chapter 6 : Properties of Polylactide Microcomposites

6.1 Introduction
This chapter describes PLA-based microcomposites that were prepared by melt blending the components at optimum processing conditions. PLA-based microcomposites were loaded with two types of natural (unmodified) MMT, Cloisite® Na⁺ and Cloisite® Ca⁺⁺DEV. The Cloisite® Na⁺ grade is water dispersible whereas the Cloisite® Ca⁺⁺DEV grade is not. The properties of the PLA microcomposites with up to 20 wt % loading were measured. The measured properties are morphology, rheology, thermal and mechanical properties.

6.2 Morphology properties
As for the nanocomposites, the morphology of microcomposites was also investigated by SAXS, SEM and TEM. Cloisite® Na⁺ is a pristine hydrophilic nanoclay (Cai et al., 2008). Their intrinsic hydrophilicity also makes them incompatible with hydrophobic polymers (Fischer, 2003, Olad, 2011, Muzny et al., 1996). It is well established in the literature that the degree of delamination and the dispersion of MMT platelets in the matrix are significantly affected by the chemistry of the clay surface (Dennis et al., 2001b).

6.2.1 Small-angle x-ray scattering (SAXS)
In Figure 6.1 and Figure 6.2, the SAXS diffractograms of Cloisite® Na⁺, Cloisite® Ca⁺⁺ and their corresponding microcomposites are presented for the range of 20 between 0.6 ° and 14 °. The natural MMT alone displayed a weak SAXS peak around 20 = 7.5 ° for Cloisite® Na⁺ and 20 = 5.9 ° for Cloisite® Ca⁺⁺, which corresponds to the d-spacing of d₀₀₁ = 1.2 nm and 1.5 nm, respectively. However no diffraction peaks were observed for either type of microcomposite. The SAXS pattern of PLA-Na and PLA-Ca microcomposites did not show any peaks corresponding to either the Cloisite® Na⁺ or Cloisite® Ca⁺⁺ or a possible intercalation. Pluta et al. (2002) attributed the absence in the XRD pattern of a diffraction peak to low amount of Cloisite® Na⁺ (3 wt %) dispersed in the PLA matrix. However in our composites system absence of expected peaks was observed at much higher filler loadings (up
to 20 wt %). The absence of a peak may therefore be attributed to its burial under the very broad signal associated with the PLA matrix (Pluta et al., 2002).

Figure 6.1 SAXS Diffractograms: Cloisite® Na⁺ and PLA-Na microcomposites

Figure 6.2 SAXS Diffractograms: Cloisite® Ca²⁺ and PLA-Ca microcomposites
Usually, blending polymer matrices with unmodified clay leads to the synthesis of conventional composites. Intercalation does not occur as the polymer does not migrate into the hydrated Na\(^+\) interlayer space due to its hydrophobicity (LeBaron et al., 1999, Pluta et al., 2002). Therefore, the overall nanoscale dispersion of the clay in the PLA is best described by SEM.

### 6.2.2 Scanning electron microscopy (SEM)

SEM observations of fracture surfaces were carried out for a selection of formulations. SEM images of the PLA-Na and PLA-Ca composite (3.25, 5.75, 10 and 20 wt %) are shown in Figure 6.3 and Figure 6.4 at 800x magnification, respectively. From 3.25 to 20 wt % clay, as the clay concentration increases, the clay spots can be seen clearly and interparticle distance decreases, as the clay fills the available volume. The SEM micrographs also show that as the clay concentration in the composites increases, larger agglomerates of particles and larger cavities can be seen on the deformed surface, without any plastic deformation, suggesting bonding between the non-dispersed clay particles and the polymer is deficient.
Figure 6.3 SEM micrographs of samples containing (a) 3.25 wt %, (b) 5.75 wt %, (c) 10 wt % and (d) 20 wt % Cloisite® Na⁺ at 800x magnification
Figure 6.4 SEM micrographs of samples containing (a) 3.25 wt %, (b) 5.75 wt %, (c) 10 wt % and (d) 20 wt % Cloisite® Ca++ at 800x magnification
6.2.3 Transmission electron microscopy (TEM)

Melt blending polymer matrices with unmodified MMT results in the formation of a microcomposite, as most of the polymers are too highly hydrophobic to migrate into the hydrated Na+ interlayer space (Paul et al., 2003b, Paul et al., 2005b). Indeed, Pluta et al. (2002) previously reported that only microcomposites could be formed by melt blending neat PLA and unmodified MMT.

The TEM micrographs of PLA-Na-3.25 and PLA-Ca-3.25 in Figure 6.5 and Figure 6.6 at 10,000x magnification, respectively clearly show stacked and flocculated silicate layers are randomly distributed in the PLA matrix. The aggregation of clay can be seen to cluster together in large domains ranging from a few hundred nanometers to micrometers in size. Figure 6.6 shows that a small amount of the clay forms high aspect ratio particles (possibly exfoliated) although the majority retains many aggregations of clay clusters.
Figure 6.5 PLA-Na-3.25 at (a) 10,000x and (b) 30,000x magnification
Figure 6.6 PLA-Ca-3.25 at (a) 10,000x and (b) 30,000x magnification
6.3 Rheology properties

The rheology of polymer composites is affected by the level of interaction between the polymer and the filler (Huang and Han, 2006). The particular effects found by adding particles as fillers will depend strongly on the nature of the individual filler particle and the way in which these particles interact with one another and the polymer. In order for the polymer to fully wet and intercalate the clay or organoclay tactoids, it is imperative that the surface polarities of the polymer and clays or organoclays be matched (LeBaron et al., 1999). Polar-type interactions are also critical for the formation of intercalated or exfoliated nanocomposites via polymer melt intercalation (Vaia and Giannelis, 1997). Typically the level of rheological properties, such as $G'$ and $G''$, are raised with filler addition. This usually takes the form of a progressive increase in the level of the property as more filler is added (Barnes, 2003). An increase in $G'$ indicates good filler–matrix interaction (Jordan et al. (2005).

6.3.1 Rheological properties of PLA Cloisite® Na⁺ composites

The rheological properties of PLA composites filled with Cloisite® Na⁺ are compared with neat PLA in this section. The master curves for $G'$ and $G''$ of pure PLA and various PLA microcomposites with different weight percentages of Cloisite® Na⁺ loading are presented in Figure 6.7 and Figure 6.8.

The figures show that both $G'$ and $G''$ decrease as clay loading increases, for all clay loadings. At low frequencies and high clay loadings, $G'$ and $G''$ have higher slopes in the terminal region compared to neat PLA. At high frequencies, the behaviour of all the samples converges. This suggests filler–matrix interaction is poor (Jordan et al. (2005). Poor filler – matrix interaction is expected in this system as the dispersed phase (clay) is hydrophilic and the continuous phase (PLA) is hydrophobic. This is consistent with the SEM images, which revealed that as the filler loading increased, filler agglomeration occurred.
Figure 6.7 Storage modulus ($G'$) of PLA-Na microcomposites ($T_{\text{ref}}$: 175 °C)

Figure 6.8 Loss modulus ($G''$) of PLA-Na microcomposites ($T_{\text{ref}}$: 175 °C)
Figure 6.9 shows the frequency dependency of the complex viscosity ($\eta^*$) for PLA-Na microcomposites. The $\eta^*$ of the unfilled PLA is constant at low frequencies, which is typical of high molecular weight viscoelastic polymers (Barnes, 2000). The complex viscosity of the PLA-Na microcomposites decreases with increasing clay loadings at lower frequencies, suggesting a weak interaction between filler and polymer. An interconnected structure is will form in polymer composites when there is a strong interaction between polymer molecules and fillers, giving enhanced melt viscosity (Mishra et al., 2005).

As shown in Figure 6.7 - Figure 6.9, the rheological behaviour of the microcomposites reveals clear dependence on the clay loading. Intercalation does not occur as the polymer does not migrate into the hydrated Na$^+$ interlayer space due to its hydrophobicity (LeBaron et al., 1999, Pluta et al., 2002). Untreated clay platelets are difficult to homogeneously disperse in the presence of organics because they tend to form large aggregates due to the hydrophilicity of these particles. This inter-particle interactions have a major impact on the rheological properties of composites (Ph, 2008).
The higher the clay loading in the PLA matrix, the more likely clay platelets are subjected to self-aggregation. The interphase between matrix and fillers must be poor, due to the lack of connecting polymer from the microparticles to the surrounding polymer matrix. This allows more flexibility and mobility of the polymer matrix than in a well bonded samples (Kontou and Niaounakis, 2010) and the continual creation of aggregates and agglomerates. Due to the creation of aggregates, the increase of the filler content does not lead necessarily to an extra increase of the total filler surface area. Hence while the effect of increasing filler level from 0 to 5.75% is significant a further increase to 20% has a much smaller impact.

The percolation threshold of the microcomposites can be estimated from the slopes of the terminal regions of the master curves for $G'$ and $G''$. The method for this was described in section 5.4. The data are presented in Table 6.1.

![Table 6.1 Terminal regions slopes of $G'(\omega)$ and $G''(\omega)$](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G'(\omega)$</th>
<th>$G''(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Na-0</td>
<td>0.90</td>
<td>1.00</td>
</tr>
<tr>
<td>PLA-Na-3.25</td>
<td>1.08</td>
<td>1.27</td>
</tr>
<tr>
<td>PLA-Na-5.75</td>
<td>1.20</td>
<td>1.37</td>
</tr>
<tr>
<td>PLA-Na-10.00</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>PLA-Na-20.00</td>
<td>1.40</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure 6.10 shows that a distinct change in the slope of the curve takes place around 9.1 wt % clay loading region, indicating that the percolation threshold for the samples is between 8 to 10 wt %. To the author’s knowledge here has been no report on the percolation threshold for these types of system.
6.3.2 Rheological properties of PLA Cloisite® Ca\textsuperscript{++} composites

PLA filled with Cloisite® Ca\textsuperscript{++} exhibits rheological properties similar to PLA filled with Cloisite® Na\textsuperscript{+}. The master curves for $G'$ and $G''$ of pure PLA and various PLA microcomposites with different weight percentages of Cloisite® Ca\textsuperscript{++} loading are presented in Figure 6.11 and Figure 6.12.

The figures show that again both $G'$ and $G''$ decrease as clay loading increases, for all clay loadings. At low frequencies and high clay loadings, $G'$ and $G''$ have higher slopes in the terminal region compared to neat PLA. This indicates that the PLA filled with Cloisite® Ca\textsuperscript{++} also has poor filler-matrix interactions due to hydrophilicity of Cloisite® Ca\textsuperscript{++} which makes them incompatible with hydrophobic PLA.

Again this is consistent with the SEM observations of fracture surfaces, which indicated that the clay particles are poorly dispersed in the polymer matrix.
Figure 6.11 Storage modulus (G’) of PLA-Ca microcomposites (T_{ref} : 175 °C)

Figure 6.12 Loss modulus (G’”) of PLA-Ca microcomposites (T_{ref} : 175 °C)
Figure 6.13 shows the frequency dependency of the complex viscosity ($\eta^*$) for PLA-Ca microcomposites is similar to that of PLA-Na microcomposites. The complex viscosity of the PLA-Ca microcomposites decreases with increasing clay loadings at low frequencies. The slopes of the terminal regions of the master curves for $G'$ and $G''$ are presented in Table 6.2.

![Figure 6.13 Complex viscosity ($\eta^*$) of PLA-Ca microcomposites ($T_{ref}$: 175 °C)](image)

### Table 6.2 Terminal regions slopes of $G'(\omega)$ and $G''(\omega)$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$G'(\omega)$</th>
<th>$G''(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Ca-0</td>
<td>0.63</td>
<td>0.75</td>
</tr>
<tr>
<td>PLA-Ca-3.25</td>
<td>0.75</td>
<td>1.31</td>
</tr>
<tr>
<td>PLA-Ca-5.75</td>
<td>0.85</td>
<td>1.31</td>
</tr>
<tr>
<td>PLA-Ca-10.00</td>
<td>0.97</td>
<td>1.42</td>
</tr>
<tr>
<td>PLA-Ca-20.00</td>
<td>1.00</td>
<td>1.42</td>
</tr>
</tbody>
</table>
Figure 6.14 shows the distinct change in the slope of the curve takes place around 8.9 wt % clay loading region, indicating that the percolation threshold for the samples is also between 8 to 10 wt %.

![Figure 6.14 Slope of G' at low frequency as a function of Cloisite® Ca⁺⁺ loading (wt %) for PLA microcomposites](image)

6.4 Thermal properties

The thermal characteristics of PLA microcomposites were investigated using MDSC. The thermal stability of PLA microcomposites were studied using TGA.

6.4.1 Modulated differential scanning calorimeter (MDSC)

The MDSC results of PLA-Na and PLA-Ca microcomposites are shown in Table 6.3 and Table 6.4, respectively.

Increasing clay content did not significantly influence the glass transition temperature, $T_g$, of the polymer: the results for $T_g$ were the same within experimental accuracy. This is similar to the findings of Pluta et al. (2002).
From Table 6.3 and Table 6.4 it can be seen that, on the other hand, melting and crystallisation temperatures and crystallinity were sensitive to clay loading. The melting temperature, $T_m$, increased significantly (up to 6 °C) with addition of clay. The cold crystallisation temperature, $T_{cc}$, decreased significantly with addition of clay. The $T_{cc}$ of PLA-Na-20 and PLA-Ca-20 microcomposites decreased by 8 °C and 10 °C, respectively as the filler loading was increased to 20 wt %. The degree of crystallinity of PLA in the presence of clays first increased slightly then decreased (above the percolation threshold). This suggests the clay particles act as effective nucleating sites for PLA crystallisation.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_{cc}$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\chi_c$ (%)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Na-0</td>
<td>61.9</td>
<td>120.6</td>
<td>25.2</td>
<td>26.9</td>
<td>150.9</td>
<td>21.5</td>
</tr>
<tr>
<td>PLA-Na-3.25</td>
<td>61.0</td>
<td>118.6</td>
<td>27.2</td>
<td>30.1</td>
<td>149.8</td>
<td>26.1</td>
</tr>
<tr>
<td>PLA-Na-5.75</td>
<td>61.3</td>
<td>116.1</td>
<td>28.2</td>
<td>31.9</td>
<td>148.8</td>
<td>23.8</td>
</tr>
<tr>
<td>PLA-Na-10.00</td>
<td>61.1</td>
<td>112.8</td>
<td>27.0</td>
<td>32.0</td>
<td>154.0</td>
<td>23.8</td>
</tr>
<tr>
<td>PLA-Na-20.00</td>
<td>60.5</td>
<td>112.5</td>
<td>22.2</td>
<td>29.7</td>
<td>153.8</td>
<td>19.9</td>
</tr>
</tbody>
</table>

Pluta and co-workers (2002) reported the opposite: an increase in $T_m$ and a decrease in $T_{cc}$. They commented that the effect on crystallisation increased as the filler size decreased. The differences to this study may be attributed to filler size (one of Pluta’s samples contained nanofiller) and to the filler level (Pluta’s samples had only 3 wt % filler).
6.4.2 Thermogravimetric analysis (TGA)

TGA curves recorded for PLA filled with Cloisite®Na⁺ and Cloisite® Ca²⁺ show that increasing the filler content triggers a substantial decrease in thermal stability (see Figure 6.15 and Figure 6.16).

The maximum degradation temperatures decreased by 1 °C as the filler loading was increased to 5.75 wt % of Cloisite® Na⁺. The maximum degradation temperatures continued to decrease as filler level increased up to 20 wt % loading levels of Cloisite® Na⁺. This may be attributed to the Na⁺ cations present in the interlayer spaces, which are highly hydrated cations. At high temperatures, some of the bonded water is released and this could be responsible for PLA chain degradation by hydrolysis. Therefore, at higher MMT-Na content, chain cleavage by an ester hydrolysis reaction will be more pronounced, leading to the formation of much shorter PLA chains, known to degrade at lower temperature (Paul et al., 2003b).

![Figure 6.15 TA thermograms of PLA-Na microcomposites](image)

Figure 6.15 TA thermograms of PLA-Na microcomposites
For PLA-Ca microcomposites, as the Cloisite® Ca⁺⁺ level varies from 3.25 to 20 wt %, the maximum degradation temperature also decreases. This may attributed to the poor physical interaction between the organic and the inorganic components (Gacitua et al., 2005). The increase in the thermal stability can be attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix (Wen and Wilkes, 1996, Fischer et al., 1999, Zhu et al., 1999). Table 6.5 and Table 6.6 summarise the maximum degradation temperatures.
Table 6.5 Thermal degradation behaviour of PLA-Na microcomposites at various clay loadings (as determined from the Derivate Weight loss curves)

<table>
<thead>
<tr>
<th>System</th>
<th>Onset degradation temperature (°C)</th>
<th>Maximum degradation temperature (°C)</th>
<th>Residue (wt %) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Na-0</td>
<td>341</td>
<td>357</td>
<td>1.0</td>
</tr>
<tr>
<td>PLA-Na-3.25</td>
<td>339</td>
<td>358</td>
<td>3.9</td>
</tr>
<tr>
<td>PLA-Na-5.75</td>
<td>337</td>
<td>357</td>
<td>6.4</td>
</tr>
<tr>
<td>PLA-Na-10.00</td>
<td>334</td>
<td>353</td>
<td>10.3</td>
</tr>
<tr>
<td>PLA-Na-20.00</td>
<td>329</td>
<td>354</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Table 6.6 Thermal degradation behaviour of PLA-Ca microcomposites at various clay loadings (as determined from the Derivate Weight loss curves)

<table>
<thead>
<tr>
<th>System</th>
<th>Onset degradation temperature (°C)</th>
<th>Maximum degradation temperature (°C)</th>
<th>Residue (wt %) at 600 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Ca-0</td>
<td>341</td>
<td>357</td>
<td>1.0</td>
</tr>
<tr>
<td>PLA-Ca-3.25</td>
<td>339</td>
<td>356</td>
<td>4.5</td>
</tr>
<tr>
<td>PLA-Ca-5.75</td>
<td>338</td>
<td>356</td>
<td>6.8</td>
</tr>
<tr>
<td>PLA-Ca-10.00</td>
<td>336</td>
<td>355</td>
<td>10.4</td>
</tr>
<tr>
<td>PLA-Ca-20.00</td>
<td>330</td>
<td>352</td>
<td>19.8</td>
</tr>
</tbody>
</table>

To summarise, the introduction of natural MMT decreases the thermal stability of PLA. In both microcomposites the samples leave some residue, as expected.
6.5 Mechanical properties

The tensile results of pristine PLA, PLA-Na and PLA-Ca microcomposites are summarised in Table 6.7 - Table 6.8.

Table 6.7 Tensile properties of PLA-Na microcomposites at various clay loadings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Na-0</td>
<td>1110</td>
<td>57</td>
<td>7.0</td>
</tr>
<tr>
<td>PLA-Na-3.25</td>
<td>1191</td>
<td>(+8 %)</td>
<td>52</td>
</tr>
<tr>
<td>PLA-Na-5.75</td>
<td>1250</td>
<td>(+13 %)</td>
<td>50</td>
</tr>
<tr>
<td>PLA-Na-10.00</td>
<td>1310</td>
<td>(+18 %)</td>
<td>50</td>
</tr>
<tr>
<td>PLA-Na-20.00</td>
<td>1490</td>
<td>(+35 %)</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 6.8 Tensile properties of PLA-Ca microcomposites at various clay loadings

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA-Ca-0</td>
<td>1110</td>
<td>57</td>
<td>7.0</td>
</tr>
<tr>
<td>PLA-Ca-3.25</td>
<td>1160</td>
<td>(+5 %)</td>
<td>50</td>
</tr>
<tr>
<td>PLA-Ca-5.75</td>
<td>1200</td>
<td>(+9 %)</td>
<td>49</td>
</tr>
<tr>
<td>PLA-Ca-10.00</td>
<td>1300</td>
<td>(+17 %)</td>
<td>49</td>
</tr>
<tr>
<td>PLA-Ca-20.00</td>
<td>1450</td>
<td>(+31 %)</td>
<td>49</td>
</tr>
</tbody>
</table>

The tables show that modulus of the microcomposites increases monotonically with increasing clay content. The magnitude of the increase is similar for both PLA-Na and PLA-Ca composites. The increase in modulus at 20 wt % clay loading compared with the unfilled control PLA sample is around 35 % for PLA-Na and 31 % for PLA-Ca microcomposites, which is a very significant improvement. This shows the natural MMT act as a mechanical reinforcement of polymer chains in the microscale molecular level and thus give modest increases in Young’s modulus values. Composites with poor polymer-filler interaction achieve mechanical reinforcement through friction between the polymer and filler due to shrinkage on cooling (Folkes, 1982).
There are a few research reports published in recent years on PLA microcomposites based on natural MMT (Pluta et al., 2002, Paul et al., 2003b). However, the mechanical properties of the PLA microcomposites were not reported, therefore a comparison with this study is not possible.

The tensile strength and elongation at break of both PLA-Na and PLA-Ca microcomposites decreased as the clay level varied from 3.25 to 20 wt %. It is well known that the presence of agglomerates causes a decrease in strength and elongation of microcomposites (Chang et al., 2003b, Chang et al., 2003a). The tensile strength and elongation results are consistent with those reported in the SEM results (section 6.2.2), where it was observed that the number of agglomerates increased with filler level.

Young’s modulus is also known to increase with crystallinity. The crystallinity results were discussed in section 6.4.1. It was found that crystallinity first increased then decreased with filler level. The trend with crystallinity does not correlate with the linear increase in Young’s modulus seen here (Figure 6.17). This suggests that the crystallinity had little impact on modulus. The primary mechanism for modulus enhancement in these microcomposites is filler mechanical reinforcement.
Figure 6.17 Degree of crystallinity and Young’s Modulus of PLA microcomposites at various clay loadings (a) PLA-Na (b) PLA-Ca
6.6 Conclusions

Natural clay minerals are hydrophilic. Thus the process challenge of using these nanoclays is not only to disperse the nanoparticles into the PLA matrix, but also to exfoliate the platelets to achieve the maximum surface area and high aspect ratio.

As revealed by SAXS, SEM and TEM, the melt processing of PLA and natural MMT leads to formation of conventional composites, due to its hydrophobicity in the composites system. The number of agglomerates increases as the filler level increased. The PLA-Na and PLA-Ca microcomposites have similar rheological properties. They do not show any improvement in their rheological properties, attributed to poor polymer-clay interaction, because strong hydrophilicity of natural clay does not have any compatibility with the hydrophobic PLA. Both samples have a percolation threshold between 8 to 10 wt %.

Thermal stability of the microcomposites shows that increasing the natural MMT content triggers a small decrease in thermal stability. The crystallinity of the PLA matrix increases with clay loading; the nanoclay acts as a nucleator. The Young’s modulus of the microcomposites increases very significantly with increasing filler loading. This is attributed to mechanical reinforcement effect of the filler. Tensile strength and elongation at break decrease slightly, attributed to presence of agglomerates.

There is little experimental work on composites with poor filler–matrix interactions (Jordan et al., 2005). Therefore it would be beneficial to carry out further studies in this area. In the next chapter, the properties of the PLA nanocomposites and microcomposites will be compared with those of neat PLA.
Chapter 7: Comparison of PLA/MMT nanocomposites and microcomposites

7.1 Introduction
In this chapter, morphology, rheology, thermal and mechanical properties of the PLA nanocomposites and microcomposites are compared with the neat PLA.

7.2 Morphology properties
In this section, both PLA nanocomposites and microcomposites morphology properties at 3.25 wt % MMT loading are compared with the neat PLA. In order for the polymer to fully wet and intercalate the clay or organoclay tactoids, it is imperative that the surface polarities of the polymer and clays or organoclays be matched (LeBaron et al., 1999). Polar-type interactions are also critical for the formation of intercalated or exfoliated nanocomposites via polymer melt intercalation (Vaia and Giannelis, 1997).

7.2.1 Small-angle x-ray scattering (SAXS)
Figure 7.1 shows the SAXS diffractograms of Cloisite® 30B, Cloisite® Na⁺, Cloisite® Ca⁺⁺ and those corresponding to their nano and microcomposites are presented for the range of 2θ between 0.6 ° and 14 °. Cloisite® 30B has an intense peak while Cloisite® Na⁺ and Cloisite® Ca⁺⁺ have weak peaks. For the PLA-30B-3.25, the diffraction peak is shifted to lower angles indicating that the d-spacing has increased and suggests the formation of disordered intercalated structure. The diffraction peak is also much weaker, due to dilution of the filler in the polymer. The SAXS pattern of PLA-Na-3.25 and PLA-Ca-3.25 did not show any peaks corresponding to either the Cloisite® Na⁺ or Cloisite® Ca⁺⁺ or a possible intercalation. This was attributed to concealment of the small peaks by the broad PLA peak. To confirm the nanostructure of the PLA/MMT hybrids and verify the conclusions from SAXS, further studies were carried out using SEM and TEM.
7.2.2 Scanning electron microscopy (SEM)

SEM images of the neat PLA and PLA composite at 3.25 wt % MMT loading are shown in Figure 7.2 at 800x magnification. When the micrographs of the nanocomposites and microcomposites are compared, it can be seen that at the same clay content, 3.25 wt %, nanocomposites with Cloisite® 30B exhibit a lower degree of agglomeration than microcomposites. The clay spots can be easily observed in the fractured surfaces of both microcomposites (Figure 7.2 (c) and (d)). This was attributed to poor dispersion of natural MMT. To justify that the degree of agglomeration is much higher in this micro than nanocomposites samples, it is best described by TEM in the next section.
Figure 7.2 SEM micrographs of samples (a) neat PLA, (b) PLA-30B-3.25, (c) PLA-Na-3.25 and (d) PLA-Ca-3.25 800x magnification

7.2.3 Transmission electron microscopy (TEM)

Figure 7.3 shows TEM micrographs of samples (a) PLA-30B-3.25, (b) PLA-Na-3.25 and (c) PLA-Ca-3.25 at 30,000x magnification, where the dark areas represent the clay and the gray/white areas represent the PLA matrix. It is clearly seen in Figure 7.3 (a) that the PLA-30B-3.25 nanocomposite has a morphology of well dispersed organoclay aggregates with thicknesses in the nano scale, Figure 7.3 (b) and (c) shows that the natural clay in PLA-Na-3.25 and PLA-Ca-3.25 microcomposite has large aggregates of natural clay bundled
together with much greater thickness. This indicates that the organic modification of MMT Cloisite® 30B provides the possibility for PLA chains to diffuse between the layers during processing (Shyang and Kuen, 2008) allowing for dispersion of the organoclay aggregates to exfoliated or intercalated particles.

![Figure 7.3 TEM micrographs of samples](image)

Clearly, one can see that the overall morphology was influenced by the nature of the filler. Mixing of the PLA with the modified clay resulted in formation of a nanocomposite material, with characteristic intercalated peaks in SAXS and high aspect ratio tactoids or exfoliated...
layers in TEM. Mixing of the PLA with natural (unmodified) clay did not result in the formation of a nanocomposite material, as no shift of the clay’s characteristic peak was observed in SAXS, large aggregates and agglomerates were observed in TEM and SEM. This emphasizes the importance of using multiple techniques to fully characterise the composite morphology.

7.3 Rheology properties

The rheological response of polymer composites is also sensitive to filler morphology and dispersion. It has been widely used to characterise micro- and nano-composites as the terminal region is highly sensitive to morphological changes and filler dispersion (Fornes et al., 2001, Shenoy, 1999). Figure 7.4 and Figure 7.5 show the effect of the type of clay on the $G'$ and $G''$ over a range of frequencies for the PLA composites filled with 3.25 wt % as well as the neat polymer. It can be seen that PLA-30B-3.25 has a significant increase of $G'$ and $G''$ in the terminal flow region in comparison with that of neat PLA. In contrast, both PLA-Na-3.25 and PLA-Ca-3.25 show a decrease in $G'$ and $G''$ in the terminal region (low frequency) compared to neat PLA.

![Figure 7.4 Storage modulus ($G'$) of PLA composites ($T_{ref}$: 175 °C)](image)
Figure 7.5 Loss modulus ($G''$) of PLA composites ($T_{ref}: 175 \degree C$)

Figure 7.6 shows the frequency dependency of the $\eta^*$ for PLA composite. The $\eta^*$ of the PLA-30B-3.25 has a significant increase compared to neat PLA, whereas for the PLA-Na and PLA-Ca microcomposites, the $\eta^*$ drops below that of the polymer.

The low $G'$, $G''$, and $\eta^*$ in PLA-Na and PLA-Ca samples was attributed to poor polymer-filler interactions and high number of aggregates and agglomerates. The opposite result in PLA-30B was attributed to confinement of polymer chains within the MMT layers and intercalation and exfoliation of clay layers. This is consistent with the SAXS, TEM and SEM results.
Figure 7.6 Complex viscosity ($\eta^*$) of PLA composites ($T_{\text{ref}} : 175 ^\circ C$)

All polylactides are insoluble in water (Madhavan Nampoothiri et al., 2010). Clay is normally very hydrophilic. This hydrophilic character makes them suitable for polymer systems that are water soluble or dispersable such as polyvinylalcohol, polyethylene oxides, latex, and polyvinylpyrrolidone (Powell and Beall, 2006). As it is shown in Figure 7.4 - Figure 7.6, PLA-Na has the lowest performance among this nanoclay. Such behaviour can be explained by the relatively high hydrophilicity of Cloisite® Na$^+$ compared to Cloisite® 30B (Paul et al., 2005).

Percolation threshold of the PLA composites also varies widely, depending on the filler-filler and filler-polymer interaction and the degree of intercalation and exfoliation achieved within the nanocomposites. The nanocomposite sample formed a percolated network at relatively low level of filler (4.2 wt %), due to the filler’s high aspect ratio. This is consistent with other studies on PLA nanocomposites. For the microcomposite samples, the percolation threshold was much higher, around 9.10 wt % for PLA-Na and 8.90 wt % for PLA-Ca. This is consistent with the lower aspect ratio of filler in these samples.
In this study, TEM and rheological characterisation certainly strengthens the hypothesis that PLA-30B compounds were intercalated, whereas PLA-Na and PLA-Ca formed a phase-separated microstructure. It appears that PLA is a polymer that readily interacts during melt blending with a MMT organomodified with with bis-(2-hydroxyethyl) methyl (hydrogenated tallowalkyl) ammonium cations, leading to the formation of at least an intercalated structure.

7.4 Thermal properties

7.4.1 Modulated differential scanning calorimeter (MDSC)

Figure 7.7 and Figure 7.8 show the effect of the type of clay on the $T_g$ and $T_m$ results of PLA composites. Increasing clay content does not influence the $T_g$ significantly compared to the pure matrix. However, $T_m$ increased significantly for PLA composites (up to 6 °C). The increased in $T_m$ was attributed to a nucleation effect of clay filler (Lewitus et al., 2006). The increase in $T_m$ occurs at lower loadings in the nano- compared to the microcomposites. The increase is seen at a level similar to the percolation threshold, which is lower in the nano- than the microcomposites. The percolation threshold in PLA-30B was found to be 4.2 wt %, and in PLA-Na and PLA-Ca was 8.9 and 9.1 wt %, respectively.
Figure 7.7 $T_g$ of PLA composites

Figure 7.8 $T_m$ of PLA composites
From Figure 7.9, it can be seen that the degree of crystallinity of PLA increased very significantly in the presence of organoclays. The additions of unmodified clay also provide a modest increment in crystallisation of PLA. This confirms that the incorporation of clay (organoclay or unmodified) promotes PLA crystallisation.

Figure 7.9 Crystallinity of PLA composites

7.4.2 Thermogravimetric analysis (TGA)

In general, addition of filler can improve the thermal stability of the filled polymer composite systems to some extent. Based on the fact that inorganic species have good thermal stabilities, it is generally believed that the introduction of inorganic components into organic materials can improve their thermal stabilities (Wen and Wilkes, 1996). The increase in the thermal stability can be attributed to the high thermal stability of clay and to the interaction between the clay particles and the polymer matrix (Wen and Wilkes, 1996, Fischer et al., 1999, Zhu et al., 1999).

Figure 7.10 summarises the maximum degradation temperatures of the PLA composites. An increase in thermal stability with the increase in clay loading level was observed for PLA-30B
nanocomposites. In contrast to Cloisite® 30B based composites, TGA curves recorded for PLA filled with Cloisite® Na⁺ and Cloisite® Ca⁺⁺ show that increasing the filler content triggered a substantial decrease in thermal stability.

Many studies (Fukushima et al., 2009b, Kontou et al., 2011, Krishnamachari et al., 2009a) have reported that the polymer/MMT composites present higher thermal stability than that of the neat polymer matrix. The increase in thermal stability was attributed to ablative reassembling of the silicate layers, which may occur on the surface of nanocomposites, creating a protective barrier. In addition, the decomposition might also be delayed as a result of exfoliated silicate layers in the polymer matrix (Gilnian et al., 1998). This is a common behaviour observed for nanocomposites and is partly responsible for their usually improved flame-retardant properties (Alexandre and Dubois, 2000, Alexandre et al., 2001).

Conversely, the lower thermal stability of the microcomposites despite the high thermal stability of clay was attributed to poor interaction between the clay particles and the polymer matrix (Wen and Wilkes, 1996, Fischer et al., 1999, Zhu et al., 1999).

Figure 7.10 Maximum degradation temperature of PLA composites
Park et al. (2003) observed that biodegradable thermoplastic starch (TPS)/Cloisite® Na⁺ nanocomposites exhibited better thermal stability than the TPS/Cloisite 30B nanocomposites at the same clay contents. The TPS used in their work was hydrophilic. They claimed that the strong polar interaction between TPS and Cloisite® Na⁺ was responsible for this behaviour.

So, the introduction of Cloisite® 30B increases the thermal stability of PLA where the microcomposites are slight less stable. The results are in good agreement with a similar study by Pluta et al. (2002). They attributed a difference in thermal stability between nano- and microcomposites to the difference in morphology. The addition of natural clays lowers the temperature of the decomposition peak, attributed to poor dispersion of the natural clays in the PLA phase.

7.5 Mechanical properties
The tensile results of pristine PLA and PLA composites are presented in Figure 7.11 - Figure 7.12. It was found that the Young’s modulus of the composites increased monotonically with increasing clay content. At 10 wt %, the increase in Young’s modulus compared with the unfilled control PLA sample was around 54 % for PLA-30B, which is a very significant improvement. This significant improvement in modulus is consistent with the nanocomposites having an intercalated structure and a high level of polymer-silicate interaction leading to large mechanical reinforcement. This may be attributed to the surface modification treatment of Cloisite® 30B with MT2EtOH organic modifier, which allows higher degree of intercalation/exfoliation and better dispersion of filler than untreated filler, leading to high aspect ratio.

The addition of unmodified clay provided a modest improvement to the Young’s modulus of PLA. At the same 10 wt % filler loading, PLA-Na and PLA-Ca improved modulus by 18 % and 17 %, respectively. The inferior performance of the micro filler was attributed to the low interaction between the low aspect ratio microparticles and surrounding polymer matrix, as well as the creation of aggregates and/or agglomerates as shown by SEM and TEM.
In contrast to the Young’s modulus results, the tensile strength and extension decreased with the introduction of more of the inorganic phase and high aspect ratio filler. At low filler loadings the nanocomposite PLA-30B had significantly better tensile strength than the microcomposites. However once the percolation threshold of 4.2 wt % was exceeded, the performance of the nanocomposite was inferior to the microcomposite samples. A very significant decreased in tensile strength was observed for PLA-30B, particularly around the percolation threshold. At 10 wt % of clay loading, the tensile strength decreased about 47% compared to only 15 % for PLA-Na and 13 % for PLA-Ca. Tensile strength and elongation at break are very sensitive to presence of agglomerates, so these results are consistent with the SEM and TEM results, as well as the rheology results for percolation.
Figure 7.12 Tensile strength (a) and Extension (b) of PLA composites as a function of clay loading.
7.6 Conclusions

PLA properties are influenced by the nature of the filler. The organic modification of the MMT improves the morphology, rheology, thermal and mechanical properties of the neat PLA. The modification of the surface of the MMT by cationic surfactant increases the compatibility between the PLA and the clay, obtaining a composite with superior properties to those of neat matrix. In particular, Cloisite® 30B exhibits high performance due to its affinity between the clay and the matrix. Cloisite® Na⁺ and Cloisite® Ca⁺⁺ clays exhibit poorer performance, due to poor dispersion in the PLA matrix as well as poor polymer-filler interactions.

The nanoscopic dimensions result in some interrelated characteristics, which distinguish nano- from microcomposites. Nanocomposites have lower percolation thresholds compared to microcomposites. The degree of crystallinity of PLA increases very significantly in the presence of organoclay and increases the thermal stability of PLA. Addition of only a small amount of organoclay improves the Young’s modulus of PLA significantly. This shows the good compatibility of Cloisite® 30B with the PLA matrix, with its hydrophobic character, compared to Cloisite® Na⁺ and Cloisite® Ca⁺⁺. The better compatibility induced a better dispersion and stronger polymer-filler interactions.

In the next chapter, the composite theory of Halpin–Tsai is applied to calculate the Young’s modulus of the nano and microcomposite as a function of the organoclay concentration.
Chapter 8: Modelling Young’s modulus of polylactide/organoclay nanocomposites using a Halpin–Tsai micromechanical model

8.1 Introduction
In this chapter, the composite theory of Halpin–Tsai is applied to calculate the Young’s modulus of the nano and microcomposite as a function of the organoclay concentration. The objective is to evaluate whether the Young’s modulus of PLA composites (both nano and micro) can be modelled using the Halpin-Tsai micromechanical model by comparing the experimental data of the modulus to theoretical predictions made.

8.2 Modelling young’s modulus of PLA composites using a Halpin–Tsai micromechanical model
A good filler dispersion has been demonstrated to be critical for the acquisition of properties superior to those of microcomposites (LeBaron et al., 1999, Gilman, 1999), but it is still unclear how other parameters, such as the filler aspect ratio, influence the overall properties of the nanocomposites. Hence, modelling the material response would provide valuable information on the underlying physics and be useful to achieve the desired structure–property linkage. Furthermore, once the desired structure is established, modelling has the capability to assist the development of material processing (Yung et al., 2006).

The mechanical behaviour of composite materials can be predicted rather well on the basis of structural modelling. PLA/organoclay formulations have predictable elastic and viscoelastic moduli when the clay particles are well-dispersed in the polymer matrix and far apart from each other. However, as soon as particle aggregation occurs and especially where the rubbery plateau modulus is concerned, structural models fail to predict results similar to experimental data. Yung et al. (2006), suggest that careful mapping between the characteristic clay structural parameters and the conventional micromechanical model parameters is needed to improve the correlation.
The Halpin–Tsai (H-T) model was chosen for use in this work for various reasons. It is effective in predicting the stiffness of glass fibre reinforced composites. It is adaptable to different filler geometries, particularly disks. It is prevalent in the literature (Affdl and Kardos, 1976, Tandon and Weng, 1984, Shia et al., 1998). It has been satisfactorily applied to polymer based nanocomposites and was included in the thorough review of micromechanical models for composite modulus by Mohapatra et al. (2011) and Fornes and Paul (2003).

8.3 Theoretical models versus experimental data

For conventional composite systems, several theoretical frameworks, such as Halpin-Tsai, have been developed for predicting various properties of a composite based on the properties of its individual components. These frameworks are useful for evaluating the contribution of individual components and for optimizing the overall performance of a composite based on the matrix ($E_m$) and filler modulus ($E_f$), volume fraction ($\phi_f$), filler aspect ratio ($\alpha_f$) and orientation ($S$) etc. In all these theories, the underlying assumptions are (i) all components in a composite will act independently and (ii) the interaction or bonding between the matrix and fillers is strong enough for load transfer (Li et al., 2005). However, according to Li et al. (2005) none of these frameworks can be applied directly to the nanoclay reinforced nanocomposite materials, in which the roles of aspect ratio, dispersion, and orientation of the fillers are more critical compared with conventional composites. Hence there is a need to identify which models are suitable for clay-based nanocomposites.

8.3.1 Calculation using the Halpin-Tsai equations

According to the Halpin-Tsai equations,

$$\frac{E_c}{E_m} = \frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f}$$

Equation 8.1

where $\eta$ is given by

$$\eta = \frac{E_f / E_m - 1}{E_f / E_m + \zeta}$$

Equation 8.2
\( \zeta \) is a shape parameter depending on filler geometry and loading direction, as shown in Figure 2.6.

The tensile modulus of an individual MMT platelet, \( E_{MMT} \), is commonly reported in the literature as 178 GPa (Fornes and Paul, 2003, Termonia, 2007, Chen and Evans, 2005) or 170 GPa (Yasmin et al., 2006, Rodlert et al., 2004, Luo and Daniel, 2003). Chen and Evans (2006) reported the Young’s modulus of clay platelets is considered to be within the range 178–265 GPa. In this study, \( E_{MMT} \) is taken as 178 GPa as recommended by manufacturer. The measured elastic modulus of PLA polymer was 1.108 GPa. The density of the MMT is 1.98 g/cc and that of the PLA is 1.25 g/cc.

The relevant modulus for this study is \( E_\parallel \): fillers align with the direction of flow in a high shear field and this is the case in the narrow part of a tensile bar (Folkes and Russell, 1980). Ashton et al. (1969) determined that assuming \( \zeta = 2(l/t) \) provides good agreement for longitudinal modulus, where \( l \) and \( t \) are the length and thickness of the fibre. The modulus perpendicular to the fibre direction (transverse), on the other hand, was found to be relatively insensitive to fibre aspect ratio, and could be approximated by \( \zeta = 2 \) (Ashton et al., 1969).

Unlike glass fibre composites, the determination of filler aspect ratio, for layered aluminosilicate nanocomposites is not straightforward. Both average \( l \) and \( t \) can be evaluated by statistically analysing the TEM images of the composites. TEM images with magnifications in the range of 60,000x to 80,000x can provide data that represent the length and thickness of the clay particles within the matrix (Fornes and Paul, 2003, Nam et al., 2001). However this has limited accuracy. Current composite theories do not give any guidance of which aspect ratio to use when there is a distribution of lengths and thicknesses (Fornes and Paul, 2003). Fornes and Paul depicted various complications of calculating an aspect ratio from TEM micrographs. Good estimates require a thorough analysis of TEM micrographs at different magnifications and require analysing several hundred particles however; this was beyond the scope of this project.

In this study size of filler was estimated from manufacturer’s specification, XRD and TEM micrographs. Sample sizes were found to have a broad range of values. For example, Figure 8.1 and Figure 8.2 were used to estimate particle length and thickness. Figure 8.1 shows the TEM bright field image of (a) PLA-30B-4.50 and (b) PLA-30B-10.00 nanocomposites. In
these TEM photographs, the light regions represent the matrix PLA. The dark entities are the cross-section of intercalated silicate layers (Klimentidis and Mackinnon, 1986). The PLA molecules separate the clay particles into either individual layer or intercalated particles. The images show particles with a wide range of lengths from 20 to 150 nm. The actual length is likely to be longer, as when circular particles are dissected the average length of the chord is typically less than the maximum diameter, by a factor of about 30% (Lewis et al., 1996). The thickness of a single layer is 1 nm (Sinha Ray et al., 2002, Ma et al., 2003). The average thickness of a single layer in an intercalated particle was measured using XRD (section 5.3.1) as 4.6 nm. The TEMs in Figure 8.1 shows some single layers and some intercalated particles with 5 to 10 layers. Hence the thickness of these particles ranges from 20 to 50 nm. The range of observable aspect ratios is then 150 ($l/d = 150/1$ nm) to 0.4 ($l/d = 20/(4.6 \times 10)$). Such a wide range is complex to model, so literature values of clay aspect ratios were taken as a starting point in this study.

Comparison of Figure 8.1 with figures (a) and (b) shows that the length may vary to some degree with filler concentration during the composite preparation process. However, previous TEM studies indicate the variation is small (Fornes et al., 2001, Fornes et al., 2002). In some cases, these platelets may be skewed relative to one another as suggested in Figure 8.2 (Chavarria and Paul, 2004). Thus, some particles may appear to be longer than the platelets really are. These kinds of issues should be kept in mind when interpreting quantitative analyses of particle aspect ratios and in comparison of observed performance with that predicted by composite theory (Fornes and Paul, 2003).

Given the wide range of aspect ratios observed in the TEM images, literature values of aspect ratio were used as a starting point in this study.
Figure 8.1 TEM micrographs of (a) PLA-30B-4.50 (b) PLA-30B-10.00 at 30,000x magnification
Recent studies vary in estimation of aspect ratio for organoclays. Mohapatra et al. (2011) have recently reported that the aspect ratio of PLA/Cloisite® 30B is 28. Sinha Ray and Okamoto (2003) reported that the average aspect ratio of the PLA/organoclay is about 12-13. Durmus et al. (2008) reported that the average aspect ratio of the organoclay is about 2-5 before compounding. In this study a range of literature values was trialled: three different aspect ratios ($l/t = 28$, $l/t = 12$ and $l/t = 4$) were selected.

An example calculation using the Halpin-Tsai equations for the Young’s modulus of a PLA composite containing 2 wt% of Cloisite® 30B is given below.

First, the weight-fraction of the MMT must be converted to a volume fraction. Volume fraction, $V_f$:

$$V_f = \frac{W_f / \rho_f}{W_f / \rho_f + (1-W_f) / \rho_m}$$

\text{Equation 8.3}

where

$V_f$ = volume fraction of fibres

$W_f$ = weight of fibres

$W_m$ = weight of matrix

$\rho_f$ = density of fibres

$\rho_m$ = density of matrix
Using values of density for PLA and filler from the literature, the volume fraction was calculated for 2 wt % as is 0.013.

Assuming an aspect ratio of the $l/t = 4$, and solving for $\eta$:

$$\eta = \frac{(178/1.108)\times 1 - 1}{(178/1.108)\times 1 + (2\times 4)} = 0.95$$

Substituting these results into Halpin-Tsai equations,

$$\frac{E_{||}}{E_m} = \frac{1 + \zeta \eta \phi_f}{1 - \eta \phi_f} = \frac{1 + 8\times 0.95\times 0.013}{1 - 0.95\times 0.013} = 1.230$$

This compares well with the measured Young’s modulus for this sample of 1.240 GPa.

Figure 8.3 shows that increasing the aspect ratio from 4 to 28 in PLA-30B nanocomposites leads to a significant increase in reinforcement efficiency. The model results show good agreement with the measured Young’s modulus of the samples when the aspect ratio is about 4.

The Halpin-Tsai theory assumed that the filler is perfectly aligned, there is good bonding between the matrix and the filler, the matrix and the filler are isotropic, and there are no filler particle–particle interactions or agglomerations (Fornes and Paul, 2003). The theory also does not account for the effect of crystallinity level that may be changed by the filler. The good agreement between the predicted and measured moduli suggests these assumptions are valid for these composites.

The model results, that aspect ratio is $l/t = 4$, is lower than that found by Sinha Ray and Okamoto (2003) for a similar system. Aspect ratio can be estimated experimentally from TEM micrographs. As discussed above, the number of layers in intercalated particles showed a wide range widely, from around 5 to 10 layers. The average thickness of an individual layer (from SAXS) was measure as 4.6 nm. So the thickness of these particles ranges from 20 to 50 nm. The length of the samples is estimated to range from 20 to 150 nm, giving an aspect ratio of 0.4 to 7.5. Hence $l/t = 4$ is in reasonable agreement with the TEM study.
Aspect ratios reported in the literature vary widely. Sinha Ray and Okamoto (2003) reported an average aspect ratio of 12-13 for PLA/organoclay nanocomposites. Durmus et al. (2008) reported an average aspect ratio range of 2–5 for organoclay before compounding. According to Giannelis (1996), an aspect ratio of below 10 indicates undispersed or poorly dispersed particles. Luo and Daniel (2003) reported an aspect range of 100–1000 for nanocomposite systems. Yasmin et al. (2003) observed that shear mixing reduced the aspect ratio of clay platelets in epoxy by a factor ranging from 2 to 10, while Olad (2011) reported the aspect ratio of clay platelets is reduced by a factor ranging from 3 to 5. This was attributed to the milling process, which breaks the clay platelet during mixing. However, the resultant nanocomposites still exhibited significant improvement of mechanical properties. Hence the aspect ratio seen in this study is within the reported range in the literature, but the ratio is low, suggesting the particles are not as well dispersed as in other studies.

Figure 8.3 Estimation of average aspect ratio of clay tactoids in PLA-30B composites by the Halpin-Tsai micromechanical model

<table>
<thead>
<tr>
<th>l/t</th>
<th>Experimental data</th>
<th>Halpin-Tsai Equations</th>
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<tbody>
<tr>
<td>28</td>
<td></td>
<td>$E_m = 1.108$ GPa</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
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</table>

Disks

$E_{MMT} = 178$ GPa
Figure 8.4 and Figure 8.5 show that the model results show good agreement with the measured Young’s modulus of the PLA-Na and PLA-Ca samples when the aspect ratio is about 2, which is in agreement with Durmus et al. (2008), who reported that the average aspect ratio of the organoclay is about 2–5 before compounding. As the clay is unmodified, no change in aspect ratio is expected after compounding, as no intercalation or exfoliation occurs.

The aspect ratio of \( l/t = 2 \) is lower than that estimated for the composites with Cloisite 30B (\( l/t = 4 \)). A higher aspect ratio for Cloisite 30B nanocomposites is expected, as its morphology changed with compounding to an exfoliated/intercalated structure.

Direct observations for the individual platy MMT particles using atomic force microscopy (AFM) were reported by Yalcin and Cakmak (2004). These examples clearly indicate that the particles in the matrix may have complicated irregular shapes, which, in general, may not be well approximated by a single aspect ratio (Lee and Paul, 2005).

A more accurate estimate of aspect ratio by quantitative examination of multiple TEM micrographs was beyond the scope of the current study. An experimental confirmation of the estimation of the aspect ratio from the Halpin-Tsai model would be interesting so it is recommended for future work. The aspect ratio of clay inclusions should be directly calculated by measuring the length and thickness of the dark lines in TEM micrographs at different magnifications (Fornes and Paul, 2003).
Figure 8.4 Estimation of average aspect ratio of clay tactoids in PLA-Na composites by the Halpin Tsai micromechanical model

Figure 8.5 Estimation of average aspect ratio of clay tactoids in PLA-Ca composites by the Halpin Tsai micromechanical model

Halpin-Tsai Equations

E_m = 1.108 GPa

Disks
E_{MMT} = 178 GPa
8.4 Summary

A comparison of the experimental data of Young’s modulus with values predicted from a model based on the Halpin-Tsai model indicates that the aspect ratio of the clay layer is about 4 for PLA-30B, and 2 for PLA-Na and PLA-Ca. The model predicts the behaviour of PLA composites satisfactorily with the appropriate material parameters obtained from the literature. A number of assumptions and simplifications were made in the model: the good agreement suggests that these are valid for these nano and microcomposites. A more accurate estimate of aspect ratio by quantitative examination of multiple TEM micrographs is recommended.

Both experimental observations and micro-mechanical model predictions carried out in this study have clearly indicated that clay aspect ratio significantly affects the nanocomposite modulus. A high aspect ratio can lead to a significantly improved modulus.

The next chapter summarises major conclusions and recommendations for future work.
Chapter 9 : Conclusions and Recommendations

9.1 Introduction
This chapter presents a summary of the key findings and foregrounds these findings against the research questions and theoretical framework of this study. New knowledge that emerged from this study and suggestions for further research are presented.

9.2 Conclusions
The conclusions of this work can be divided into three parts. In the first part, the optimum processing conditions of PLA nanocomposites are summarised. In the second part, the properties of composites which were produced from the optimised processing conditions are summarised according to the research questions. Finally, various correlations arising from this work used to predict the properties of PLA composites are summarised.

9.2.1 Optimum processing conditions
One novel contribution of this study is the optimisation of processing conditions by using statistical analysis. Results showed that the optimum processing conditions depends on rotor speed, temperature and mixing time, and that mechanical properties vary significantly with processing conditions. Inferior properties will result if mixing conditions are not optimised. Experimental design is a useful approach to ensure mixing is optimised. The particular optimum conditions for this polymer-filler combination using a Haake rotary batch mixer were found to be at 175 ºC, 100 rpm and 7 min but these will be different for different composites or different mixers.

The interaction effect with most influence on the Young’s modulus of these PLA/organoclay nanocomposites is temperature and speed. Young’s modulus also increases quadratically with time.
### Properties of composites

In responding to the research questions of this study, the following conclusions are drawn:

<table>
<thead>
<tr>
<th>1. What is the morphology of PLA nanocomposites samples produced with various organoclay contents?</th>
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<tbody>
<tr>
<td>- An intercalated structure with some exfoliation is achieved for these PLA-30B nanocomposites as evidenced by SAXS and TEM measurement.</td>
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<tr>
<td>- PLA is a polymer that readily interacts during melt blending with a MMT organomodified with dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium cation, leading to the formation of at least an intercalated structure.</td>
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<tr>
<th>2. What is the morphology of PLA microcomposite samples produced with various natural clay contents?</th>
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</thead>
<tbody>
<tr>
<td>- A microcomposite is formed when unmodified montmorillonite, such as Cloisite® Na⁺ and Cloisite® Ca²⁺DEV, is mixed with PLA polymer. The natural unmodified clay does not show any peaks corresponding to intercalation or agglomerates in SAXS. SEM and TEM show a predominance of agglomerates and aggregates. This confirms that the morphology has a microstructure.</td>
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<tr>
<th>3. What are the thermal, mechanical and rheological properties of the samples? and 4. What are the impacts that nanofiller has on thermal, mechanical and rheological behaviour of the PLA composites compare to micro filler?</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal:</strong></td>
</tr>
<tr>
<td>- Increasing clay content does not influence the $T_g$ significantly compared to the pure matrix. $T_m$ increases significantly for PLA composites. These changes indicate that the filler does not affect chain flexibility but it does have a</td>
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nucleation effect.

- Degree of crystallinity of PLA increases very significantly in the presence of organoclays. The additions of unmodified clay also provide a modest increment in crystallisation of PLA. This confirms that the incorporation of clay (organoclay or unmodified) promotes PLA crystallisation.

- Thermal stability increases with clay loading level in PLA-30B nanocomposites but microcomposites with Cloisite® Na⁺ and Cloisite® Ca++ decreases in thermal stability. This reflects the level of dispersion of the filler in the polymer. Good dispersion of thermally stable clay nanoparticles promotes thermal stability of the composite. Poor dispersion of clay microparticles combined with poor interaction between filler and polymer decreases thermal stability of the composite.

**Mechanical:**

- Addition of organoclay, such as Closite30B to PLA, enhances Young’s modulus significantly. At 10 wt %, the increase in Young’s modulus compared with the unfilled control PLA sample was around 54 %. This reflects the increase in aspect ratio after processing, with formation of exfoliated layers and intercalated tactoids, due to the strong interaction between the PLA matrix and the modified silicate layers.

- Addition of unmodified clay to PLA provides a modest improvement to the Young’s modulus. At the same 10 wt % filler loading, PLA-Na and PLA-Ca improved modulus by 18 % and 17 %, respectively. The inferior performance of the micro filler reflects the low level of interaction between the polymer and filler, as well as the lower aspect ratio of micro- compared to nanoparticles.

- In contrast to the Young’s modulus results, the tensile strength and extension decreased with the introduction of both modified and unmodified clay loading, due to presence of agglomerates, particularly above the percolation threshold.
Rheology:

- PLA-30B nanocomposite shows a significant increase in key rheology parameters, $G'$, $G''$, and $\eta^*$, in the terminal flow region in comparison with that of neat PLA, indicating good dispersion and interaction between filler and polymer. In contrast, both PLA-Na and PLA-Ca microcomposites show a decrease in $G'$, $G''$, and $\eta^*$ in the terminal region (low frequency) compared to neat PLA, indicating poor dispersion and interaction.

- Cloisite 30B forms a percolated network in PLA at relatively low level of filler (4.2 wt %). The untreated clay forms a percolation threshold at a higher level, around 9%. This is consistent with the aspect ratio of micro filler being lower than that of nanofiller.

5. How can the mechanical properties be predicted from knowledge of the structure?

- Halpin-Tsai model can be used for both nano and microcomposites to predict values of modulus in good agreement with measured values. A suitable aspect ratio is needed to ensure a good fit between model and experimental data.

9.2.3 Various correlations arising from this work

A comparison of the experimental data of Young’s modulus with values predicted from a model based on the Halpin-Tsai model indicates that the aspect ratio of the clay layer is about 4 for the modified clay, Cloisite® 30B, and around 2 for the unmodified clay, Cloisite® Na⁺ and Cloisite® Ca++. These values of aspect ratio are within the range of published literature. The ratios are in the lower part of the published range, and indicate that both the nano- and micro filler are not well dispersed in the polymer. For polymer nanocomposite systems, the aspect ratio of nanoplatelets can play an important role on their mechanical performance. A high aspect ratio leads to significantly improved modulus.
9.3 Recommendations

Based on the findings of this study, the following are recommended as future work in this area:

- Investigations of barrier properties and biodegradability of the composites.
- Consider other DOE, such as CCD, to determine the optimum processing conditions to process PLA since only one type of DOE was investigated in this work.
- A more accurate estimate of aspect ratio by quantitative examination of multiple TEM micrographs is recommended.
- Compared with other predictions micromechanical model of properties in composites.
REFERENCES


BALKCOM, M., WELT, B. & BERGER, K. 2002. *Notes from the Packaging Laboratory: Polylactic Acid--an Exciting New Packaging Material*, University of Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, EDIS.


*Polymer*, 29, 2229-2234.

Films: Enhanced Wettability from Surface-Confined Photografting and Increased 
Degradation Rate Due to an Artifact of the Photografting Process. *Macromolecules*, 
37, 9151-9159.

calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects 

properties of polylactide/montmorillonite clay nanocomposites. *Journal of Applied 
Polymer Science*, 118, 1489-1493.

Experimental trends in polymer nanocomposites—a review. *Materials Science and 
Engineering: A*, 393, 1-11.

JULIEN, J. M., BÉNÉZET, J. C., LAFRANCHE, E., QUANTIN, J. C., BERGERET, A., 
LACRAMPE, M. F. & KRAWCZAK, P. 2012. Development of poly(lactic acid) 
cellular materials: Physical and morphological characterizations. *Polymer*.

JUSTICE, R. S., SCHAEFER, D. W., VAIA, R. A., TOMLIN, D. W. & BUNNING, T. J. 
2005. Interface morphology and phase separation in polymer-dispersed liquid crystal 

The Processing and Characterization of MWCNT/Epoxy and CB/Epoxy Nanocomposites Using Twin Screw Extrusion. *Polymer-Plastics Technology and 
Engineering*, 49, 1207-1213.

KIERSNOWSKI, A., DĄBROWSKI, P., BUDDE, H., KRESSLER, J. & PIGOWSKI, J. 
2004. Synthesis and structure of poly(ε-caprolactone)/synthetic montmorillonite nano- 

KLIMENTIDIS, R. E. & MACKINNON, I. D. R. 1986. High-resolution imaging of ordered 

KOJIMA, Y., USUKI, A., KAWASUMI, M., OKADA, A., FUKUSHIMA, Y., KURAUCHI, 
T. & KAMIGAITO, O. 1993. Mechanical properties of nylon 6-clay hybrid. *Journal 
of Materials Research*, 8, 1185-1189.

KOLYBABA, M., TABIL, L. G., PANIGRAHI, S., CRERAR, W. J., POWELL, T. & 
The Society for engineering in Agriculture, food and biological systems. Paper Number: 
RRV03-0007. An ASAE Meeting Presentation.


KONTOU, E., NIAOUNAKIS, M. & GEORGIPOULOS, P. 2011. Comparative study of 
PLA nanocomposites reinforced with clay and silica nanofillers and their mixtures. 

KOO, J. H. 2006. *Polymer nanocomposites: processing, characterization, and applications*, 

KOPINKE, F. D., REMMLER, M., MACKENZIE, K., MÖDER, M. & WACHSEN, O. 

KRIKORIAN, V. & POCHAN, D. J. 2003. Poly (L-Lactic Acid)/Layered Silicate 
15, 4317-4324.


LEE, S., KIM, C. H. & PARK, J. K. 2006. Improvement of processability of clay/polyolactic nanocomposites by a combinational method: In situ polymerization of L-lactide and


NATUREWORKS LLC 2005. Processing Guides: Crystallizing and Drying of PLA. NatureWorks LLC.


TOKIWA, Y. & CALABIA, B. 2006. Biodegradability and biodegradation of poly(lactide). Applied Microbiology and Biotechnology, 72, 244-251.


APPENDIX A - The analysis result and MW distribution curve of sample before processing:

![Sample Information](image)

<table>
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APPENDIX B - The analysis result and MW distribution curve of sample after processing: