REINFORCEMENT OF PLASTICIZED POLY(LACTIC ACID) WITH TITANIUM DIOXIDE NANOFILLER

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REINFORCEMENT OF PLASTICIZED POLY(LACTIC ACID) WITH TITANIUM DIOXIDE NANOFILLER

ABSTRACT

The study aimed to investigate the reinforcement of plasticized poly(lactic acid) (PLA) with titanium dioxide (TiO_2) nanofiller. In this research, solvent casting and thermocompression methods are adopted to prepare PLA nanocomposites with different percentages of TiO_2 at 0.5, 2.0, 3.5, 5.0, and 7.0 %·w/w that dispersed in PLA solution using a mechanical mixer and ultrasonication technique. The composites were characterized using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Results showed that tributyl citrate (TBC) plasticizer reduced the brittle failure and increased the flexibility of PLA whilst TiO_2 nanofiller improved the crystallization of PLA composites as evidenced in DSC results at slow scanning rate. The presence of 3.5 %·w/w TiO_2 in plasticized PLA increased the glass transition temperature (T_g) from 41.75 °C to 42.22 °C indicating restricted mobility of polymer chains. The storage modulus improved from 2.36 GPa to 2.85 GPa due to the good dispersion of TiO_2 in the polymer matrix, as proven in SEM results. Thermal analysis proved that the crystallinity of PLA increased with the addition of TBC and TiO_2 from 24.98 % to 36.57 % at optimum loading of 7.0 %·w/w and 3.5 %·w/w, respectively. However, agglomeration of nanoparticles was formed at higher filler loading (>3.5 %·w/w), which reduced its properties. TiO_2 was distributed uniformly throughout the polymer matrix, acted as a reinforcement agent that improved the thermomechanical properties and thermal stability of the composites. In conclusion, the incorporation of plasticizer and nanofiller increased flexibility, improved thermomechanical properties, thermal behavior, and thermal stability of the PLA nanocomposites at optimum 7.0 %·w/w TBC and 3.5 %·w/w TiO_2. The implication of the study is that modification of PLA in the acquirement of improved flexibility, toughness and strength has potential in the packaging industry due to PLA biodegradability and compostability.

PENGUKUHAN PEMPLASTIK ASID(POLILAKTIK) DENGAN PENGISINANO TITANIUM DIOKSIDA

ABSTRAK

Kajian ini bertujuan untuk mengkaji pengukuhan pemplastik asid(polilaktik) (PLA) dengan pengisinano titanium dioksida (TiO_2). Dalam kajian ini, kaedah acuan pelarut dan mampatan terma digunakan untuk menyediakan komposit nano PLA dengan peratusan TiO_2 berbeza pada 0.5, 2.0, 3.5, 5.0 dan 7.0 %·w/w yang tersebar dalam larutan PLA menggunakan pengadun mekanikal dan teknik ultrasonik. Komposit dicirikan menggunakan analisis mekanikal dinamik (DMA), kalorimetri pengimbasan perbezaan (DSC), analisis gravimetri terma (TGA) dan mikroskop elektron imbasan (SEM). Hasil kajian ini menunjukkan pemplastik tributyl citrate (TBC) mengurangkan kegagalan rapuh dan meningkatkan kelenturan PLA manakala pengisinano TiO_2 memperbaiki penghabluran komposit PLA seperti yang dibuktikan dalam hasil DSC pada kadar imbasan perlahan. Kehadiran 3.5 %·w/w TiO_2 dalam pemplastik PLA meningkatkan suhu peralihan kaca (T_g) daripada 41.75 °C kepada 42.22 °C menunjukkan pergerakan rantai polimer yang lebih terhad. Modulus storan meningkat daripada 2.36 GPa kepada 2.85 GPa disebabkan oleh penyebaran TiO_2 yang baik dalam matrik polimer seperti yang dibuktikan dalam keputusan SEM. Analisis termal membuktikan bahawa pengkristalan PLA meningkat dengan penambahan TBC dan TiO_2 daripada 24.98 % kepada 36.57 % pada kandungan optimum 7.0 %·w/w TBC dan 3.5 %·w/w TiO_2. Walau bagaimanapun, penggumpalan partikel nano terbentuk pada kandungan pengisi yang tinggi (>3.5 %·w/w), yang telah mengurangkan sifat-sifat komposit PLA. TiO_2 disebarkan secara seragam ke seluruh matrik polimer, bertindak sebagai ejen penguat yang meningkatkan sifat termomekanikal dan kestabilan terma komposit. Kesimpulannya, penambahan bahan pemplastik dan pengisinano meningkatkan kelenturan, memperbaiki sifat-sifat termomekanikal, sifat terma dan kestabilan terma komposit nano PLA pada kandungan optimum 7.0 %·w/w TBC dan 3.5 %·w/w TiO_2. Implikasi kajian ini ialah pengubahsuaian PLA bagi mendapatkan komposit yang lebih lentur, kukuh dan kuat berpotensi digunakan dalam industri pembungkusan kerana sifat PLA yang biodegradasi dan boleh kompos.

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GENERAL ABBREVIATIONS & NOMENCLATURE

ΔH_c	Enthalpy of crystallization
ΔH_{cc}	Enthalpy of cold-crystallization
ΔH_m	Enthalpy of fusion
ΔH_m^*	Enthalpy of crystalline PLA
dw_{max}	Maximum rate of degradation
E'	Storage modulus
E''	Loss modulus
mrr	Melting, recrystallization and remelting
T_c	Crystallization temperature
$T_{c,\ on}$	Onset of crystallization temperature
T_{cc}	Cold-crystallization temperature
$T_{d,\ onset}$	Onset of degradation temperature
$T_{d,\ max}$	Maximum degradation rate temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{m1}	Melting peak at low temperature
T_{m2}	Melting peak at high temperature
W_L	Weight loss
χ_c	Crystallinity

ATBC	Acetyl tributyl citrate
ATEC	Acetyl triethyl citrate
$CaCO_3$	Calcium carbonate
CEO	Cinnamon essential oil

CFA	Chemical foaming agent
ChNs	Chitin nanocrystals
CNC	Cellulose nanocrystal
CNF	Cellulose nanofibers
CNT	Carbon nanotubes
CO_2	Carbon dioxide
DBP	Di-n-butyl phthalate
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
EDX	X-ray energy dispersive
EeRSO	Epoxidized rubber seed oil
EPA	Environmental Protection Agency
EPO	Epoxidized palm oil
ESO	Epoxidized soy oil
EVO	Epoxidized vegetable oil
FDA	Food and Drug Administration
FESEM	Field emission scanning electron microscopy
GRAS	Generally Recognized as Safe
HDPE	High density poly(ethylene)
HDT	Heat deflection temperature
HNT	Halloysite nanotubes
IC	Industrial composting
IR	Infrared
LDPE	Low density poly(ethylene)
MMT	Montmorillonite
MWCNT	Multi-walled carbon nanotubes
PA	Polyamide
PAN	Poly(acrylonitrile)
PBS	Poly(butylene succinate)
PCL	Poly(caprolactone)

PE	Poly(ethylene)
PEG	Poly(ethylene glycol)
PET	Poly(ethylene terephthalate
PFA	Physical foaming agent
PGA	Poly(glycolic acid)
PHAs	Poly(hydroxyl alkanoates)
PHB	Poly(hydroxybutyrate)
PHV	Poly(hydroxyl valerate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PP	Poly(propylene)
PS	Poly(styrene)
PTMC	Poly(trimethyl carbonate)
PVC	Poly(vinyl chloride)
PVOH	Poly(vinyl alcohol)
ROP	Ring-opening polymerization
TEC	Triethyl citrate
TBC	Tributyl citrate
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
TiO_2	Titanium dioxide
UV	Ultraviolet
ZnO	Zinc oxide

CHAPTER 1

INTRODUCTION

1.1 Overview

In recent decades, due to the diminishing of petrochemical resources and increase in environmental concerns by plastics, the use of biodegradable plastics prepared from renewable resources materials have been attracting more interest in the public research, scientific community and industrial worlds (Arjmandi, Hassan, Haafiz, Zakaria & Inuwa, 2014; Avella, Buzarovska, Errico, Gentile & Grozdanov, 2009). Biodegradable plastics have undergone extensive research since the 1970s because using biodegradable resources instead of petroleum-based resources is one of the latest available solutions to the environmental problems caused by the disposal of plastic wastes (Nair & Laurencin, 2007; Li, He & Inoue, 2003). Biodegradation is a process when a polymer is degrading down in natural environments that includes the changes in chemical structure, loss of mechanical and structural properties, and finally, changing into other compounds such as carbon dioxide (CO_2), water, minerals, biomass, and humic materials (Jamshidian, Tehrany, Imran, Jacquot & Desobry, 2010).

Polymers commonly known as plastics are widely used in many different applications including in industrial and medicines due to their versatile properties. Plastics can be either natural or synthetic and can be derived from either renewable or non-renewable resources. Plastics are widely used not only as packaging materials, but also in agriculture, the food industry, and even in pharmaceutical and clinical sectors (Anuar et al., 2017). It is almost impossible to live without plastics in our daily life in this modern society. Since the early 1990s, the evolution of the bioplastics industry has changed directions dramatically. Hence, the latest generation is moving towards durable and degradable bioplastics having a high biobased content (Nagarajan, Mohanty & Misra, 2016).

Today, biodegradable polymer plastics have been widely used in food packaging and agriculture because these polymers give some advantages such as low molecular weight, low density, environmentally friendly, cheaper cost availability, and good thermal properties (Kumar, Tyagi & Sinha, 2011). Besides, the emergence of novel biomedical technologies has led to the need for biodegradable materials platforms including tissue engineering, regenerative medicine, gene therapy, controlled drug delivery, and bio-nanotechnology. The end-product of these biodegradable materials also have been commonly used in furniture, food, and clothing industries (Ali, Awale, Fakhruldin & Anuar, 2016).

Among the various possible routes to eliminate environmental pollution by plastics wastes, biodegradability and bio-recyclability of polymer from renewable resources such as poly(lactic acid) (PLA), are regarded as attractive solutions, and it has become a rather widely adopted opinion that biodegradable polymers have a well-grounded role in solving the waste problems. This is because previously expensive PLA-polymers now have a good chance of being popularized in such a low-priced especially in food packaging (Jacobsen, Fritz, Degée, Dubois & Jérôme, 1999).

1.2 Research Background

PLA is a biodegradable polymer that appears to be one of the most attractive applications in agriculture and as packaging material because of its facile availability, good biodegradability, good heat sealability, good barrier properties, and good mechanical properties (Rydz, Musioł, Zawidlak-Węgrzyńska & Sikorska, 2018; Tang, Kumar, Alavi & Sandeep, 2012; Jamshidian et al., 2010). PLA is a class of semicrystalline biodegradable polymer that is derived from renewable resources such as corn, sugarcane, and tapioca through condensation polymerization of lactic acid that comparable to those of traditional petroleum-based polymers because of its strength and stiffness (Righetti et al., 2019). PLA can be processed by typical manufacturing methods such as film casting, injection moulding, extrusion, thermoforming, and fibre spinning (Nampoothiri, Nair & John, 2010).

A huge range of mechanical, thermal and physical properties, degradation rate, structural morphology and other physical properties can be achieved when PLA is copolymerized with other monomers, blending with other biodegradable polymers, with the addition of plasticizer/s and reinforced with nucleating agents. By improving PLA processability, mechanical and thermal properties, it is an important challenge to be afforded before sending this production to the market and in fact, PLA resins are nowadays marketed for different applications (Armentano et al., 2015; Avella et al., 2009).

In general, biocomposites can be obtained by blending natural fibers with bio-based polymers that produced an ecological and low-cost alternative to conventional petroleum-derived materials (Righetti et al., 2019). PLA is often blended with other polymers, fibre and filler to increase biodegradability, to modify the physical and mechanical properties (e.g., strength, elastic modulus), and to reduce costs (Chieng, Ibrahim, Yunus & Hussein, 2014a; Khanam & AlMaadeed, 2014). However, the brittleness and low glass transition temperature (T_g) of the PLA blend is a major drawback in many applications (Righetti et al., 2019). Therefore, a low molar mass plasticizer such as tributyl citrate (TBC), epoxidized palm oil (EPO) and di-n-butyl phthalate (DBP) is used to remedy this limitation. These plasticizers are miscible with PLA at compositions less than 30 %·w/w, effectively reducing the T_g and in turn improving the elongation at break (Ali et al., 2016; Anuar et al., 2016; Sejidov, Mansoori & Goodarzi, 2005). On the other hand, plasticization is often used to enhance biopolymers' processability and other properties needed for food packaging applications (Arrieta, Fortunati, Dominici, López & Kenny 2015).

Nanofillers have been widely used as the reinforcement and nucleating agents to enhance physical, mechanical and thermal properties, chemical resistance, surface appearance, heat distortion temperature, flame retardancy and electrical conductivity (Adeosun, Lawal, Balogun & Akpan, 2012) of the composites. Physical properties of the polymers such as mechanical properties, thermal stability, and barrier properties to oxygen and moisture as a result of the reinforcement effect of nanomaterials can be enhanced by the incorporation of nanomaterials into compatible polymers by creating nanocomposites which have a high surface area to volume ratios (Baek, Kim, Marcy, Duncan & O'Keefe, 2018; Mihindukulasuriya & Lim, 2014; Duncan, 2011; Silvestre, Duraccio & Cimmino, 2011). These advantages can be accomplished with the addition of low loading of nanofiller because of its large surface area and high ratio of the nanoparticles. This effect also largely depends on a few factors such as the shape of the particles, dispersion of the nanoparticles in the polymer matrix and the interaction between the nanofiller and the bulk polymer (Alberton, Martelli, Fakhouri & Soldi, 2014).

Much research has been performed to modify PLA composite properties with organic and inorganic fillers such as montmorillonite (MMT), clay, silica, carbon black, calcium carbonate ($CaCO_3$), zinc oxide (ZnO), graphite, carbon nanotubes (CNT), halloysite nanotubes (HNT), titanium dioxide (TiO_2), cellulose nanocrystal (CNC), talc, and metal salts of phenyl phosphoric acid as reinforcing agents (Arrieta et al., 2015; Alberton et al., 2014; Han et al., 2014; Yu et al., 2012; Barrau et al., 2011; Zhijun, Xingxiang, Ning & Jianming 2009; Wen et al., 2009; Wang, Zhang, Ma & Fang, 2008; Tsuji, Takai & Saha, 2006; Lei, Zhang, Rong & Friedrich, 2005). These researchers found that the existence of nanofiller in polymer composites can control the biodegradation rate and enhance the properties of PLA with good reinforcing capabilities for bio-based polymers. Besides, coupling the renewable resources based monomeric building block and inherent compostability and biodegradability of the various polymers has led to a definite focus being directed into single-use disposable product markets (Lunt, 1998).

1.3 Problem Statement

The usage of plastic materials in daily life especially in food packaging is inseparably due to their anti-corrosive, lightweight and high durability features properties. However, most of the plastics are non-biodegradable (synthetic packaging) materials and this will contribute to serious environmental pollution due to the increase in waste disposal problems. Although synthetic packaging film being replaced by eco-friendly packaging films is just impossible to achieve, the use of bioplastics at least requires the future for specific applications like food packaging. Petrochemical-based plastics such as polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polyvinylchloride (PVC), polystyrene (PS), polyamide (PA) have been increasingly used as packaging materials because of their large availability at relatively low cost and due to their good mechanical performance such as tensile and tear strength, carbon dioxide, good barrier oxygen, heat sealability and so on (Siracusa, Rocculi, Romani & Dalla Rosa, 2008). However, the use of these materials caused the declining oil and gas resources and in turn increasing oil and gas prices (Adeosun et al., 2012). Others effect include global warming, uneconomical costs in their recycling, environmental incineration and consumer toxicity risks (Adeosun et al., 2012; Jamshidian et al., 2010; Siracusa et al., 2008; Mohanty, Misra & Hinrichsen, 2000; Chandra & Rustgi, 1998; Amass, Amass & Tighe, 1998).

Confronting with this situation, it is of high importance to develop the polymer packaging material based on biodegradable polymers with controlled properties in the packaging industry in order to relieve the dependence on petrochemical-based polymers and alleviate solid waste disposal problems (Huang et al., 2014; Bordes, Pollet & Avérous, 2009; Ray & Bousmina, 2005). Polyolefin is one of the selected hydrocarbon polymers used for food packaging applications because of its flexibility, toughness and excellent barrier properties (Siracusa et al., 2008). Although hydrocarbon polymers give positives advantages such as incineration with energy recovery and can be mechanically recycled if clean, they are not biodegradable. On the other hand, according to a study by the Institute of Bioplastics and Biocomposites (2016), biodegradable polyesters, biodegradable starch blends and polyhydroxyalkanoates (PHAs) are examples of biodegradables polymers which contributed 10.8 %, 9.4 % and 3.6 % respectively for the production of bioplastics and used mostly for packaging applications (Mangaraj, Yadav, Bal, Dash & Mahanti, 2019).

PLA is a biodegradable material that is degraded slowly and released a low level of non-toxic gases. Under the environmental conditions, it can degrade into methane, water and carbon dioxide, over some time (Castro-Aguirre, Iñiguez-Franco, Samsudin, Fang, & Auras, 2016; Dil, Virgilio & Favis, 2016; Wang et al., 2016; Campoccia et al., 2015). Hence, recently PLA is widely used to replace the conventional non-biodegradable plastics because of its excellent properties including biodegradability, high modulus, strength and transparency, good heat sealability, excellent flavour and aroma barrier, high surface energy allowing easy printability, resistance to fatty foods and dairy products which equivalent to PET, and have the flexural modulus which higher than PS (Lunt, 1998).

However, semicrystalline PLA is brittle, exhibits a slow crystallization rate, rapid degradation rate, poor thermal stability, poor mechanical properties, low barrier properties and show relatively low resistance to oxygen and water vapor permeation compared with conventional non-degradable polymer resins (Zhao et al., 2019; Singh, Maspoch & Oksman, 2019; Chen & Dou, 2019; Kang et al., 2018; Armentano et al., 2015; Yee, Ching, Rozali, Hashim & Singh, 2016; Yu, Dean & Li, 2006). Therefore, various approaches, including copolymerization, plasticization, blending with other polymers, and the incorporation of organic or/and inorganic fillers have been used to improve the flexibility, toughness, and barrier properties of neat PLA (Kratochvı´l & Kelnar, 2017; Ebadi-Dehaghani, Barikani, Khonakdar & Jafari, 2015; Shi & Dou, 2015; Ahmed, Varshney, Auras & Hwang, 2010).

The most valuable method to overcome PLA weaknesses is by blending PLA with plasticizer and nucleating agent. Generally, the addition of plasticizer into PLA reduces the T_g and strength of the PLA composites, improved elongation at break and enhanced the crystallization ability of PLA. Meanwhile, filler/s that act as a nucleating agent has been applied to further enhance some properties such as thermal stability, mechanical and barrier properties (Marra, Silvestre, Kujundziski, Chamovska & Duraccio, 2017).

Numerous investigations have been conducted on improving the mechanical and physical properties of PLA composites with the help of nanofiller. The PLA/TiO_2 composites prepared by solution blow spinning (SBS) found that TiO_2 nanoparticles influenced the crystallinity of the composites. The thermal behavior of nanocomposites produced by the SBS technique and the casting method are similar (Costa, Brichi, Ribeiro & Mattoso, 2016). Efforts also focused on improving properties of embedded PLA and nanofiller (Chen & Dou, 2019; Righetti et al., 2019; Baek et al., 2018), PLA and plasticizer (Singh et al., 2019; Zhao et al., 2019; Kang et al., 2018; Maiza, Benaniba, Quintard & Massardier-Nageotte, 2015; Chieng et al., 2014b; Shirai et al., 2013), however still not satisfactory in improving physical, thermal and mechanical properties, thus limiting their applications (Shankar & Rhim, 2018).

To the best of our knowledge, no study has been carried out on the incorporation of TBC plasticizer and TiO_2 nanofiller for tailoring the dynamic mechanical properties of PLA composites. In this research, the reinforcement of TiO_2 nanofiller and inclusion of TBC plasticizer into PLA matrix aims to improve the thermal stability and thermomechanical properties that consequently alter the morphology and crystallization behavior of PLA composites. Plasticizer was used to reduce the brittleness of PLA while the nucleating agent was introduced to promote the crystallization by providing nucleation sites in the polymer chains. The good dispersion of nanofillers influences the physical and mechanical properties of PLA (Wu, Wu & Zhang, 2017; Li, Dou, Bai & Lu, 2015; Chen, Yao, Gu & Pan, 2013; Papageorgiu, Achilias, Nanaki, Beslikas & Bikiaris 2010). Besides, PLA can be readily cast into thin films upon dissolution in a solvent (Anuar et al., 2017).

1.4 Research Aim

The aim of this research is to investigate the reinforcement of plasticized poly(lactic acid) with TiO_2 nanofiller on the thermal stability, thermomechanical, thermal properties and morphology of PLA composites.

1.5 Objectives

The objectives of this research are:

i. To prepare plasticized PLA with and without nanofiller by using solvent casting and thermocompression method.

ii. To characterize the thermal stability, thermomechanical and thermal properties of plasticized PLA with and without nanofiller.

iii. To study the morphology of plasticized PLA with and without nanofiller.

1.6 Research Question

i. Does the incorporation of plasticizer and nanofiller in PLA matrix improve the thermal stability, thermomechanical and thermal properties of PLA composites?

1.7 Rationale

Durable bioplastics are required for multi-use long-term applications in electronics, automotive and other industries (Nagarajan et al., 2016). At the same time, consumers demand a high quality of bioplastics in food packaging that has a long shelf life and the requirements for recognizing the packaging to observe the foodstuff aspect (Armentano et al., 2015). The solution to the environmental problems caused by plastics waste is also being developed by the use of polymer composites from renewable resources to maintained sustainable ecological technology (Adeosun et al., 2012; Pandey, Chu, Lee & Ahn 2007; Ray & Bousmina, 2006).

PLA is widely applied in the medical apparatus, textiles, food packages, and automotive interiors, as well as agricultural materials (Foruzanmehr, Vuillaume, Elkoun & Robert, 2016; Li et al, 2015; Huang et al., 2014; Wu et al., 2011). In biodegradable packaging, PLA is used for bottles, yogurt cups, and candy/sweet wrappers. This is because PLA film for food packaging has high transparency, available in the market, easy to be processed, economically competitive and environmentally benign characteristics (Arrieta et al., 2015; Armentano et al., 2013; Auras, Harte & Selke, 2004). It also has been used for food service ware, lawn and food waste bags, coating for paper and cardboard, and fiber for clothing, carpets, sheets and towels and wall coverings. In biomedical applications, it is used for sutures, prosthetic materials and materials for drug delivery. For example, TiO_2 nanoparticles and PLA nanofibers have been accepted for new nanomaterials that let's drug molecules quickly self-assemble on the surface of the nanocomposite (Avella et al., 2009). Therefore, PLA material has a promising future with the potential to replace conventional petrochemical-based plastics such as PE, PP, and PET in various applications.

In addition, the blending of PLA with plasticizers and nanofiller is a practical strategy to improve flexibility and toughness, increase thermal stability and mechanical strength of PLA composites. Nanofiller such as TiO_2 received a lot of attention because of its good thermal stability, environmental compatibility, non-toxicity and low price. Meanwhile, lactide monomer such as TBC is the best plasticizing agent for polylactide because lactide and polylactide have a close chemical relationship to each other and in fact, the plasticizing effect of plasticizer reduced the T_g of the polylactide by the presence of lactide in PLA polymer (Jacobsen & Fritz, 1996). This research is mainly focused on improving the thermal stability, thermomechanical and thermal properties as well as the morphology of PLA that has the potential to be used in the development of packaging applications.

1.8 Thesis Structure

This thesis has five main sections. The first section is Chapter 1 which an introduction to the thesis that contains the aim, objectives and problem statement as shown in Figure 1.1. Chapter 2 is a Literature Review explaining the biodegradable polymers, modification of PLA polymer with plasticizer and nanofiller and the application of PLA polymer in food packaging. Materials, methods and all characterization techniques used in this research are outlined in Chapter 3. The composites were prepared by the solvent casting and thermocompression method. Thermal stability, thermomechanical, thermal properties, and structural morphology are characterized using TGA, DMA, DSC and FESEM. The fourth section is Chapter 4 which covers the results and discussion of the thermal stability, thermomechanical, thermal properties and morphology of PLA composites. The results are divided into three compositions of samples which are plasticized PLA, PLA nanocomposites and plasticized PLA nanocomposites. Plasticized PLA samples are prepared with various TBC content (5.0, 7.0 and 10.0 %·w/w) in the PLA matrix. The second composition which is PLA nanocomposites used different TiO_2 loading (0.5, 2.0, 3.5, 5.0 and 7.0 %·w/w) without the addition of TBC. Plasticized PLA nanocomposites are the last composition prepared with the optimum TBC content at 7.0 %·w/w reinforced with 0.5, 2.0, 3.5, 5.0 and 7.0 %·w/w of TiO_2. Chapter 5 as the last section involves conclusions and recommendations for further research.

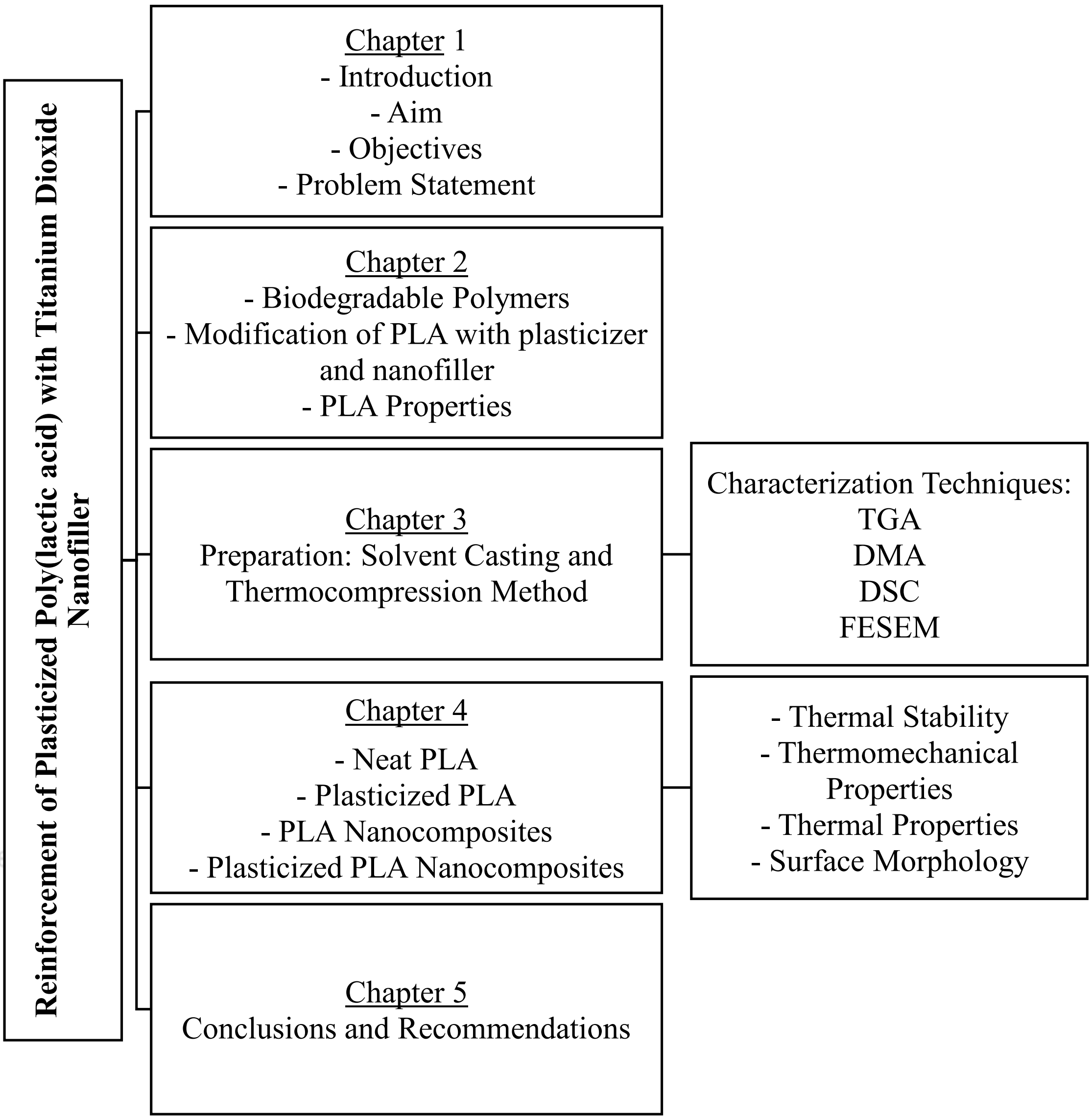

Figure 1.1. Flow chart of thesis structure