THERMOMECHANICAL, THERMAL PROPERTIES AND STRUCTURAL MORPHOLOGY OF POLY (LACTIC ACID) REINFORCED WITH TITANIUM OXIDE NANOFILLER

MOHAMMED ZORAH HASSAN

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MOHAMMED ZORAH HASSAN

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ABSTRACT

The aim of this study was to investigate the thermomechanical, thermal properties and structural morphology of modified poly (lactic acid) (PLA) reinforced with titanium oxide (TiO_2) nanofiller. The PLA composites were prepared by solvent casting followed by hot press method using tributyl citrate (TBC) as a plasticizer and TiO_2 nanofiller for reinforcement. The thermomechanical, thermal behavior and structural morphology of PLA composites were characterized using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and field emission scanning electron microscopy (FESEM). The crystallinity and transparency of the composites were studied using X-ray diffraction analysis and UV-Vis transmittance spectroscopy. Results showed TBC acts as a successful plasticizer that increased flexibility of the composite with improved crystallinity from 17.52 % to 38.56 % at the optimum loading of 7.0 w/w % TBC. The cross-section morphology of the composites revealed a good dispersion of TiO_2 nanofiller in PLA matrix at low loading (0.5 to 3.5 w/w %). The presence of the nanofiller has improved the thermal stability and thermomechanical properties of the nanocomposites at low loading with 40 % improvement of storage modulus due to good dispersion of the nanofiller as shown in the SEM results. The glass transition temperature of the composites has shifted from 50.0 °C to 54.2 °C indicating restricted mobility of the polymer chains in the presence of the nanofiller. The transparency was excellent for plasticized PLA but decreased with the addition of the nanofiller as showed by the transmittance spectra. In conclusion, incorporation of plasticizer and the nanofiller improved the thermomechanical and thermal properties of PLA nanocomposites which exhibited optimum results at 3.5 w/w % TiO_2. The implication of this study is that the modified PLA reinforced with TiO_2 nanoparticles offer promising application as a food packaging due to the improved thermomechanical properties, thermal stability and crystallinity.

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ABSTRAK

Kajian ini bertujuan untuk mengkaji sifat termomekanikal, sifat termal dan struktur morfologi poli (laktik asid) (PLA) yang telah diubah suai dan diperkuatkan dengan partikel nano titanium dioksida (TiO_2). Komposit PLA telah disediakan melalui kaedah acuan pelarut dan tekanan mampat panas menggunakan tributyl citrate (TBC) sebagai bahan pemplastik dan partikel nano TiO_2 sebagai penguat. Sifat termomekanikal, sifat termal dan struktur morfologi komposit PLA dicirikan dengan menggunakan analisis mekanikal dinamik (DMA), kalorimetri pengimbasan perbezaan kalorimeter (DSC), analisis gravimetri terma (TGA) dan mikroskopi pengimbas elektron (SEM). Penghabluran dan kelutsinaran komposit dikaji dengan analisis pembelauan sinar-X dan spektroskopi transmisi UV-Vis. Dapatan kajian menunjukkan TBC berjaya mengurangkan kerapuhan serta meningkatkan fleksibiliti PLA komposit dengan peningkatan penghabluran daripada 17.52 % kepada 38.56 % pada tahap optimum 7.0 w/w % TBC. Analisis morfologi keratan rentas komposit menunjukkan partikel nano TiO_2 terserak dengan baik dalam matrik PLA pada kandungan rendah (0.5 hingga 3.5 w/w %). Penambahan partikel nano ini juga telah meningkatkan kestabilan terma dan sifat termomekanikal komposit nano dengan peningkatan modulus storan sebanyak 40 % disebabkan oleh penyerakan partikel nano yang baik seperti yang yang ditunjukkan pada mikrograf SEM. Suhu peralihan kaca komposit meningkat daripada 50.0 °C kepada 54.2 °C menunjukkan kehadiran partikel nano telah menghadkan pergerakan rantai-rantai polimer dalam komposit. Transmisi spektra menunjukkan kelutsinaran PLA terplastik adalah sangat baik tetapi sifat ini berkurangan dengan pertambahan partikel nano. Kesimpulannya, penggabungan bahan pemplastik dan partikel nano telah berjaya meningkatkan sifat thermomekanikal dan sifat termal komposit nano PLA di mana ia memberikan keputusan optimum pada 3.5 w/w·% TiO_2. Implikasi kajian ini menunjukkan bahawa PLA yang diubahsuai telah diperkuat dengan partikel nano TiO_2 boleh diaplikasi sebagai bahan pembungkusan makanan yang lebih baik kerana kekuatan mekanikal, kestabilan sifat termal dan juga kelutsinaran yang lebih baik.

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LIST OF SYMBOLS AND ABBREVIATIONS

ΔHc	Enthalpy of crystallization
ΔHcc	Enthalpy of cold-crystallization
ΔHm	Enthalpy of fusion
E'	Storage modulus
E''	Loss modulus
E^*	Complex modulus
T_c	Crystallization temperature
T_{cc}	Cold crystallization temperature
T_{onest}	The onset of degradation temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{m1}	Melting peak at low temperature
T_{m2}	Melting peak at high temperature
T_{max}	Maximum rate of weight loss
X_c	Crystallinity
ASTM	American society for testing of materials
ATBC	Acetyl tributyl citrate
$CaCO_3$	Calcium carbonate
Da	Dalton (unit)
DMA	Dynamic mechanical analyser
DSC	Differential scanning calorimetry
ESO	Epoxidized soybean oil
EPO	Epoxidized palm oil
GPa	Gigapascal
GO	Graphene oxide
HDPE	High density PE

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ISO	International standards organization
LDPE	Low density PE
MPa	Megapascal
NPs	Nanoparticles
MCC	Microcrystalline cellulose
PBAT	Poly (butylene adipate-co-terephthalate)
PCL	Poly(caprolactone)
PCl_5	Phosphorous pentachloride
PE	Poly(ethylene)
PEG	Poly (ethylene glycol)
PET	Poly(ethylene terephthalate)
PHA	Poly(hydroxyl alkanoates)
PHB	Poly(3-hydroxybutanoate)
PHV	Poly (hydroxyvalerate)
PEA	Poly(ester amide)
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
PASP	Polyaspartic acid
PVC	Polyvinylchloride
PLL	Poly(L-lysine)
pPLA	Plasticized PLA
Ag NPs	Silver nanoparticles
ROP	Ring opening polymerization
$SOCl_2$	Thionyl chloride
TBC	Tributyl citrate
TEC	Triethyl citrate
Ti	Titanium
TGA	Thermogravimetric analysis

THF	Tetrahydrofuran
TPS	Thermoplastic starch
TiO_2	Titanium oxide
ZnO	Zinc oxide
UV-Vis	Ultraviolet–visible

CHAPTER 1

INTRODUCTION

1.1 Introduction

The generic word polymer that refers to the plastics owing to their versatile attributes is widely used for varieties of industrial and medical applications (Mathur, 2018). In the modernized world, the dependence on plastic has been exponentially increasing in daily life. To meet various industry sectors, polymeric, synthetic materials have been constantly being improved to facilitate their processing capacity, great versatility, low-cost, durability, mechanical properties and their resistance to chemical and biological attacks.

On the contrary, petroleum-derived plastics are not environmentally friendly due to slow decay after the use, waste-related landfilling, non-biodegradability, pollution, etc. (Mitra, 2014; Faruk, Bledzki, Fink, & Sain, 2012; Fortunati et al., 2012). Proposed solutions for managing this problem caused by polymeric materials include reuse, recycling and replacing conventional petroleum-based polymers to biodegradable polymers. The use of biodegradable polymers is becoming a very interesting alternative, attracting both the interest of public and scientific community (Gowman, Picard, Lim, Misra, & Mohanty, 2019).

1.2 Research Background

In the 21st century industrial and technological era, conventional plastics are inseparable from daily life applications because of their omnipresence with low-cost, excellent anti-corrosive, light-weight and high durability. However, most of these plastics are non-biodegradable. Thus, extensive usages of plastics remain an environmental threat in terms of waste disposal related landfilling and varied pollution (Kamdem, Shen, & Nabinejad, 2019; Râpă et al., 2016; Burgos et al., 2014).

Conventional plastics have been dominating the packaging industry because of their abundance, lightness, transparency, flexibility, durability and low cost. Additionally, plastics are very stable and tolerant against external biotic and abiotic stresses (Roohi et al., 2018; Rydz, Sikorska, Kyulavska & Christova, 2015). However, the decomposition process of plastics are very slow and remain in the environment for years, thereby continuing a significant concern. Therefore, environmentally friendly, biodegradable, sustainable, transparent, cost effective materials alternative to plastics has been continuously demanded in packaging industry.

Biopolymer has attracted attention due to its biodegradability and compostability. Biodegradable polymers such as cellulose, poly(lactic acid), poly(glycolic acid), poly(3-hyroxybutanoate), polycaprolactone and poly(ethylene succinate), have been considered as the most promising materials to replace conventional polymers in various application. Biodegradable polymer in the contact of this study is poly(lactic acid) (PLA), a linear aliphatic polyester that was obtained from renewable sources such as starch and sugar. Excellent physicochemical and barrier properties of PLA are similar to some petroleum-based polymers including polypropylene (PP) and poly(ethylene terephthalate) (PET), make it practical for different applications (Lizundia, Penayo, Guinault, Vilas, & Domenek, 2019; Carbonell-verdu, Samper, Garcia-garcia, Sanchez-nacher, & Balart, 2017a; Farah, Anderson & Langer, 2016a). Due to the outstanding sustainability and biodegradability of PLA, it has become a very attractive material in various industries.

PLA is a unique biopolymer with excellent thermomechanical and non-toxic character, which is very suitable for food packaging and medical products including implant devices, tissue scaffolds, and internal sutures (Haider, Völker, Kramm, Landfester & Wurm, 2019; Hassouna et al., 2011). Because of its non-toxicity, the PLA can degrade slowly by releasing non-hazardous gases at a very low level (Krishnaiah et al., 2016; Yokohara & Yamaguchi, 2008). Meanwhile, the tensile strength and Young's modulus of PLA are comparable to several other commercial polymers including PP, polyethylene (PE) and polystyrene (PS), which make it potential for various applications.

Despite promising prospects, some properties of PLA, such as high brittleness, low thermal stability, slow crystallization rate and low gas barrier, which limit its applications in certain industries (Chaos et al., 2019; Ahmad et al., 2019). For the successful implementation of PLA in consumer applications, it should have similar or better mechanical properties than conventional petroleum-based polymers.

The modification of PLA with different plasticizers has been explored as a means to lower the glass transition temperature (T_g) and increase the flexibility and ductility of PLA and to reduces the energy required for crystallization, thereby increasing the crystallization rate (Chen & Dou, 2019). This has been achieved by addition of plasticizers such as citrate esters, oligomeric lactic acid, poly (ethylene glycol) (PEG) epoxidized soybean oil (ESO) and epoxidized palm oil (EPO), that are commonly used to improve the toughness of brittle polymers (Luzi et al., 2019; Mahmud et al., 2019; Singh, Maspoch, & Oksman, 2019 ; Awale et al., 2018). The addition of plasticizers increase flexibility and ductility, whilst decrease the mechanical properties and thermal stability of PLA (Ahmad et al., 2019; Mihai et al., 2018; Maiza, Benaniba, & Massardier-Nageotte, 2016) Studies involving the modification of PLA that have a good balance between flexibility and mechanical strength are still under development (Lee, Choi, Choi & Ha, 2019; Hassouna et al., 2011). Therefore, a new approach to enhance the toughness and ductility with minimal strength loss and thermal stability is required.

Nanotechnology is recognized as one of the most promising avenues of technology development for the 21st century material research studies. In this approach, the incorporation of nanofillers as a nucleating agent can be used to improve thermomechanical properties of biodegradable nanocomposites polymer. A polymeric nanocomposites is a material composed of two or more phases in which the major component is the polymer that forms a continuous matrix wherein nanoparticles are dispersed. It is necessary that the nanofiller and the polymer be compatible in order to obtain a homogeneous dispersion of the nanofiller in the polymer matrix. The nanocomposites become especially important in food packaging because materials with improved specific properties can be obtained; such as mechanical resistance, thermal stability, and the barrier properties with respect to pure polymer and conventional composites (Peelman et al., 2013; Arora & Padua, 2010). The reinforcements for polymer matrix can be organic or inorganic nanoparticles such as silver, titanium oxide (TiO_2), zinc oxide (ZnO), graphene oxide (GO) and organoclays. PLA based nanocomposites properties were found to exhibits significant improvements at a low loading of nanofiller (Lopes et al., 2019; Avolio et al., 2018; Yoo, Shin, Yoon & Park, 2014)

1.3 Problem Statement

PLA is one of the eco-friendly biodegradable polyesters; its raw material is derived from starchy crops, such as corn, potato, sugar beet, and so on. PLA shows similar properties to some plastic materials used in food packaging, such as PS and PET (Chung et al., 2018). It is currently becoming economically competitive alongside commonly manufactured plastics. However, in industrial implementation, it encounters numerous problems associated with slow crystallization, high brittleness, low thermal stability and low impact resistance (Farah, Anderson, & Langer, 2016a; Silverajah et al., 2012). These disadvantages result from the structure and composition of the PLA macromolecular chains, the ratio of optical isomers, and many other factors. Therefore, the poor rigidity and strong fragility of PLA that limits its broad array of usages must be improved.

These unsatisfactory properties must be improved or modified to widen the potential application of this biopolymer. Several methods of modifying the polymer properties have been adopted such as the addition of plasticizers, nanofillers, copolymerization or blending with other flexible polymers (Alakrach et al., 2019). For example, blending PLA with other biopolymers, mixing with food grade plasticizer/s or incorporating reinforcement fillers into the PLA matrix improved PLA properties (Hassan et al., 2012). Various nanofillers such as carbon black (Zhang et al., 2020), calcium carbonate ($CaCO_3$) (Avolio et al., 2018) , ZnO (Vasile et al., 2017), graphite (Valapa, Pugazhenthi, & Katiyar, 2015), silica (Dorigato, Sebastiani, Pegoretti, & Fambri, 2012), silver (Li et al., 2017), clays (Nieddu et al., 2009), carbon nanotubes (Zhou, Lei, Yang, Li, & Ren, 2018), and TiO_2 (Mallick et al., 2018) have been incorporated into PLA to improve its mechanical and physical properties. It has been acknowledged that the insertion of nanofillers can improve thermal stability. Nanofillers enhanced mechanical properties by restricting the mobility of polymer chains. Activations with dopants, sensitizers, modifiers or embedments were shown to soften PLA, enhance its mechanical and thermal properties and make the resultant nanocomposites useful for industrial applications such as food packaging without compromising the too much transparency and biodegradability (González, Olmos, Lorente, Vélaz, & González-Benito, 2018). The improvement of the thermal stability, physical and thermomechanical properties of biodegradable polymer PLA blends are the main concern in this study. The mechanical and physical properties of plasticized PLA reinforced nanocomposites are related to their structures and morphologies. Several techniques have been developed to modified polymer films including spin coating process, extrusion injection processing (for a thick film), melt blending and solvent casting (Sharma, Singh, Majumdar & Butola, 2019; Mallick et al., 2018; Buong et al., 2014; Haafiz et al., 2013; Man et al., 2012). However, the comprehensive characterizations of tributyl citrate (TBC) and TiO_2 reinforced PLA nanocomposites prepared by solvent casting followed by hot press technique has not been reported.

In this study, plasticizer TBC and TiO_2 nanoparticles were used to modify the thermomechanical, thermal properties and structural morphology of PLA. TiO_2 was chosen as a nanofiller due to its chemical inertness, non-toxicity, good thermomechanical properties and good thermal stability (Díez-Pascual & Díez-Vicente, 2015; Sakka, Bouaziz & Ben Ayed, 2014). Mechanical mixer and ultrasonicator were used to mix and disperse the nanoparticles in PLA matrix. The sample was prepared using solution casting followed by hot press techniques. The composites were characterized to evaluate the effect of the nanoparticles and plasticizer on the thermomechanical and thermal properties of the PLA, as well as the morphology of the composites.

1.4 Research Objectives

i) To prepare PLA and PLA /TiO_2 nanocomposites with and without plasticizer *via* solvent casting followed by hot press techniques.

ii) To characterize the thermomechanical properties, crystallinity and thermal properties of the PLA and PLA /TiO_2 nanocomposites with and without plasticizer.

iii) To determine the impacts of plasticizer and nanoparticle on the morphology and thermal behavior through melting and crystallization of the PLA and PLA / TiO_2 nanocomposites with and without plasticizer.

1.5 Research Significance

PLA has received much attention due to increasing environmental concerns and decreasing fossil fuel resources, with excellent properties including biodegradability, high modulus, strength and transparency. PLA is inherently clear, naturally glossy, resistant to moisture and grease, which makes it useful for recyclable and biodegradable packaging, food service ware, waste bags, coating for paper/cardboard, fibre for clothing and in biomedical applications as sutures, prosthetic materials and materials for drug delivery.

In the market, PET is one of the conventional petroleum-based polymers that has been widely used in packaging. PLA possess good mechanical and thermal properties and its stiffness is similar to PET, however PLA is more brittle and does not have any reactive side-chain groups. Thus, the major challenges to the widespread use of PLA are its brittleness and lack of readily reactive-chain group.

Reinforcement of polymer composites with nanoparticles is a way of improving PLA properties including its mechanical and thermal properties, however, such composites often have high brittleness and low flexibility. On the other hand, PLA blend with plasticizer significantly reduced PLA brittleness, yet such composites are often of moderate strength and have slow crystallization rate. Thus, in this research TBC plasticizer and TiO_2 nanofiller were used to modified biodegradable PLA with improving thermomechanical and thermal properties, flexibility, crystallinity as well as balance its brittleness and toughness.

1.6 Thesis Structure

This thesis consists of five chapters. Introduction to the work including research background, problem statement, objectives and research significance are presented in Chapter 1. Chapter 2 provides the detail and critical literature review related to this research interest. It includes the introduction of biodegradable polymers, biological degradation of polymers, synthesis of PLA, properties and modification of PLA. Applications of such biodegradable plastics as nanocomposites for food packaging are also explained in this chapter. Chapter 3 describes the research methodology starting from the preparation methods, characterizations and analysis techniques. The research findings and discussion are presented in Chapter 4. Chapter 5 concludes the research with recommendations for future works.