



**UNIVERSITI PUTRA MALAYSIA**

***PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/  
POLY( $\epsilon$ -CAPROLACTONE)/ GLYCIDYL METHACRYLATE BLENDS  
AND THE EFFECTS OF ELECTRON BEAM IRRADIATION ON THE  
BLENDS***

**CHEE WEI KIT**

**FS 2013 55**



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**By**

**CHEE WEI KIT**

**Thesis Submitted to the School of Graduate Studies,  
Universiti Putra Malaysia, in Fulfilment of the  
Requirements for the Degree of  
Master of Science**

**December 2013**

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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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**CHEE WEI KIT**

**December 2013**

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This research focused on blending of Poly(lactic acid) (PLA) with Poly( $\epsilon$ -caprolactone) (PCL) in order to overcome the brittle character of PLA matrix. Properties of PLA was successfully tuned to ductile however poor compatibility between these polymers limited the extend of improvement. Thus, Glycidyl Methacrylate (GMA) was utilized as interfacial compatibilizer to improve the interfacial compatibility of the non-miscible components. Besides, the effects of electron beam irradiation on mechanical properties of compatibilized blends were studied as well. The properties of PLA/PCL blends were improved significantly by addition of GMA by 3 wt%. FT-IR spectra indicated slight interaction between GMA and PLA matrix, in agreement with the improvement in mechanical properties. Elongation at break of the blend increased dramatically from 17.1% to 327% indicating better dispersion of PCL in PLA matrix as well as improvement interfacial adhesion. Decrease in flexural strength and modulus upon addition of GMA designated that the specimens were tuned from rigid to deformable. Besides, significant increase in impact strength from 418.36 J/m to 802.35 J/m was also recorded upon addition of GMA.

Thermal properties of the blends were studied via Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA). TGA revealed addition of 3 wt% GMA resulted slight improvement in thermal stability of the blend. In addition, DMA analysis showed that glass transition temperature ( $T_g$ ) of PLA in the blend shifted significantly to a lower temperature region with addition of GMA, indicating improved compatibility of the components. Scanning electron microscopy (SEM) was utilized to study the fracture surface morphology of the blends. The random and fibrous structure of PLA/PCL blend was tuned to a finer dispersion morphology upon addition of GMA.

From water absorption analysis, it can be deduced that the addition of GMA influence the water uptake affinity of the blends to slightly higher level. However, the total increment in weight due to water absorption was considered minor (less than 1%). Soil burial degradation analysis revealed that the rate of degradation of PLA was relatively low. Besides, the addition of GMA did not significantly influenced the rate of degradation.

Mechanical study on the irradiated specimens showed that the compatibilized blends were still remained ductility upon irradiation up to 10 kGy. Besides, slight increment was recorded on tensile strength when irradiation dosage varied from 10 to 15 kGy. Elongation at break dropped remarkably with increasing irradiation dosage up to 25 kGy, following by gradual decrement in tensile strength and modulus. However, blends added with GMA showed better resistivity upon irradiation, noted by high tensile strength and modulus values were retained upon irradiated at 25 kGy of dosage. FT-IR analysis revealed no shift in wavenumber occurred as a function of irradiation, indicating no interactions occurred. Water absorption analysis showed that irradiated specimens absorbed less water, however soil burial degradation test recorded no enhancement on the rate of degradation of the specimens upon irradiation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PENYEDIAAN DAN PENCIRIAN POLI(ASID LAKTIK)/  
POLI( $\epsilon$ -KAPROLAKTON)/ CAMPURAN GLYSIDIL METAKRILAT DAN  
KESAN SINARAN ELEKTRON TERHADAP CAMPURAN POLIMER**

Oleh

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Kajian ini memberi tumpuan kepada campuran Poli(asid laktik)(PLA) dan Poli( $\epsilon$ -kaprolakton)(PCL) untuk mengatasi ciri-ciri kerapuhan PLA. PLA telah berjaya diubahsuai menjadi mulur, bagaimanapun ketidakserasian antara polimer-polimer ini menghadkan tahap peningkatan. Oleh itu, Glysidil Metakrilat (GMA) telah digunakan sebagai agen penyerasian untuk meningkatkan keserasian antara komponen-komponen tersebut. Selain itu, kesan-kesan sinaran alur elektron terhadap sifat-sifat mekanik campuran polimer tersebut turut dikaji. Sifat-sifat campuran PLA/PCL menunjukkan peningkatan ketara dengan penambahan GMA sebanyak 3 wt%. FT-IR spektrum menunjukkan interaksi antara GMA dan PLA matriks, sehubungan dengan peningkatan pada sifat-sifat mekanik. Pemanjangan pada takat putus yang meningkat secara mendadak daripada 17.1% kepada 327% menunjukkan penyebaran komponen PCL yang lebih menyeluruh di antara matriks PLA serta peningkatan daya lekatan. Penurunan dalam kekuatan lenturan dan modulus apabila penambahan GMA menunjukkan bahawa spesimen mengalami tegasan kuat dalam proses ubah bentuk. Selain itu, peningkatan yang ketara dalam daya impak daripada 418.36 J/m ke 802.35 J/m juga tercatat sebagai kesan penambahan kandungan GMA dalam campuran polimer tersebut.

Sifat haba daripada campuran dikaji melalui analisis Termogravimetrik (TGA) dan Analisis Mekanikal Dinamik (DMA). TGA mendedahkan bahawa penambahan 3wt% GMA menyebabkan sedikit peningkatan terhadap kestabilan haba polimer tersebut. Di samping itu, analisis DMA menunjukkan bahawa suhu peralihan kaca ( $T_g$ ) PLA dalam campuran beralih dengan ketara ke kawasan suhu yang lebih rendah sebagai kesan penambahan GMA, menunjukkan peningkatan keserasian di antara komponen-komponen polimer. Imbasan mikroskop elektron (SEM) telah digunakan untuk mengkaji morfologi permukaan putus dalam campuran polimer. Struktur rawak dan berserabut gabungan PLA/PCL telah berubah kepada penyebaran morfologi yang lebih halus kesan daripada penambahan GMA.

Keputusan daripada analisis penyerapan air menyimpulkan bahawa penambahan GMA mempengaruhi penyerapan air polimer campuran PLA/PCL ke tahap yang lebih tinggi. Walau bagaimanapun, jumlah kenaikan dalam berat kesan penyerapan air dianggap kecil (kurang daripada 1%). Analisis biodegradasi tanah menunjukkan bahawa kadar degradasi PLA adalah agak rendah. Selain itu, penambahan GMA tidak mempengaruhi kadar degradasi dengan ketara.

Kajian mekanikal terhadap spesimen dedahan sinaran elektron menunjukkan bahawa kemuluran campuran polimer masih kekal sehingga tahap sinaran 10 kGy. Selain itu, kenaikan sedikit dicatatkan pada kekuatan tegangan apabila dos sinaran mencapai 10 hingga 15 kGy. Pemanjangan pada takat putus menurun dengan mendadak akibat peningkatan dos sinaran sehingga 25 kGy, berikutan dengan susutan secara beransur-ansur dari segi kekuatan tegangan dan modulus. Walau bagaimanapun, campuran polimer ditambah dengan GMA menunjukkan rintangan yang lebih baik kepada penyinaran, ternyata oleh kekuatan tegangan yang tinggi dan modulus berkekalan pada tahap sinaran 25 kGy. Analisis FT-IR menunjukkan tiada perubahan terhadap pendedahan sinaran, menunjukkan tiada interaksi berlaku. Analisis penyerapan air menunjukkan bahawa spesimen dedahan sinaran kurang menyerap air, namun keputusan analisis biodegradasi tanah mencatatkan tiada peningkatan terhadap kadar degradasi spesimen oleh sinaran elektron.

## ACKNOWLEDGEMENT

First of all, I would like to express the deepest appreciation to my committee chairperson Dr. Nor Azowa Ibrahim for continually and convincingly conveyed a spirit of adventure throughout my research pathways.

Special thanks of gratitude to Dr. Norhazlin Zainuddin for continual guidance and informative support given whenever obstacles were met. In addition, my grateful thanks to Mr. Faizal Mohd. Abd. Rahman for experience advices and opinions given proceeding the particular research. I would also like to extend my thanks to the technicians of the laboratory of Chemistry Department, Faculty of Science for their kindly assistance and resources for this period of study. Besides, a token of appreciation to Mr. Zahir from Department of Process and Food Engineering for his kind assistance and help. Not forgetting on Mr. Chieng Buong Woei and Mr. Then Yoon Yee for their constant supports and assistance throughout my study. I would also like to show my appreciation to Fundamental Research Grant Scheme(FRGS) and Research Management Centre(RMC) of UPM for providing financial support which were crucial for my study.

Also special dedication to Ms. Sim Biow Ing for her encouragement and supports given throughout the research period. Last but not least, I owe my deepest gratitude to my family who always supported my spiritually throughout my life.





I certify that an Examination Committee has met on 6 December 2013 to conduct the final examination of Chee Wei Kit on his thesis entitled "Preparation and Characterization of Poly(lactic acid)/ Poly( $\epsilon$ -caprolactone)/ Glycidyl Methacrylate Blends and The Effects of Electron Beam Irradiation on The Blends" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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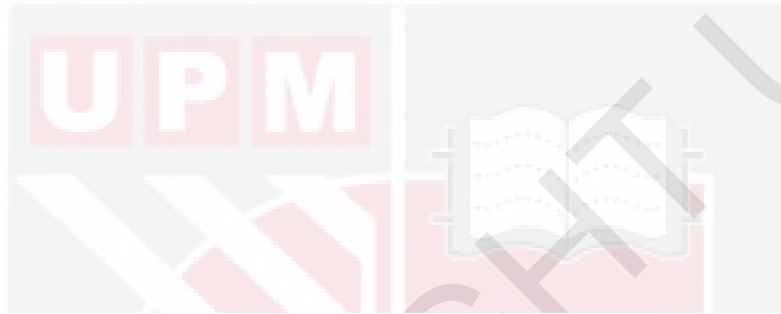
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## LIST OF ABBREVIATIONS/ NOTATIONS

BF	Bamboo Flour
DCP	Dicumyl Peroxide
DMA	Dynamic Mechanical Analysis
DMAP	4-dimethylaminopyridine
DSC	Differential Scanning Calorimetry
DTG	Derivative Percentage Weight Thermogram
$E''$	Loss Modulus
EB	Electron Beam Irradiation
EGMA	Poly(ethylene-glycidyl methacrylate)
EPO	Epoxidized Palm Oil
ESO	Epoxidized Soy Bean Oil
$E'$	Storage Modulus
FT-IR	Fourier Transform Infrared Spectroscopy
GMA	Glycidyl Methacrylate
GPC	Waters Gel Permeation Chromatography
J/m	Joule per Meter
kGy	Kilogray
LDI	L-lysine-diisocyanate
LDPE	Low Density Poly(ethylene)
LTI	Llysine-triisocyanate
MA	Maleic Anhydride
MPa	Megapascal
MeV	Mega-electron volt
MP	Multiple Plasticizers
mPOE	Glycidyl Methacrylate Grafted Poly(ethylene octane)
NMR	Nuclear Magnetic Resonance
OTR	Oxygen Transmission Rate

Pa	Pascal
PBAT	Poly( butylene adipate-co-terephthalate)
PBGA	Poly(1,3-butylene glycol adipate)
PBS	Poly(butylene succinate)
PCL	Poly( $\epsilon$ -caprolactone)
PEG	Poly(ethylene glycol)
PE	Poly(ethylene)
PHB	Poly(hydroxybutyrate)
Phr	Parts Per Hundred
PLA <sub>70</sub> PCL <sub>30</sub> -g-AA	Acrylic Acid Grafted PLA <sub>70</sub> PCL <sub>30</sub>
PLA-b-PCL	Poly(lactic acid)/Poly( $\epsilon$ -caprolactone) Block Copolymer
PLA-b-PEG-b-PLA	Poly(D,L-lactic acid)-b-poly(ethylene glycol) Copolymer
PLA-EI	Injected and Extruded PLA
PLA-I	Injected PLA
PLA-PCL-PLA	Poly(lactic acid)/Poly( $\epsilon$ -caprolactone)/ Poly(lactic acid) Triblock Copolymers
PLA	Poly(lactic acid)
PP	Poly(propylene)
ROP	Ring opening polymerization
SEM	Scanning Electron Microscopy
TAIC	Triallyl Isocyanurate
$\tan \delta$	Tangent Delta
$T_c$	Crystallization Point
$T_{final}$	Final Degradation Temperature
TGA	Thermogravimetric Analysis
$T_g$	Glass Transition Point
$T_{max}$	Rapid Decomposition Temperature
$T_m$	Melting Point
TMPTA	Trimethylpropane Trimethacrylate
$T_{onset}$	Onset Degradation Temperature

TPA	Thermoplastic Starch
TPO-MAH	TPO-grafted maleic anhydride
TPO-PLA	Thermoplastic Oolyolefin Elastomer-graft-poly(lactide)
TPO	Thermoplastic Polyolefin
Wt%	Weight Percentage
$\Delta H_c$	Heat of Crystallization
$\Delta H_m$	Heat of Fusion



# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Recently, massive usage of polyolefin plastics in commercial as well as industrial purpose have created a major setback on the landfills. Besides, the non-biodegradability properties of polyolefin has even increase the difficulties in handling the problem. Many solutions had been applied in order to overcome this major drawback including recycling, incineration, and waste disposal. However, none of these has made a significant impact towards reducing this environmental issues. Recycling of plastics was not a major choice as the recycled products were not in feasible properties as the main products due to the nature characteristic of plastics. In addition, incineration of plastics eventually will release toxic gases and vapors which were proven to be extremely hazardous. Lastly, plastics disposal in the landfills will be the least chosen as the non-biodegradability issues will create a serious environmental pollution (Simões *et al.*, 2009).

In order to overcome this phenomenon, biodegradable polymers have been introduced as a replacement towards the polyolefin plastics. Being fully biodegradable into simple organic elements of carbon, hydrogen and oxygen, these polymers immediately attracts the attention various industrial and commercial fields in recent years. Currently, there are a few types of biodegradable polymers namely poly(lactic acid), poly( $\epsilon$ -caprolactone), poly(butylene succinate), poly( butylene adipate-co-terephthalate) and poly(hydroxybutyrate).

Poly(lactic acid) (PLA) being the most promising biodegradable plastic attributable to a few primary advantages such as fully derived from renewable resources (mainly corn, wheat, or rice), biocompatibility with respect to biomedical application, and low production cost with respect to other biodegradable polymers. The repeating unit of PLA is shown in Figure 1.

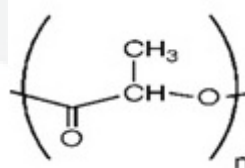


Figure 1. Repeating unit of PLA

The synthesis of PLA started from the polymerization process of its monomer, lactic acid. Basically, there are three methods in synthesis of PLA (Fig. 2). The most conventional way is via condensation polymerization of lactic acid monomer to yield low molecular weight polymeric chains which are usually brittle and mostly unusable. The second method is via azeotropic dehydrative condensation of lactic acid monomer. This method can yield high molecular weight PLA without the use of

any chain extenders. Finally, the main process which is mainly practiced in industrial scale is via ring opening polymerization (ROP) of lactides to obtain a very high molecular weight polymer chains. This method was patented by Cargill (US) in 1992, (Avérous, 2008).

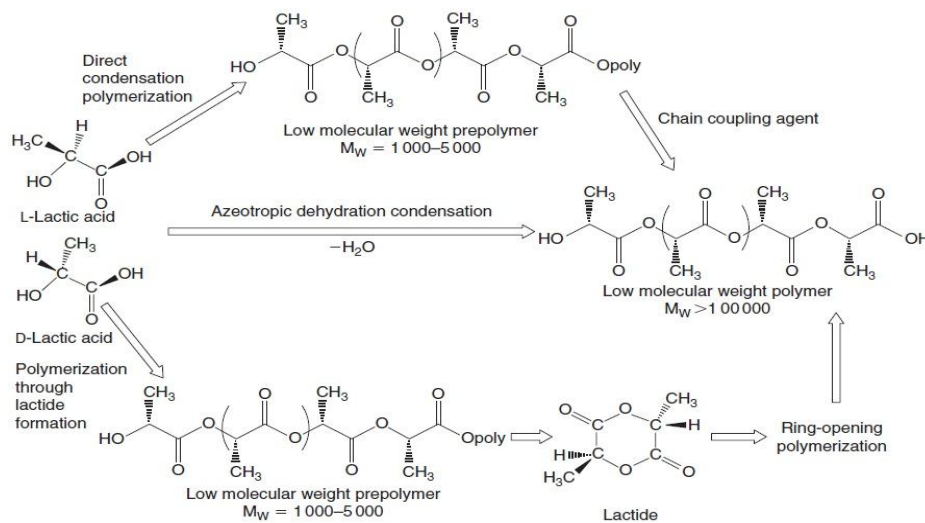


Figure 2. Synthesis Methods of PLA (Avérous, 2008)

However, being the most promising biodegradable plastics, there were a few major drawbacks in the properties of PLA including brittleness, high stiffness and low toughness which limits its application in various fields (Simões *et al.*, 2009). The drawback of PLA can be overcome by blending with other polymers.

Blending of polymers has become another conventional method in tuning the properties of the main matrix by introducing a latter polymer which inherit a specific interesting characteristic. By blending the two phase system, one can obtain the desired characteristic of both the polymers by altering the total ratio of each polymer. As mentioned above, PLA exhibits very high tensile strength and its stiffness limited to the extend especially in film and packaging applications. Thus, PLA was blended with other polymers which exhibits elastomeric properties to impart the flexibility and toughness to the main matrix. Besides, another strategy for blending PLA is to reduce the production cost since the material cost for PLA is yet significantly higher than that of those petroleum-based plastics. Various polymers from biodegradable up to petroleum based have been used in this blending method to improve the properties of PLA. Biodegradable polymers including poly(butylene succinate), poly(butylene adipate-co-terephthalate), and poly( $\epsilon$ -caprolactone) are often being used as the blending target due to the elastomeric properties they exhibited. Therefore, the brittle characteristic and low impact strength of PLA can be easily tuned to ductile and tough by introducing those elastomers into the main matrix. Besides, PLA is also being blended with polyolefin mainly poly(ethylene) (PE) and poly(propylene) (PP) in order to reduce the production cost of PLA while maintaining its high tensile strength properties (Ren, 2011). However, the core challenge of polymer blending is the miscibility of the components in the blend. Most of the polymers remain immiscible upon blending and thus existed in two phase system, where the

continuous phase is referred to the main matrix, whereas the dispersed phase is the latter polymer that being added. The properties of the target blend is mainly achieved by varying the ratio of the main matrix and the polymer being added. Due to the immiscibility problem, most blends have poor interfacial adhesion between the matrices, thus resulting a poorer properties than that of expected.

Various modification methods have been tried by various authors (Park and Im, 2002, Broz *et al.*, 2003, Bramfeldt *et al.*, 2007, Reddy *et al.*, 2008, Yokohara and Yamaguchi, 2008, Ozkoc and Kemaloglu, 2009, Jain *et al.*, 2010) including the addition of compatibilizers, chemical grafting of a reactive functional group onto the backbone of polymeric chains, addition of nanoclay to improves the interfacial adhesion between the polymers and so on.

Poly( $\epsilon$ -caprolactone) (PCL) is an aliphatic polyester obtained from petrochemical processes. However, it is readily biodegradable in numerous environment conditions. Besides that, it is non-toxic, therefore suitable for many uses, provided its mechanical and environmental properties are adapted. PCL has become a promising choice for blending with PLA because of its ductility which could tune PLA matrix from rigid to ductile. The repeating unit of PCL is shown in Figure 3 below:

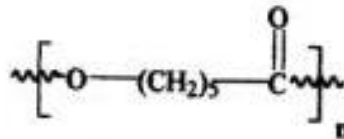


Figure 3: Repeating Unit of PCL

Glycidyl Methacrylate (IUPAC name: 2,3-epoxypropyl methacrylate) (GMA) is a molecule with reactive epoxy group attached. Due to the reactive epoxy ring, it is used mainly in epoxy resins. GMA is introduced as compatibilizer to enhance the poor interfacial adhesion between non-miscible PLA and PCL matrices. The structure of GMA is shown as in Figure 4.

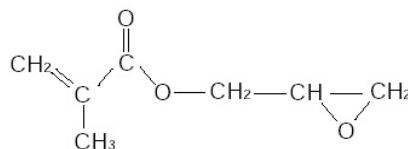


Figure 4. Structure of GMA

Besides the usage of compatibilizers, electron beam irradiation (EB) technique can be used to induce interaction between two polymers. Generally, EB is a type of ionizing energy which is low penetration and high dosage rates. The beam is highly charged of electrons and produced by the acceleration and conversion of electricity.



When the beam passes beneath the products (in this case polymer specimens), energy from the electron is absorbed. The energy absorption process alters chemical bonds or biological bonds within the specimens and thus the material is said to be sterilized. Furthermore, in polymeric materials, cross-linking process or polymer branching between the polymers could occur. The energy that is being absorbed is quantified by the term "radiation absorbed dose". In this study, the facility for EB is provided by Malaysia Nuclear Agency.

## **1.2 Problems statement**

The massive production and application of non-degradable plastics in industrial and commercial fields have created numerous environmental issues including reproducibility, pollution and waste disposal problems. To overcome these environmental harms, bio-based polymers were introduced as the potential substitute mainly for the advantages including fully biodegradable and produced from renewable resources. Poly(lactic acid) possesses high potential in industrial and commercial usages. However, the brittleness and low toughness characteristics limited its application widely. Poly( $\epsilon$ -caprolactone) is introduced to tune PLA matrix from brittle to ductile, but the extent of modification was limited by non-compatibility and poor interfacial adhesion of these polymers. Thus, this research aims to improve the compatibility of the immiscible polymers. In addition, radiation effects towards the blends are also further discussed in this topic.

## **1.3 Objectives of the study**

1. To modify brittle PLA matrix by adding PCL via melt blending method.
2. To improve the mechanical and impact properties of PLA/PCL blends by addition of GMA as reactive compatibilizing agent.
3. To study the effects of EB on PLA/PCL/GMA blend through radiation exposure at various irradiation doses.
4. To characterize the PLA/PCL/GMA and irradiated blends by means of mechanical, thermal, morphological, biodegradability, water absorption and gas permeability properties.

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