



UNIVERSITI PUTRA MALAYSIA

***DEVELOPMENT OF GRAPHENE-BASED POLY(LACTIC ACID)
NANOCOMPOSITES***

CHIENG BUONG WOEI

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BERILMU BERBAKTI

**DEVELOPMENT OF GRAPHENE-BASED
POLY(LACTIC ACID) NANOCOMPOSITES**

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**DOCTOR OF PHILOSOPHY
UNIVERSITI PUTRA MALAYSIA**

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By

CHIENG BUONG WOEI

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

July 2014

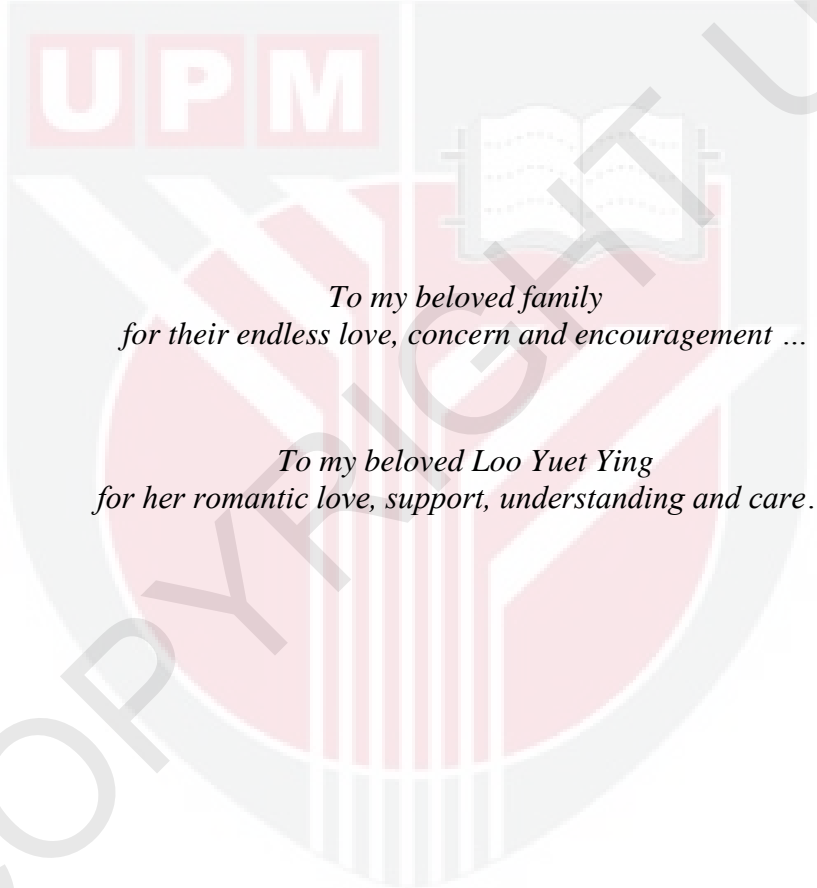
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DEDICATION

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*To my beloved family
for their endless love, concern and encouragement ...*

*To my beloved Loo Yuet Ying
for her romantic love, support, understanding and care...*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

DEVELOPMENT OF GRAPHENE-BASED POLY(LACTIC ACID) NANOCOMPOSITES

By

CHIENG BUONG WOEI

July 2014

Chairman : Nor Azowa bt Ibrahim, PhD
Faculty : Science

The present research aims to develop a material that having balanced properties between strength and flexibility. The plasticized poly(lactic acid)s (PLA) were prepared by melt blending technique using Brabender internal mixer. The effects of three different plasticizers, (i) Epoxidized Palm Oil (EPO), (ii) Epoxidized Palm and Soybean Oil (EPSO), (iii) poly(ethylene glycol) (PEG), and their loadings on plasticized PLA were studied. PLA plasticized with EPO, EPSO, and PEG show optimum plasticization effect at 5 wt%, 5 wt% and 10 wt% plasticizer loading, respectively. PLA plasticized with hybrid plasticizer (PEG:EPO) was also performed. Hybrid plasticizer with ratio (2:1) had good miscibility with PLA. Glass transition temperature (T_g) of the plasticized PLAs obviously decreased since plasticizer increased the chain mobility of PLA. On the other hand, a novel co-plasticization and synergistic plasticization effects of the two kinds of plasticizers were achieved in the studied PLA system.

However, the major drawbacks of this plasticization were the substantial decrease in the strength and modulus of the plasticized PLAs. Hence, a plasticized PLA nanocomposite was developed to get balanced properties. The synthesized Reduced Graphene Oxide (rGO) and Graphene Nanoplatelets (xGnP) were employed as graphene-based nanofiller in this study to prepare the plasticized PLA nanocomposites. rGO was synthesized from GO using green tea extracts from *Camellia sinensis* as a novel reducing agent.

Preliminary investigation was carried out to optimize the operation condition for graphene-based PLA nanocomposites preparation by Response Surface Methodology (RSM) coupled with Central Composite Design (CCD). The effects of variables

including graphene loading, temperature, speed and time on tensile strength were examined and optimized. The prepared plasticized PLA nanocomposites exhibited a significant improvement in mechanical properties at 0.3 wt% xGnP loading. The enhancement to some extent of the mechanical properties of the plasticized PLA/xGnP nanocomposites ascribed to the homogeneous dispersion and orientation of the xGnP in the polymer matrix and strong interfacial interactions between both components. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) results proved the enhancement of tensile strength and elongation at break. Addition of rGO into PLA and plasticized PLA substantially enhanced the stiffness and toughness without deteriorating elasticity, comparing to xGnP nanocomposites. In addition, the investigation of the thermal properties by means of Thermogravimetric Analysis (TGA) has found that the presence of rGO in the system is very beneficial for improving thermal stability of the PLA and plasticized PLA. SEM micrographs of the rGO nanocomposites display homogenous and good uniformity fracture surface. TEM images revealed that the rGO remained intact as graphene sheet layers and were dispersed well into the polymer matrix, and it was confirmed by X-ray Diffraction (XRD) result which shows no graphitic peak in the XRD pattern.

Water absorption, oxygen transmission rate, water vapour transmission rate, biodegradability as well as antibacterial activity of the plasticized PLA nanocomposites, all showed improved properties with the incorporation of xGnP compared to the pristine PLA and plasticized PLAs.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN NANOKOMPOSIT POLI(ASID LAKTIK) BERASASKAN GRAFENA

Oleh

CHIENG BUONG WOEI

Julai 2014

Pengerusi : Nor Azowa bt Ibrahim, PhD
Fakulti : Sains

Kajian ini bertujuan untuk membangunkan satu bahan yang mempunyai ciri yang seimbang antara kekuatan dan fleksibiliti. Poli(asid laktik) (PLA) yang diplastikkan telah disediakan oleh teknik pengadunan leburan menggunakan Brabender pencampur dalaman. Kesan tiga pemplastik yang berbeza, (i) minyak sawit epoksida (EPO), (ii) minyak sawit dan soya epoksida (EPSO), (iii) poli(etilena glikol) (PEG) dan kandungan mereka pada PLA yang diplastikkan telah dikaji. PLA diplastikkan dengan EPO, EPSO, dan PEG menunjukkan kesan pemplastikan optimum masing-masing pada 5 wt%, 5 wt% dan 10 wt% pemplastik. PLA diplastikkan dengan pemplastik hibrid (PEG:EPO) turut dilakukan. Pemplastik hibrid dengan nisbah (2:1) mempunyai kebolehcampuran yang baik dengan PLA. Suhu peralihan kaca (T_g) PLA yang diplastikkan jelas berkurangan disebabkan pemplastik meningkatkan mobiliti rantai PLA. Selain itu, pemplastikan bersama dan kesan pemplastikan sinergi kedua-dua jenis pemplastik ini telah dicapai dalam sistem PLA yang dikaji.

Walau bagaimana pun, kelemahan utama pemplastikan ini adalah penurunan yang ketara kekuatan dan modulus bagi PLA yang diplastikkan. Oleh itu, nanokomposit PLA yang diplastikkan telah dibangunkan untuk mendapatkan ciri yang seimbang. Grafena terturun (rGO) yang disintesis dan Grafena Platelet Nano (xGnP) telah digunakan sebagai pengisi nano yang berasaskan grafena dalam kajian ini untuk menyediakan nanokomposit PLA yang diplastikkan. rGO telah disintesis daripada GO menggunakan ekstrak teh hijau daripada *Camellia sinensis* sebagai ejen penurun yang baru .

Siasatan awal telah dijalankan untuk mengoptimumkan keadaan operasi persediaan nanokomposit PLA berasaskan grafena dengan kaedah tindakbalas permukaan (RSM) dengan reka bentuk komposit pusat (CCD). Kesan pembolehubah termasuk kandungan grafena, suhu, kelajuan dan masa kepada kekuatan tegangan telah diperiksa dan dioptimumkan. Nanokomposit PLA yang diplastikkan mempamerkan peningkatan yang ketara dalam sifat mekanik pada kandungan xGnP 0.3% mengikut jisim. Peningkatan dalam sifat-sifat mekanik yang nanokomposit PLA/xGnP yang diplastikkan dapat menunjukkan penyebaran dan orientasi xGnP yang homogen dalam matriks polimer dan interaksi antara muka yang kukuh antara kedua-dua komponen. Keputusan mikroskopi pengimbasan elektron (SEM) dan mikroskopi transmisi elektron (TEM) membuktikan peningkatan kekuatan tegangan dan pemanjangan pada takat putus. Penambahan rGO ke dalam PLA dan PLA yang diplastikkan dengan ketara meningkatkan kekakuan dan keliatan tanpa merosotkan keanjalan, berbanding dengan nanokomposit xGnP. Di samping itu, penyiasatan sifat haba melalui analisis termogravimetri (TGA) telah mendapati bahawa kehadiran rGO dalam sistem adalah sangat bermanfaat untuk meningkatkan kestabilan terma PLA atau PLA yang diplastikkan. Mikrograf SEM nanokomposit rGO memaparkan permukaan patah yang homogen dan seragam. Mikrograf TEM mendedahkan bahawa rGO kekal utuh sebagai lapisan grafena dan telah tersebar dengan baik ke dalam matriks polimer, dan disahkan dengan keputusan pembelauan sinar-X (XRD) yang tidak menunjukkan puncak grafitik dalam corak XRD.

Penyerapan air, kadar penghantaran oksigen, kadar penghantaran wap air, kebolehbiorosotan serta aktiviti anti-bakteria bagi semua nanokomposit PLA yang diplastikkan menunjukkan ciri yang lebih baik dengan penambahan xGnP berbanding dengan PLA dan PLA yang diplastikkan.

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I certify that a Thesis Examination Committee has met on 1 July 2014 to conduct the final examination of Chieng Buong Woei on his thesis entitled "Development of Graphene-Based Poly(lactic acid) Nanocomposites" 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 Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Abdul Halim bin Abdullah, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mansor bin Hj Ahmad @ Ayob, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohamad Zaki bin Abd Rahman, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Sabu Thomas, PhD

Professor
Mahatma Gandhi University
India
(External Examiner)

NORITAH OMAR, PhD

Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 July 2014

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Nor Azowa bt Ibrahim, PhD

Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohd Zobir Hussien, PhD

Professor
Institute of Advance Technology
Universiti Putra Malaysia
(Member)

Dato' Wan Md Zin Wan Yunus, PhD

Professor
Centre for Defence Foundation Studies
Universiti Pertahanan National Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean
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Signature: _____
Name of
Chairman of
Supervisory
Committee: **Nor Azowa Ibrahim**

Signature: _____
Name of
Member of
Supervisory
Committee: **Mohd Zobir Hussein**

Signature: _____
Name of
Member of
Supervisory
Committee: **Dato' Wan Md Zin Wan Yunus**

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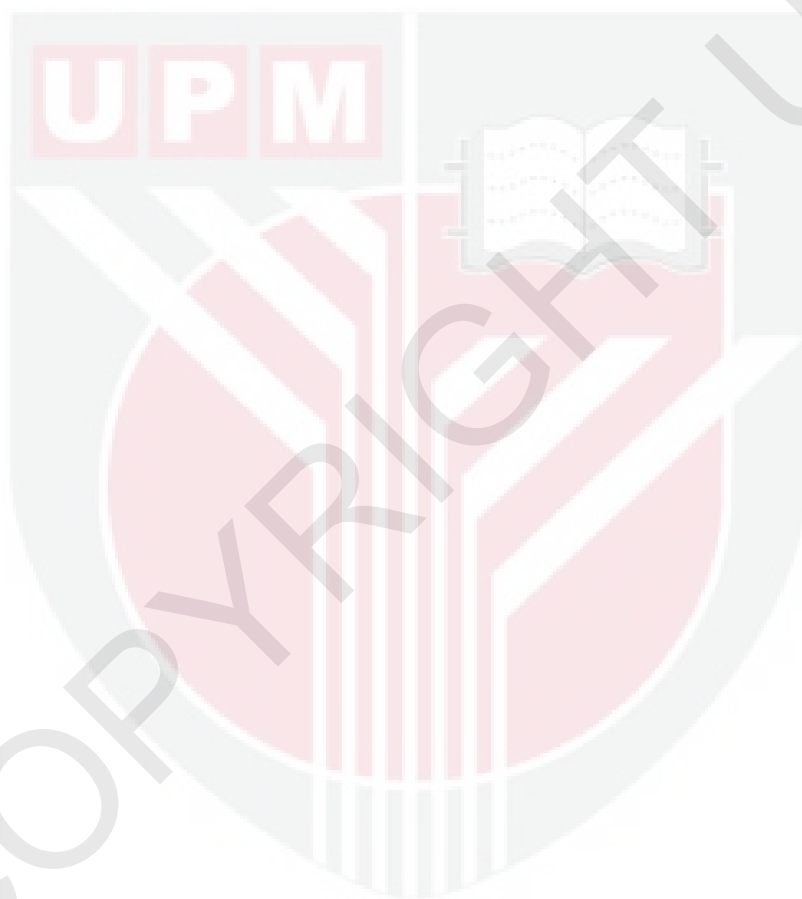
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LIST OF ABBREVIATIONS

CCD	Central composite design
CNT	Carbon nanotubes
EPO	Epoxidized Palm Oil
EPSO	Mixture of Epoxidized Palm Oil and Soybean Oil
EVO	Epoxidized vegetable oils
DTG	Derivative thermogravimetric
GO	Graphene oxide
HDPE	High density polyethylene
MMT	Montmorillonite
OOC	Oxirane oxygen content
OTR	Oxygen transmission rate
PBAT	Poly(butylene adipate-co-terephthalate)
PBGA	Poly(1,3-butylene glycol adipate)
PBS	Poly(butylene succinate)
PC	Polycarbonate
PCL	Poly(ϵ -caprolactone)
PE	Polyethylene
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
rGO	Reduced Graphene Oxide
rpm	Revolutions per minute
T_{onset}	Onset temperature
T_{cc}	Cold crystallization temperature
T_{m}	Melting temperature
T_{max}	Maximum degradation temperature
T_{50}	50% degradation temperature
T_{g}	Glass transition temperature
TEGO	Thermal exfoliated graphene oxide
xGnP / GNP	Graphene Nanoplatelets
WVTR	Water vapour transmission rate
wt%	Weight percentage
λ	Lambda

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Human beings depend a lot on great invention of science. One of the inventions is polymer which greatly brings many benefits to our mankind. Very few polymers are used commercially in their pure state without any additives. Several types of material are added to most of polymers to improve or modify their properties, such as plasticizers added to lower the glass transition or reduce the amount of crystallinity which softens the final product (Chen *et al.*, 2011), silanes or other bonding agents added to composite to induce the bonding between polymers (Xie *et al.*, 2010), finely divided rubber is added to brittle polymers to toughen them (Manson and Sperling, 1976), both glassy and rubbery polymer are cross-linked to improve elastomer behavior or to control swelling (Borin *et al.*, 2012), carbon black or silicas are added to rubber formulations to improve tear resistance and raise the modulus (Litvinov *et al.*, 2011), fillers are added to reduce price and etc (Bitinis *et al.*, 2011).

However, these polymer materials are non-biodegradable, thus widely use of these polymers for disposable applications significantly damaging the earth's ecosystem. The environmental effect of polymer plastic wastes brings global concern to a worrying status. Considerable attention has been paid to biodegradation polymers, mainly owing to increase interest for preservation of environment. Many efforts have been made to solve problems generated by plastic waste, particularly by one-time-use disposable commodity materials. Most of the research attention was focused on the replacement of petroleum-based plastics by biodegradable material with similar mechanical properties. Biodegradable polymers have been considered as most promising materials for this purpose. One of the most promising and attractive biodegradable polymer being developed is poly(lactic acid) (PLA) (Bajpai *et al.*, 2014), which are manufactured from lactic acid that in turn is produced from starch. Although production processes for lactic acid and PLA are well known, very few processes have been commercialized and still the cost of PLA is not competitive with synthetic plastics.

Scientific and technological researchers focused on the theory and practice of biopolymers, renewable-based monomers, fillers and additives as well as sustainable polymer blends and composites with possible application in packaging, agriculture, automotive or biomedicine. Packaging materials should have good mechanical properties, thermal stability, hinder gain or loss moisture, prevent microbial contamination and act as a barrier against permeation of water vapour and gases (Figure 1.1). Packaging materials are not only used as containers but also acts as protective

barriers with some innovative functions. There has been ever increasing effort in the development of different kinds of packaging materials in order to enhance their effectiveness in keeping the goods quality with improved convenience for final use (Rhim *et al.*, 2013).

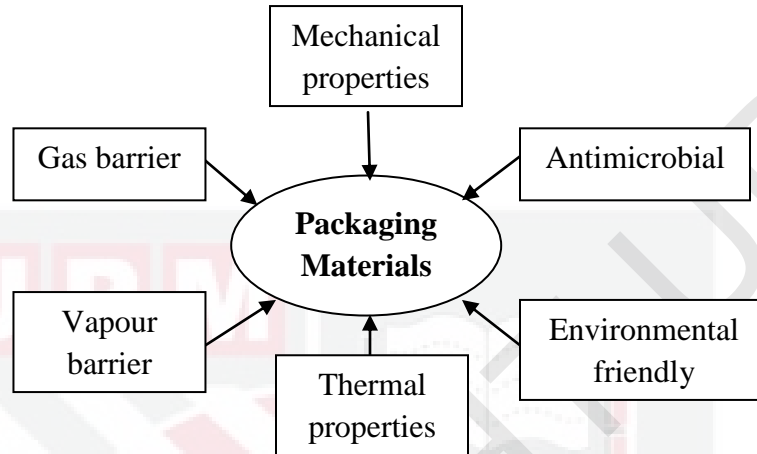


Figure 1.1 General properties required for packaging materials

One of the methods to improve biodegradable polymers is to develop nanocomposites. Nanotechnology is recognized as one of the most promising avenues of technology development for the 21st century. In the materials industry, the development of polymer nanocomposites is one of the rapidly expanding areas for applications. Nanocomposites constitute one of the most developed areas of nanotechnology. These materials being refer to composite components with nanoscale dimensions. Commonly, such fillers have at least one dimension in nanometer range and typically 1 to 20 nm (Komarneni, 1992), such as montmorillonite, carbon nanotubes, and graphite derivatives.

1.2 Graphite

Graphite crystallizes in hexagonal structure (Figure 1.2) in which each carbon atom is bound covalently to its three neighbors. Therefore, only three of the four valences of the carbon atom are saturated. The fourth electron of the atoms remains unbound, and becomes delocalized across the hexagonal atomic sheets of carbon. As these electrons are mobile, graphite shows electrical conductivity within the layers, but perpendicularly to the layers graphite is an insulator. Within the layers are strong covalent bonds, whereas in between the layers are weak van der Waals bonds, and consequently it is possible to cleave pieces of monocrystalline graphite. These single layers of graphite are known as graphene, which discover by Geim and Novoselov in 2004 (Novoselov *et al.*, 2004).

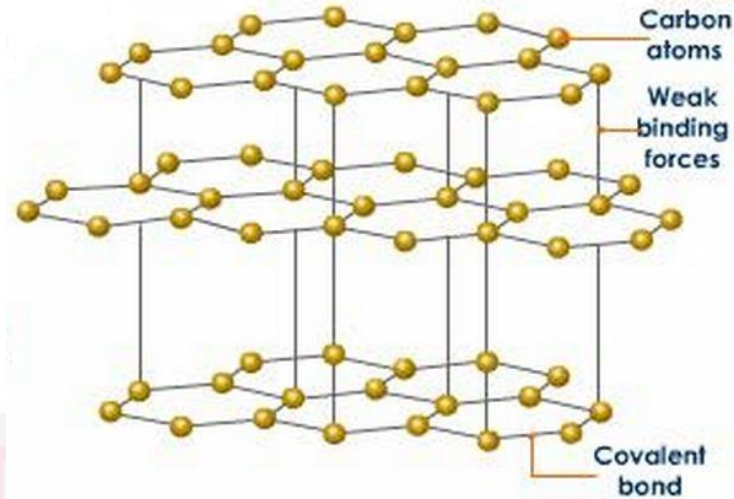


Figure 1.2 Structure of graphite

Graphene, a one-atom-thick two dimensional honeycomb layer of sp^2 bonded carbon, can be used as a potential alternative nano-reinforcement filler to both clay and carbon nanotubes. Graphene combines layered structure of clays with superior mechanical and thermal properties of carbon nanotubes, which can provide excellent functional property enhancements (Kalaitzidou *et al.*, 2007a). Since graphite is the stiffest material found in nature, having a modulus several times higher than clay, and given its excellent strength, electrical and thermal conductivity, it ought to have similar properties to carbon-based nanomaterials (Kuila *et al.*, 2010). Furthermore, graphene is much cheaper than either single-walled or multi-walled carbon nanotubes.

1.3 Problem Statements

Traditionally, all plastics have been manufactured from non-renewable petroleum resources, and these plastics are non biodegradable. Conventional disposal methods include incineration and secured landfill, which are associated with many environmental problems, such as production of dioxins.

Raw materials produced from petrochemicals are becoming more and more expensive because of the increase in oil price and the lower supply. Furthermore, the distinct durability of the petrochemical-based plastics which makes them ideal for several applications especially in packaging, is now leading to waste disposal problem, as these materials are not biodegradable.

The inherent brittleness of PLA has been a bottleneck for its large scale commercial applications. Numerous approaches such as plasticization, blending with other polymers

have been adopted to improve the toughness of brittle PLA. However, the major drawbacks of these methods are the substantial decreases in the strength and modulus of the toughened PLA. Meanwhile, the development of nanocomposites can enhance the tensile strength and tensile modulus but sacrifices the flexibility and elongation at break. So, a PLA-based material having balanced properties is still elusive (Figure 1.3).

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.

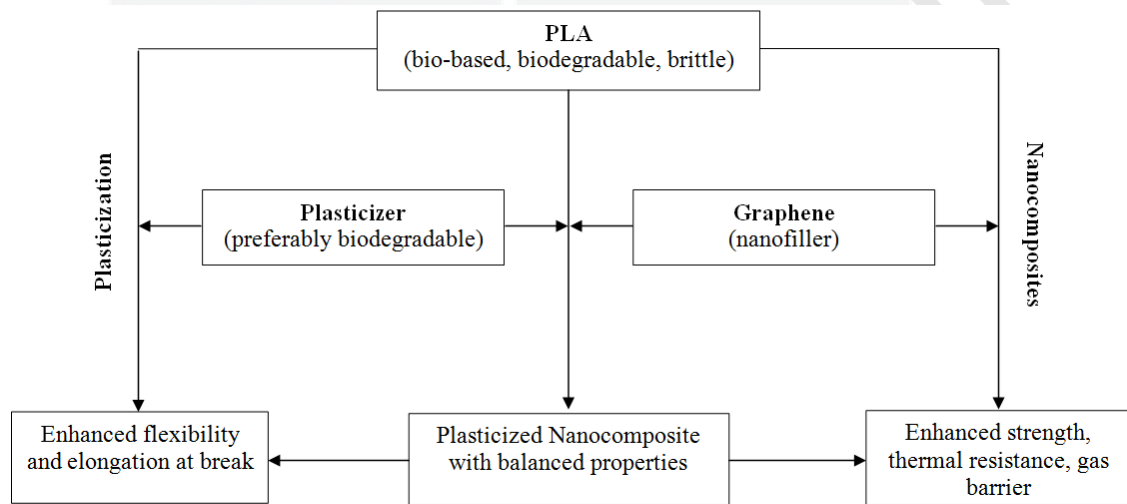


Figure 1.3 Improvement of PLA by plasticization or nanocomposites development

1.4 Scope of the Study

This research addresses the study in the area of advanced material from biodegradable polymer, PLA and graphene nanoplatelets. The aim of this study is to produce improved and balanced characteristics of PLA via melt blending technique. The response surface methodology (RSM) in conjunction with the central composite design (CCD) was employed to statistically evaluate and optimize the melt blending parameters for composites preparation. The plasticization using three different plasticizers, epoxidized palm oil (EPO), epoxidized palm and soy bean oil (EPSO) and poly(ethylene glycol) (PEG) was study and compared to pristine PLA. Hybrid plasticizers in combination of EPO and PEG were also studied to improve the flexibility of PLA. Graphene based materials such as graphene nanoplatelets (xGnP) and reduced graphene oxide (rGO) were used as nanofillers in the nanocomposites preparation. Evaluation of plasticized PLA and its graphene-based nanocomposites include mechanical properties (tensile, flexural and impact), thermal properties (thermogravimetric and differential scanning calorimetric analysis), morphology (scanning electron microscopy and transmission

electron microscopy), physical testing (water absorption, gas permeability, biodegradability) and etc. was reported in this study.

1.5 Objectives

The objectives of this study are:

1. To prepare and characterize PLA plasticized with EPO, EPO and PEG plasticizers.
2. To optimize parameter for melt blending method in polymer nanocomposite preparation by RSM method.
3. To prepare and characterize plasticized PLA/xGnP nanocomposites.
4. To prepare and characterize plasticized PLA with hybrid plasticizers and its nanocomposites.
5. To synthesize graphene oxide and reduced graphene oxide as nanofiller in PLA nanocomposites.
6. To prepare and characterize PLA/rGO and plasticized PLA/rGO nanocomposites.

1.6 Organization of the Thesis

The thesis is divided into 10 chapters. Chapter 1 is the introduction of the thesis which given general idea for the global issues of non-biodegradable polymer and the important of biodegradable nanocomposites are described here. Besides, the problem statement regarding the conventional polymer is mentioned together with the objectives of the research study. In the Chapter 2 Literature reviews section, the general process for polymer nanocomposites production, techniques used for the preparation and effect of nanofiller were explained. Chapter 3 is the methodology section which discussed the method and materials that use in this research. Chapter 4 to 9 discussed the results and discussion for each type of plasticizers that used to plasticizes PLA as well as multiple plasticizers. Synthesis of GO and rGO which use as nanofiller was reported. Development of graphene-based PLA nanocomposites also discussed here. The last chapter is the overall conclusion of the thesis and recommendation for future research based on the understanding and knowledge generated in the present study.

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