UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLY(LACTIC ACID) WITH EPOXIDIZED PALM OIL

V.S.GIITA SILVERAJAH

FS 2012 79
PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLY(LACTIC ACID) WITH EPOXIDIZED PALM OIL

V.S.GIITA SILVERAJAH

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA
2012
PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLY(LACTIC ACID) PLASTICIZED EPOXIDIZED PALM OIL

By

V.S.GIITA SILVERAJAH

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

September 2012
Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLY(LACTIC ACID) WITH EPOXIDIZED PALM OIL

By

V.S.GIITA SILVERAJAH

September 2012

Chairman : Nor Azowa binti Ibrahim, PhD
Faculty : Science

Conventional plastics such as polyethylene, polypropylene, and polyethylene terephthalate persist for many years after disposal. They are inappropriate for applications intended for short time such as packaging, which increases the plastic waste disposal. The accumulation of plastic waste in landfills results in long-term environment, economic and waste management problems which need immediate resolution. Rising environmental concerns have directed research to the development of biodegradable polymer materials.

Poly(lactic acid) (PLA) has a large potential as a biodegradable plastic. However, PLA has low toughness, low tensile elongation and high brittleness which limited its applications. In this research PLA was incorporated with three different samples of epoxidized palm oil (EPO). The plasticized PLA were prepared by melt blending technique using Brabender internal mixer. The effects of three different samples of EPO and their loadings on plasticized PLA were studied. Further, the optimum EPO loading with enhanced properties of PLA were determined.
Results displayed the overall properties of PLA were improved with the addition of EPO. The optimum EPO loading with enhanced mechanical and thermal properties of PLA is 1 wt%. PLA/1 wt% EPO(3) showed excellent properties compared to PLA/1 wt% EPO(1), PLA/1 wt% EPO(2) and neat PLA. The tensile strength, flexural strength, impact strength and elongation at break were improved by 13%, 25%, 23% and 77%, respectively compared to neat PLA. This reveals good stress transfer of the material. Addition of 1 wt% EPO(3) also significantly decreased the storage modulus while increased the loss factor of DMA analysis.

XRD analysis reveals an increase in the amorphous phase of the PLA/1 wt% EPO(3), whereas an increase in the crystalline phase of PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2). Thermal properties of the plasticized PLA were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). From the results, there is significant improvement about 27% on the thermal stability of plasticized PLA with the addition of 1 wt% EPO. Further, the DSC results illustrate a decrease in the glass transition temperature due to plasticizing effect of EPO. The surface morphology of the PLA/1 wt% EPO(3) fracture surface obtained from tensile test shows a smooth surface without voids and aggregation, indicating good interaction between PLA and EPO(3). This is in agreement with the significant improvement of mechanical properties.

The environmental degradation behaviors on the physical properties of plasticized PLA were studied with special reference to the influence of ageing conditions like water sorption and biodegradability. From water uptake analysis, it can be inferred that the 1 wt% plasticized PLA absorb lesser water than neat PLA. The soil burial
test was carried out for 6 months, and the results indicate that EPO loading slightly promotes degradation of the plasticized PLA. Thus, PLA/1 wt% EPO(3) can be considered as an alternative to the conventional plastics used. Additionally, EPO can be seen as a potential useful plasticizer.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN POLI(ASID LAKTIK) DIPLASTIK DENGAN MINYAK SAWIT EPOKSIDA

Oleh
V.S.GIITA SILVERAJAH

September 2012

Pengerusi : Nor Azowa binti Ibrahim, PhD
Fakulti : Sains

Plastik konvensional seperti polietilena, polipropilena, dan polietilena terephthalat akan masih wujud beberapa tahun selepas ianya dilupuskan. Plastik seumpama ini tidak sesuai untuk penggunaan jangka masa yang pendek seperti pembungkusan, yang meningkatkan pembuangan sisa plastik. Oleh itu, penimbunan sisa plastik di tapak pelupusan memerlukan resolusi serta-merta kerana ia mengakibatkan pencemaran, masalah ekonomi dan pengurusan sisa. Kesedaran terhadap alam sekitar yang semakin meningkat telah mendorong kepada penyelidikan dan pembangunan bahan polimer biodegradasi.

Poli(laktik asid) (PLA) mempunyai potensi yang tinggi sebagai polimer biodegradasi. Namun demikian, PLA sangat rapuh serta tidak mempunyai kekuatan dan keupayaan pemanjangan yang tinggi. Oleh itu, penyelidikan ini memberi tumpuan dalam mengintegrasikan PLA dengan tiga jenis sampel minyak sawit epoksida (EPO). PLA yang diplastik dengan EPO telah disediakan dengan teknik pengadunan lebur menggunakan alat pengadun dalaman ‘Brabender’. Kesan
penggunaan tiga jenis sampel EPO dan kandungannya dikaji pada PLA yang telah dihasilkan. Seterusnya, kandungan EPO yang optimum dengan peningkatan ciri-ciri PLA telah ditentukan.

Keputusan menunjukkan keseluruhan ciri-ciri PLA telah ditingkatkan dengan penambahan EPO. Kandungan optimum EPO yang menunjukkan peningkatan dalam ciri mekanikal dan terma PLA adalah 1% mengikut berat. PLA/1% EPO(3) telah menunjukkan ciri yang sangat baik berbanding dengan PLA/1% EPO(1), PLA/1% EPO(2) dan PLA tulen. Kekuatan regangan, flektural, hentaman dan keupayaan pemanjangan telah bertambah baik, masing-masing sebanyak 13%, 25%, 23% dan 77% berbanding dengan PLA tulen. Ini menunjukkan pemindahan ketegangan yang baik oleh bahan tersebut. Penambahan 1% EPO(3) juga menunjukkan penurunan ketara dalam modulus penyimpanan, sementara peningkatan dalam faktor kehilangan daripada analisis DMA.

Analisis XRD mendedahkan fasa amorfus (fasa tak berbentuk) PLA/1% EPO(3) telah meningkat, manakala bagi PLA/1% EPO(1) and PLA/1% EPO(2) fasa kristalnya telah bertambah. Sifat terma bagi PLA yang diplastik dengan EPO telah dikaji dengan menggunakan analisis termogravimetri (TGA) dan analisis kalorimetri pengimbas pembezaan (DSC). Daripada hasil kajian, PLA dengan penambahan 1% EPO telah menunjukkan peningkatan dalam kestabilan terma yang jelas sebanyak 27%. Di samping itu, hasil pemerhatian DSC turut menunjukkan penurunan dalam suhu peralihan kaca disebabkan kesan liat daripada EPO. Pemerhatian morfologi pecahan permukaan ujian regangan PLA/1% EPO(3) menunjukkan permukaan yang licin tanpa kekosongan (liang) dan pengagregat, menandakan interaksi yang baik.
di antara PLA dan EPO(3). Hasil ini selari dengan peningkatan ketara dalam ciri-ciri mekaniknya.

Kesan degradasi persekitaran terhadap ciri fizikal dan mekanikal PLA yang diplastik dengan EPO telah dikaji dengan melibatkan ujian penyerapan air dan biodegradasi sampel. Merujuk kepada analisis penyerapan air, PLA dengan 1% EPO menyerap kurang air berbanding PLA tulen. Ujian biodegradasi tanah telah dijalankan selama 6 bulan, dan hasil kajian menunjukkan bahawa kandungan EPO menggalakkan degradasi PLA. Oleh yang demikian, PLA/1% EPO(3) boleh dianggap sebagai alternatif kepada plastik konvensional yang sedang digunakan. Selain itu, EPO juga boleh dilihat sebagai agen liat yang berpotensi.
ACKNOWLEDGEMENTS

First of all, I want to express my deepest appreciation to my project supervisor Dr. Nor Azowa Ibrahim, co-supervisors Professor Dato’ Dr. Wan Md Zin Wan Yunus, Dr. Norhazlin Zainuddin and Dr. Hazimah Abu Hassan for their supervision, brilliant ideas, technical guidance and superb tolerance throughout the course of this work.

Much appreciation is extended to Advanced Oleochemical Technology Division (AOTD), Malaysian Palm Oil Board (MPOB) for kindly providing the materials used in this study. Special thanks to all the laboratory assistants and staffs in the Faculty of Science, Universiti Putra Malaysia for their sincere contribution that has made this research work possible. I would like to thank Ms. Kosheela Devi Poo Palam from AOTD and the staffs in Malaysian Institute for Nuclear Technology Research (MINT), Bangi for their unfailing assistance.

I would like to express my deepest gratitude to my beloved parents, Punethn Superminium and friends who have always believe in me, and endured with me during difficult times. I also would like to dedicate my gratitude to all my colleagues in Polymer Group Research whose help, suggestions, encouragement and companion are of great help in sustaining the morale and enthusiasm.

Last but not least, I would like to convey my deepest appreciation to examiners for their guidance to improvise this thesis. Financial support from Research University Grant Scheme (RUGS), Universiti Putra Malaysia and MyMaster are gratefully acknowledged.
I certify that A Thesis Examination Committee has met on 26th September 2012 to conduct the final examination of V.S.Giita Silverajah on her thesis entitled “Preparation and Characterization of Plasticized Poly(lactic acid) with Epoxidized Palm Oil” in accordance with the Universities and University College 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.

Members of the Thesis Examination Committee were as follows:

Prof. Madya Dr. Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Prof. Madya Dr. Mansor bin Haji Ahmad, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
/Internal Examiner

Prof. Madya Dr. Mohamad Zaki bin Abdul Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
/Internal Examiner

Prof. Madya Dr. Ishak bin Ahmad, PhD
Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
/External Examiner

______________________________
SEOW HENG FONG, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:
This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of Supervisory Committee were as follows:

Nor Azowa Ibrahim, PhD  
Senior Lecturer  
Faculty of Science  
Universiti Putra Malaysia  
(Chairman)

Norhazlin Zainuddin, PhD  
Lecturer  
Faculty of Science  
Universiti Putra Malaysia  
(Member)

Wan Md Zin Wan Yunus, PhD  
Professor  
Chemistry Department  
National Defence University of Malaysia  
(Member)

Hazimah Abu Hassan, PhD  
Director  
Advanced Oleochemical Technology Division (AOTD)  
Malaysian Palm Oil Board (MPOB)  
(Member)

BUJANG BIN KIM HUAT, PhD  
Professor and Dean  
School of Graduate Studies  
Universiti Putra Malaysia

Date:
DECLARATION

I declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

_________________________
V.S.GIITA SILVERAJAH
Date:
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ABSTRACT</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRAK</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>vii</td>
</tr>
<tr>
<td>APPROVAL</td>
<td>ix</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xiv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xvii</td>
</tr>
</tbody>
</table>

CHAPTER

1 INTRODUCTION
   1.1 Background of Study       1
   1.2 Scope of Study            3
   1.3 Objectives of Study       4

2 LITERATURE REVIEW
   2.1 Biodegradable Polymer     5
   2.2 Poly(lactic acid)         7
      2.2.1 Synthesis of Poly(lactic acid) 9
      2.2.2 Properties of Poly(lactic acid) 10
      2.2.3 Biodegradability of Poly(lactic acid) 11
      2.2.4 Application           14
   2.3 Plasticizer               16
      2.3.1 Theory of Plasticization 19
      2.3.2 Interaction of Plasticizer on Blend Components 20
      2.3.3 Plasticization of Blend Components 23
      2.3.4 Processing Technique 25
   2.4 Epoxidized Palm Oil (EPO) 26
      2.4.1 Preparation of Epoxidized Palm Oil 27
      2.4.2 Effect of Oxirane Oxygen Content (OOC) on the Properties of Epoxidized Oil 31
      2.4.3 Application of Epoxidized Palm Oil 33
   2.5 Modification of Poly(lactic acid) 34

3 MATERIALS AND METHODS
   3.1 Materials
      3.1.1 Poly(lactic acid) 38
      3.1.2 Epoxidized palm oil 38
   3.2 Methods
      3.2.1 Preparation of Plasticized PLA 39
      3.2.2 Tensile Properties 40
      3.2.3 Flexural Properties 40