UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/POLY(BUTYLENE SUCCINATE)/GRAPHENE OXIDE COMPOSITE

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PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/POLY(BUTYLENE SUCCINATE)/GRAPHENE OXIDE COMPOSITE

By

NURAINI BINTI MD SUKUR

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PREPARATION AND CHARACTERIZATION OF POLY(LACTIC ACID)/POLY(BUTYLENE SUCCINATE)/GRAPHENE OXIDE COMPOSITE

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The present research study the effect of graphene oxide (GO) on the properties of poly(lactic acid)/poly(butylene succinate), (PLA/PBS). GO was synthesized from graphite through modified Hummers' method. The synthesized GO was characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetric analysis (TGA). FTIR and XRD results proved that GO was successfully synthesized. XRD showed that a new broad peak at 12.9˚ emerged with the occurrence of graphite layer oxidation.

PLA/PBS blends were prepared via melt blending technique. FTIR spectra revealed shifting of functional group peaks to lower wavenumber indicating chemical interaction occurred between PLA and PBS. Tensile strength and modulus decreased with increasing amount of PBS due to PBS elasticity. SEM micrographs of PLA/PBS blends showed immiscibility with more than 20 wt.% of PBS content. Thermal properties of PLA/PBS blend improved with the addition of PBS. From the mechanical and morphological studies, PLA with 20 wt.% PBS loading was chosen as optimum ratio and used for the preparation of PLA/PBS/GO composites.

The PLA/PBS/GO composites were prepared via melt blending technique. The mechanical property of the composites improved with the addition of 0.1 wt.% of GO. Thermal analysis of the composites also revealed significant improvement in thermal stability compared to PLA/PBS blend and pristine PLA. SEM micrographs results revealed rougher surfaces when more GO loaded to the PLA/PBS blend.

Furthermore, the PLA/PBS/GO composite with 0.1 wt.% GO loading was more water resistance than PLA/PBS blend because GO can act as barrier to the composite. Biodegradability test revealed that the PLA/PBS/GO has the lowest weight lost compared to PLA/PBS blend and neat PLA.

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PENYEDIAAN DAN PENCIRIAN KOMPOSIT POLI(ASID LAKTIK)/POLI(BUTILIN SUKSINAT)/GRAFIN OKSIDA

Oleh

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Matlamat kajian ini adalah untuk mengetahui kesan penggunaan grafin oksida (GO) ke atas sifat poli(asid laktik)/poli(butilin suksinat), (PLA/PBS). Grafin oksida telah disintesis daripada grafit melalui kaedah Hummer yang diubahsuai. GO yang disintesis telah dicirikan menggunakan spektroskopi Inframerah transformasi Fourier (FTIR), pembelauan sinar-X (XRD), mikroskopi elektron imbasan (SEM), dan analisis termogravimetri (TGA). Keputusan FTIR dan XRD menunjukkan GO telah berjaya disintesis. XRD menunjukkan puncak lebar baru telah muncul di 12.9˚ dengan kejadian pengoksidaan lapisan grafit.

Adunan PLA/PBS telah disediakan melalui teknik mengadun lebur. Spectrum FTIR mendedahkan pengalihan puncak kumpulan berfungsi ke nombor gelombang yang lebih rendah menunjukkan berlakunya interaksi kimia di antara PLA dan PBS. Kekuatan tegangan dan modulus menurun dengan dengan meningkatnya kandungan PBS kerana sifat elastik PBS. SEM mikrograf daripada PLA/PBS mempamerkan ketidakbolehcampuran dengan kandungan PBS lebih daripada 20 wt.%. Sifat terma adunan PLA/PBS meningkat dengan penambahan PBS. Daripada kajian mekanik dan morfologi, PLA dengan penambahan 20 wt.% PBS dipilih sebagai nisbah optima untuk penyediaan komposit PLA/PBS/GO.

Komposit PLA/PBS/GO telah disediakan melalui teknik mengadun lebur. Sifat mekanik komposit meningkat dengan penambahan 0.1 wt.% GO. Analisis terma komposit juga mendedahkan peningkatan pada kestabilan terma berbanding dengan PLA asli dan adunan PLA/PBS. Keputusan mikrogaraf SEM mendedahkan permukaan yang lebih kasar apabila lebih banyak GO ditambah kepada adunan PLA/PBS.

Tambahan pula, komposit PLA/PBS/GO dengan GO sebanyak 0.1 wt.% lebih tahan air berbanding campuran PLA/PBS oleh kerana GO bertindak sebagai penghalang kepada komposit. Ujian biodegradasi mendedahkan PLA/PBS/GO mempunyai pengurangan berat terendah berbanding campuran PLA/PBS dan PLA.

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

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This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CAGR	Compund annual growth rate
CNT	Carbon nanotube
DCPDCE	Dicyclopentadiene bisphenol dicyanate ester
DNA	Deoxyribonucleic acid
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric
EPO	Epoxidized palm oil
FTIR	Fourier transform infrared spectroscopy
GO	Graphene oxide
HBPGO	Hyperbranced polysiloxane functionalized-graphene
KDC	Kenaf-derived cellulose
M_w	Molecular weight
PA	Polyamide
PBAT	Polybutyrate
PBS	Poly(butylene succinate)
PEG	Poly(ethylene glycol)
PPO	Poly(phenylene oxide)
PVC	Poly(vinyl chloride)
PBAT	Polybutyrate
RNA	Ribonucleic acid
T_c	Crystallization temperature
T_{deg}	Final degradation temperature
T_g	Glass transition temperature
T_m	Melting temperature
T_{max}	Maximum degradation temperature
T_{onset}	Onset temperature
TGA	Thermogravimetric analysis
UATR	Universal attenuated total reflectance
UP	Unsaturated polyester
wt.%	Weight percentage
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Overview of Study

Polymer has become one of the most essential materials used in our live. In fact, most of the things around us are made up of polymer. Polymer can be defined as a large molecule which are made up of repeating structural units or monomers bonded by the same type of linkage. Different type of monomers and how they are linked together will form polymers with different properties. Polymers can exist naturally or synthetically. Examples of naturally occurring polymers include starch, silk, asbestos, as well as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). While examples of synthetic polymers are nylon, Teflon, silicon, poly(vinyl chloride) (PVC), and poly(ethylene terephthalate) (PET).

Due to the wide range of its properties, the application of polymers now extends from packaging, adhesives, automotive, textiles, electrical, agricultural, optical, to even medicine and biomedical. However, most of the materials are made from non-renewable sources such as petroleum and crude oil because of the availability at lower cost and having better properties than the polymer derived from renewable sources. The extensive use of the non-renewable sources materials now leads to environmental problems such as the decrement of petroleum stock and accumulation of domestic waste. It is not just the non-renewable sources that concern the community, the plastic waste generated is also not naturally degradable, takes years to decompose, and even gives off toxic gasses (e.g. dioxin) when incinerated.

Due to the alarming concerns, many research have been carried out to counteract the problems. One of the ways is by substituting the non-biodegradable polymers derived from non-renewable sources with biodegradable polymers derived from renewable sources. Biodegradable polymers from renewable sources play an important role in reducing the world dependency on petroleum-based materials and also help to alleviate solid waste disposal problems. Biodegradable polymers are polymers that can be broken down by the action of enzymes and/or microorganism into natural byproducts such as water, gasses (nitrogen and carbon dioxide), inorganic salts, and biomass. Biodegradable polymers from renewable sources can be categorized into three categories which are natural occurring polymers, synthetic polymers, and microbial fermentation derived polymers as depicted in **Figure 1.1** (Ramani, 2005).

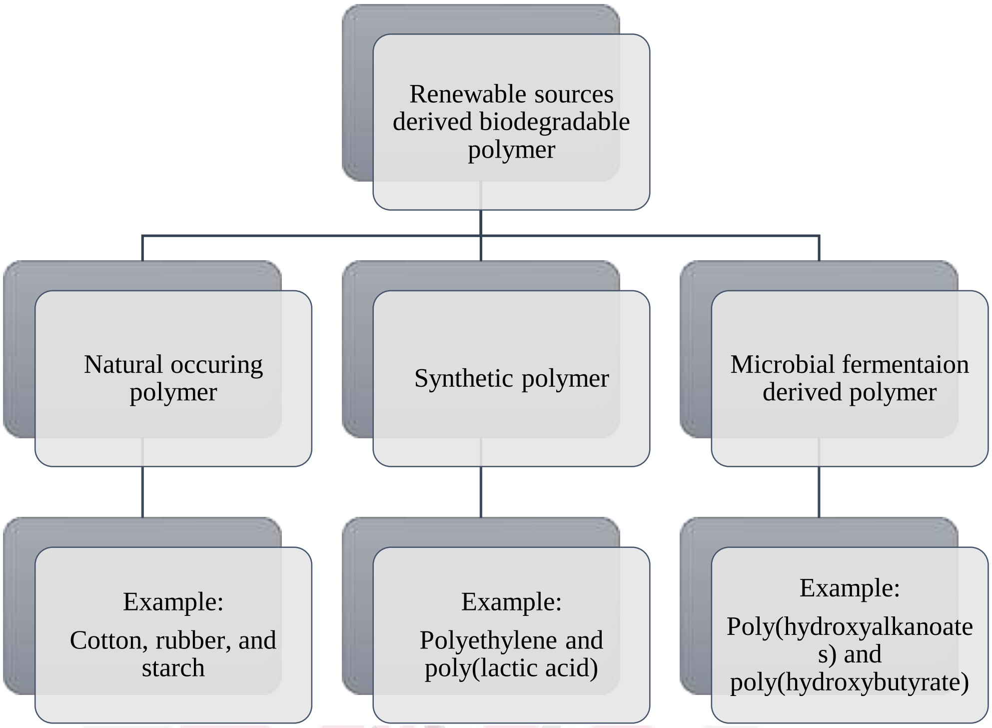

Figure 1.1: Types of renewable sources derived biodegradable polymer
(Ramani, 2005)

Poly(lactic acid) (PLA) is one of the most interesting and promising polymers used by researchers to achieve those goals as it is made from agricultural products and most importantly readily biodegradable (Gruber and Brien, 2002). PLA has very good properties such as good visual appearance, high mechanical strength and barrier properties, as well as low toxicity, which makes PLA flexible to be implied in various fields (Fang and Hanna, 1999). PLA also does not emit toxic gasses such as nitrogen oxide when burned and only one-third of the combustion heat generated by polyolefins that do not damage the incinerator and at the same time save energy.

The increasing appreciation of various intrinsic properties of PLA, coupled with knowledge of how such properties can be enhanced to achieve compatibility with manufacturing, thermoplastic processing, and end-use requirements has fuelled technological and commercial interest in PLA. Up to this day, development activities have spread throughout all countries at a compound annual growth rate (CAGR) of 19.5% from 2013 to 2020. Major applications will be packaging, building and construction products, automotive components, appliances materials and electrical/electronic parts.

Even though this type of polymer can help in the environmental problems, it is not very favourable in the industrial market because of the availability of petroleum at lower cost and better biochemical inertness of petroleum based-materials compared to the renewable source derived-polymer. Besides that, some of the properties of the biodegradable polymer are rather too weak compared to conventional polymers. For example, PLA possess poor mechanical properties and high rittleness. Therefore, in order to compete with these conventional materials, modifications such as blending and composite formation have to be carried out to the polymers to improve the properties (Yu *et al.*, 2006).

Poly(butylene succinate) (PBS) is a potentially valuable polyester to replace the petroleum based materials because of its biodegradability, compostability, and good mechanical and thermal properties (Fujimaki, 1998). It is derived from the polycondesation reaction of succinic acid with 1,4-butanediol (Okada, 2002). PBS has been utilized in various applications such as laminates, blown bottles, foamed sheet, films, and injection-molded materials. Due to its high flexibility and crystallization rate, PBS is usually applied as modifier or plasticizer to enhance the deformation of PLA such as brittleness and low crystallization rate (Stoyanova *et al.*, 2014). Unfortunately, polymer blend tend to be immiscible due to the large mixing enthalpy which then lead to deterioration of the mechanical properties (Cao *et al.*, 2011). Furthermore, blending PLA with plasticizer such as PBS, PEG, and epoxidized palm oil would lead to decrement in tensile strength as well as tensile modulus although it does improve the elongation at break. Therefore, in order to overcome these problems, the polymer blend need to be reinforced by adding the third component such as filler. Fillers are commonly added to the polymer blend to enhance the properties of the materials (Gacitua *et al.*, 2005). Some examples of fillers are mica, graphene, kaolin, graphene oxide, feldspar, talc, ground calcium carbonate, and carbon black. Graphene oxide has drawn a great interest in research and composite productions mainly due to its unique electronic and material properties. The addition of graphene oxide as filler for composite production could offer desired properties to the polymer due to its excellent mechanical properties such as hardness, high Young's modulus, and flexibility, along with its large aspect ratio and lower cost production compared to carbon nanotube. Furthermore, presence of oxygen functionalities on graphene oxide would eventually help to interact non-covalently with other polymers (Zhao *et al.*, 2014).

1.2 Research Approach

This present work represents attempts toward introducing graphene oxide (GO) as filler to the biodegradable poly(lactic acid) (PLA)/poly(butylene succinate) (PBS) blend. The introduction of filler to the polymer as reinforcement agent is common for renewable sources based-polymers since most of them have drawbacks of low softening temperature and low modulus. Therefore, the main objective of this research is to improve the properties of PLA/PBS blend by incorporating GO as filler in the blend. GO is a monolayer of sp^2-hybridized carbon atoms arranged in a flat honeycomb structure. It is similar to graphene but has several oxygen containing group functionalities attached to it such as hydroxyls, epoxides, and carbonyls. GO can be synthesized from natural graphite flakes which is cheap and abundant. Aside from that, GO is easier to manufacture compared to graphene. Thus, it can compete with other types of filler in the term of cost production. Due to its improvement of mechanical and thermal properties of many composites, GO has been chosen as filler to improve the properties of PLA/PBS blend.

This research is divided into three stages. Starting with the synthesis of GO from graphite flakes using modified Hummer’s method and followed by preparation of PLA/PBS blend and determination of optimum ratio. PBS is added to PLA as a plasticizer in order to improve the flexibility of PLA. Finally, introduction of GO into the optimum ratio of PLA/PBS blend by melt blending technique. PLA and PBS are expected to interact with each other due to the presence of hydroxyl group for both of the polymer. Evaluation of mechanical, thermal, morphological and physical properties of the neat PLA, PLA/PBS blend, and PLA/PBS/GO composite were investigated.

1.3 Objectives

The objectives of this study are to:

1. prepare and optimize PLA blends with PBS as a plasticizer based on the mechanical properties.

2. prepare PLA/PBS/GO composites with different percentages of GO loading.

3. characterize the neat PLA, PLA/PBS blend and PLA/PBS/GO composites in terms of mechanical, thermal stability, and morphological properties.

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