PROPERTIES AND BIODEGRADABILITY OF LOW DENSITY POLYETHYLENE/THERMOPLASTIC SOYA SPENT POWDER (TSSP) BLENDS ADDED SPEAR GRASS POWDER AS PRO-OXIDANT

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by

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TABLE OF CONTENTS

PAGE

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

B1	Brown isolate
DEG	Diethylene glycol
DS	Degree of substitution
DSC	Different scanning calorimetry
E_b	Elongation at break
EG	Ethylene glycol
ENR 50	Epoxidised natural rubber with 50 mol% epoxidation
EPO	Epoxidised palm oil
ESO	Epoxidised soya bean oil
FTIR	Fourier transform infrared
G1	Green isolate
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
PBAT	Poly(butylenes adipate-co-terephthalate)
PCL	Poly-ε-caprolactone
PDA	Potato dextrose agar
PE	Polyethylene
PEG	Polyethylene glycol
PE-g-MA	polyethylene-grafted maleic anhydride
PG	Propylene glycol
PHBV	Poly(hydroxybutyrate-co-valerate)
PP	Polypropylene

PS	Polystyrene
PVA	Poly(vinyl alcohol)
PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
SPI	Soya protein isolate
SSP	Soya spent powder
TEG	Triethylene glycol
TGA	Thermogravimetric analysis
TPS	Thermoplastic starch
TSSP	Thermoplastic soya spent powder
UTM	Universal Testing Machine
W1	White isolate
WG	Waste gelatine
WGESO	Wheat gluten epoxidised soya bean oil

LIST OF NOMENCLATURES

NH_4NO_3	Ammonium nitrate
$MgSO_4.7H_2O$	Magnesium sulphate heptahydrate
K_2HPO_4	Pottasium hydrogen phosphate
$CaCl_2.2H_2O$	Calcium chloride dihydrate
KCl	Pottasium chloride
Thiamine-HCL	Thiamine hydrochloride
Pb	Plumbum
Cu	Copper
Zn	Zinc
Cd	Cadmium
Mn	Manganese
Fe	Ferum

LIST OF SYMBOLS

%	percentage
kg/capita	kilogram per capita
°C	degree celcius
g/cm^3	gram per cubic centimetre
$mgkg^{-1}$	miligram per kilogram
g	gram
h	hour
µm	micrometer
wt%	weight percentage
mm/min	millimetre per minute
kV	kilo volt
mg	miligram
°C/min	degree celcius per minute
ΔH^{*}_{f}	heat fusion for 100% crystalline polyethylene
ΔH°_{f}	heat of fusion for semicrystalline polyethylene
L	litre
ml	mililitre
cm^3	cubic centimetre
mm^3	cubic milimetre
cm^{-1}	reciprocal wavelength
MPa	mega pascal

Sifat-Sifat dan Keupayaan Biodegradasi oleh Campuran Polietalina Berketumpatan Rendah/Termoplastik Serbuk Hampas Soya Bersama Serbuk Lalang Ditambah sebagai Pro-Oksida

ABSTRAK

Pembuangan sampah merupakan suatu masalah persekitaran yang serius dan menjadi cabaran terbesar dalam pengurusan sisa pembuangan. Keazaman yang tinggi untuk menghasilkan polimer yang 'mesra alam' telah mendorong para penyelidik untuk menjalankan kajian mengenai polimer terbiodegradasi melalui campuran polimer semulajadi ke dalam bahan plastik yang tidak terbiodegradasi. Termoplastik merupakan suatu bahan yang dihasilkan melalui gabungan pemplastik ke dalam polimer semulajadi contohnya kanji. Oleh yang demikian, dalam kajian ini, suatu percubaan untuk menggabungkan polimer semulajadi berdasarkan protein iaitu hampas soya ke dalam matrik polietalina berketumpatan rendah telah dijalankan. Kajian ini menyiasat pengaruh gliserol terhadap sifat-sifat campuran yang tersedia daripada kandungan polietalina berketumpatan rendah yang divariasikan daripada 5 sehingga 25 peratus kandungan. Serbuk lalang (1.5 peratus) yang bertindak sebagai pro-oksida telah ditambah ke dalam campuran polietalina berketumpatan rendah/hampas serbuk soya dan polietalina berketumpatan rendah/termoplastik hampas serbuk soya. Pendedahan kepada persekitaran semulajadi dan penanaman ke dalam tanah telah dijalankan selama 9 bulan untuk mengenal pasti tahap potensi polimer yang terhasil untuk mereput dalam persekitaran yang berbeza. Hasilnya, campuran polietalina berketumpatan rendah/termoplastik hampas serbuk soya menunjukkan kekuatan tegangan dan pemanjangan pada takat patah yang lebih tinggi berbanding campuran polietalina berketumpatan rendah/ hampas serbuk soya selepas pendedahan kepada persekitan dan penanaman di dalam tanah. Walaubagaimanapun, selepas penambahan serbuk lalang, kekuatan tegangan dan pemanjangan pada takat patah untuk kedua-dua campuran menurun. Imej mikrograf SEM menunjukkan terdapat penghasilan retak, lubang dan kolonisasi kulat pada permukaan polietalina berketumpatan rendah/ hampas serbuk soya dan polietalina berketumpatan rendah/ termoplastik hampas serbuk soya. Bagi analisa pengimbasan kalorimeter pula, polietalina berketumpatan rendah/hampas serbuk soya menghasilkan penghabluran yang lebih tinggi (15.65% untuk 25 peratus kandungan) berbanding polietalina berketumpatan rendah/termoplastik hampas serbuk soya (14.76%) untuk peratus kandungan yang sama. Kestabilan terma untuk setiap campuran menurun daripada 451°C bagi polietalina berketumpatan rendah asli dengan pertambahan 25 peratus kandungan hampas serbuk soya (269 °C) dan termoplastik hampas serbuk soya (284°C). Sebanyak tiga jenis mikroorganisma telah berjaya diasingkan. *Aspergillus fumigatus* daripada genus *Aspergillus* mencatatkan peningkatan sel berat kering yang paling tinggi iaitu sebanyak 56% melalui proses fermentasi.

Properties and Biodegradability of Low-Density Polyethylene/Thermoplastic Soya Spent Powder (TSSP) Blends Added Spear Grass Powder as Pro-Oxidant

ABSTRACT

Plastic waste is a serious environmental problem and become an enormous challenge to waste management. A high determination to produce eco-friendly polymer has led the researchers to investigate about biodegradable polymers by adding natural polymer into the non-degradable plastic material. Thermoplastic is a material that produced by incorporating the plasticizer into the natural polymer, ie starch. Therefore in this research, an attempt was made by incorporating protein based natural polymer which was soya spent powder (SSP) into LDPE matrix. This study investigated the influence of glycerol on the properties of blends prepared from low density polyethylene (LDPE) with different SSP content varied from 5 to 25 wt%. Spear grass powder as a natural pro-oxidant (1.5 wt%) has been added into LDPE/SSP and LDPE/TSSP blends. Natural weathering test and soil burial test were performed for 9 months period to determine the potential of this polymer to degrade in different surroundings. As a result, LDPE/TSSP blends showed higher strength and elongation at break (E_b) compared to LDPE/SSP blends after weathering and composting. However, after the addition of spear grass powder, the tensile strength and E_b of LDPE/TSSP blends decreased. Scanning electron microscopy (SEM) micrographs showed the formation of crack, pores and fungus colonization on of LDPE/SSP and LDPE/TSSP blends surfaces. For differential scanning calorimetry (DSC) analysis, LDPE/TSSP blends presented higher crystallinity (15.65% for 25 wt% TSSP) compared to LDPE/SSP blends for the same blends ratio (14.76%). The thermal stability for each blends decreased from 451 °C (for neat LDPE) with an increase of 25 wt% of SSP (269 °C) and TSSP (284 °C) content. Three different strains have been successfully isolated in this study. *Aspergillus fumigatus* from the genus of *Aspergillus* encountered the highest percentage increment of cell dry weight (mg) which is 56% through the fermentation process.

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, the disposal of plastic waste is a serious environmental issue that still meets the dead end. Most of the solid waste is contributed by petroleum-based plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC). Apart from that, 40% of the plastic that used in the packaging application is from polyethylene (Sung, 2010). Table 1.1 illustrates generation of solid waste in East Malaysia.

Table 1.1: Generation of solid waste in East Malaysia (Pusat Perbadanan dan Pengurusan Sisa Pepejal Awam, 2014)

Year	Amount (Tonnes per day)
2005	17 000
2012	22 000
2013	30 000-33 000

Average generation of solid waste for one person is about 1.25 kg/capita a day (Pusat Perbadanan dan Pengurusan Sisa Pepejal Awam, 2014). Figure 1.1 demonstrates the components of solid waste. Plastic contributes about 25% from the components of solid waste. This indicates the high amount of plastic waste disposal based on the statistic generation of solid waste in East Malaysia.

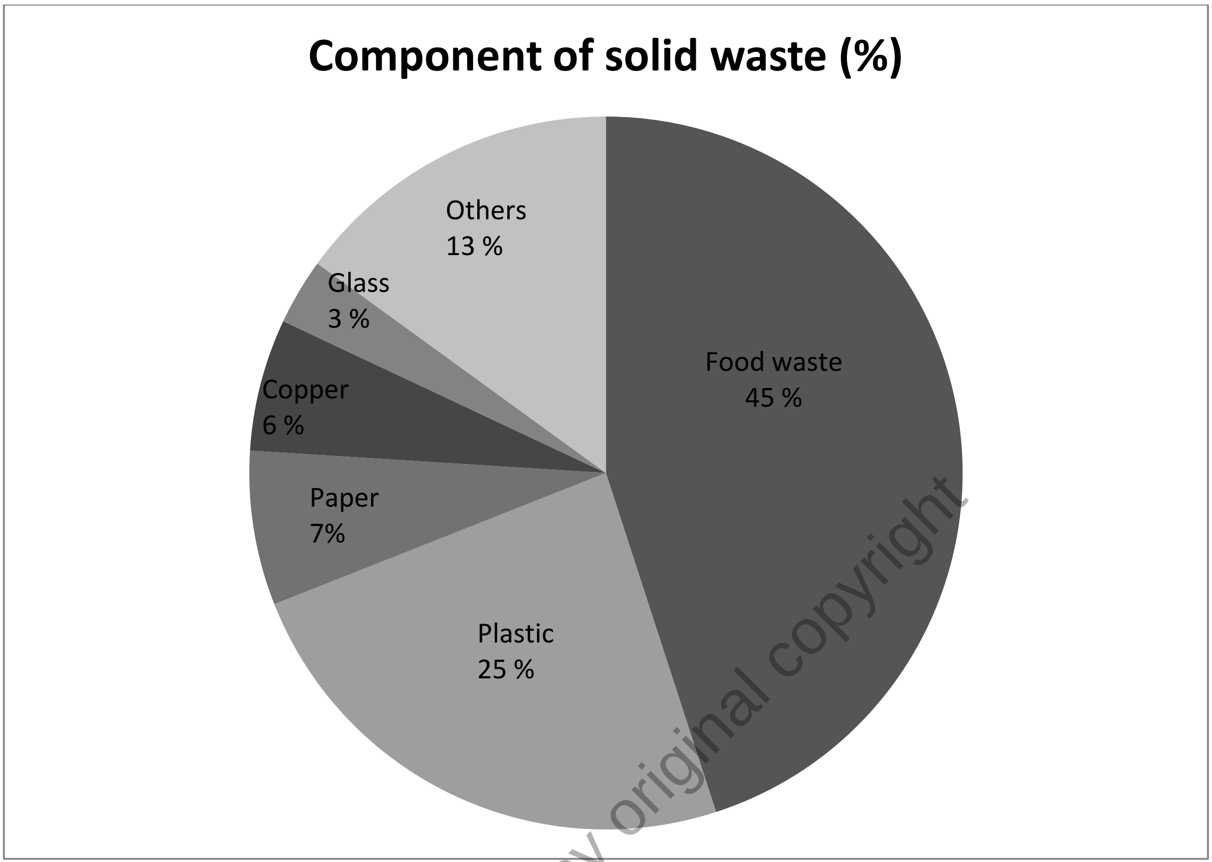

Figure 1.1: Component of solid waste (%) (Pusat Perbadanan dan Pengurusan Sisa Pepejal Awam, 2014)

Polyethylene is not biodegradable and last for many years upon disposal. In the present studies of biodegradability of PE, the researchers have jump into conclusion that the number of bacteria that can degrade PE is based on its molecular weight (Luckacahan et al., 2006). They defined the high molecular weight PE cannot be biodegraded since it comprises of many branches that hardly to break down. PE takes hundreds years to completely degrade and highly resistant due to chemical and environmental degradation (Otake et al., 1995).

By introducing natural polymer into the non-degradable plastic, a low cost of degradable polymer can be produced (Sam et al., 2010). Nevertheless, most of the researches focused on the starch that rich in polysaccharide. Danjaji et al. (2002) blended sago-starch with the linear low density polyethylene (LDPE) and Sabetzadeh et al. (2015) used thermoplastic starch as a filler in linear low density polyethylene/ low density polyethylene. However, there are only few studies that incorporate the protein based natural polymer in the non-biodegradable polymer (Kaur et al., 2009). Soya protein-based polymer is another potential natural polymer instead of starch-based biodegradable natural polymer. Soya spent powder (SSP) is an abundant biomaterial because it is the by-product from soya oil production. Therefore, the cost of SSP is cheaper than soya protein isolate and soya protein concentrate (Tian et al., 2009). However, it needs intense transformation to disrupt its native structure and to become thermoplastic. A thermoplastic is described as a polymer that softens or melts on heating, and returns to a solid state on cooling.

Today, most of the researchers are focusing on thermoplastic starch (TPS). Nevertheless, there is lack of research are carried on thermoplastic based protein. Plasticizers are inert organic compound, used as polymer additives which have low molecular weight, high boiling points and low pressures. The incorporation of plasticizers is to improve the mechanical properties such as flexibility and tensile strength (Rahman & Brazel, 2004). A good plasticizer means that it has a good compatibility with polymer, which depends on polarity, solubility, structural configuration and molecular weight of plasticizer. Plasticizing agents that were commonly used included water and glycerol (Famá et al., 2006; Alves et al., 2007), polyethylene glycol (Parra et al., 2004) and other polyols, such as sorbitol, mannitol and sugars (Talja et al., 2008; Kechichian et al., 2010). Some researchers found that glycerol is the best plasticizer for water soluble polymers due to the presence of hydroxyl group in the glycerol (Bertuzzi et al., 2007; Müller et al., 2008). This hydroxyl group provides the hydrogen bonds in polymeric chains which increase the tensile strength and present more flexible structure to the blends. According to Wang et al. (2004), they observed that the tensile properties of the LDPE/rich starch blends slightly increased after the incorporation of glycerol to the starch.

Pro-oxidant is a substance that accelerates the oxidation process of another substance. In this context, spear grass powder (*Imperata cylindrica*) was incorporated into the LDPE/TSSP blends to enhance the biodegradability of the polymer. Spear grass powder contains some metal compounds i.e cuprum, zinc, mangan and ferum (Okonmah & Agbogidi, 2013). The usage of spear grass powder can be considered as green, low-cost and non-toxic pro-oxidant. The previous study by Sharma et al. (2001) found that the incorporation of manganese stearate as the key pro-degradent has increased the rate of degradation tremendously. Therefore, it was proven that the pro-oxidant can accelerates the degradation process by inducing the oxidative reaction in the polymer chains.

In this study, LDPE were blended with SSP and TSSP in various blends ratios. The properties of these two blends after subjected to natural weathering and soil burial for 9 months were compared to determine their biodegradability. Spear grass powder was added to the blends in order to fasten the degradation rate of the materials. This study also included isolation and identification of microorganism that contribute in the degradation of the blends from soil burial test. The purpose of the identification is to find out the key microorganism which involved in the biodegradation of the LDPE/TSSP blends. In addition, this research is strengthening by the biodegradability study through the liquid state fermentation. From this method, the biodegradability of the blends is evaluated from biomass profile of the selected microorganisms.