PREPARATION, CHARACTERIZATION AND DEGRADATION OF LINEAR LOW DENSITY POLYETHYLENE / RAMBUTAN PEEL FLOUR BIOCOMPOSITES

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by

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LIST OF ABBREVIATIONS

AA	Adipic acid
AAc-g-PLDPE	Acrylic acid grafted LDPE after plasma treatment
CaSt	Calcium stearate
CA	Citric acid
Co	Cobalt
CO_2	Carbon dioxide
CS	Cobalt stearate
DSC	Differential scanning calorimetry
E_b	Elongation at break
Fe	Iron
FTIR	Fourier transform infrared
GLU	Glutaraldehyde (GLU)
H_2O	Water
HDPE	High density polyethylene
HF	Hemp fiber
HMTA	Hexamethylenetetramine
MA-g-PLDPE	Maleic anhydride grafted LDPE after plasma treatment
Mn	Manganese
MSW	Municipal solid waste
NaOH	Sodium hydroxide
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene

PCL	Polycaprolactone
PE	Polyethylene
PE-g-MA	Polyethylene-grafted-maleic anhydride
PET	Polyethylene terephthalate
PGA	Poly (glycolic acid)
PLA	Poly (lactic acid)
PMMA	Polymethylmethacrylate
PP	Polypropylene
PS	Polystyrene
PSW	Plastic solid waste
PVC	Polyvinyl chloride
PVOH	Poly (vinyl alcohol)
RPF	Rambutan peel flour
RWF	Rambutan skin waste flour
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TPS	Thermoplastic strach
TPSS	Thermoplastic sago starch
UTM	Universal Testing Machine
UV	Ultra violet

LIST OF SYMBOLS

%	percentage
wt %	weight percentage
Mt	metric ton
g	gram
kg	kilogram
mg	milligram
°C	degree celcius
°C/min	degree celcius per minute
nm	nanometer
µm	micrometre
MPa	mega pascal
GPa	giga pascal
h	hour
L	litre
ml	milimetre
g/cm^3	gram per cubic centimeter
Da	Dalton
kV	kilo volt
$\Delta H *_f$	heat fusion for 100% crystalline polyethylene
$\Delta H°_f$	heat of fusion for semi crystalline polyethylene
cm^{-1}	reciprocal wavelength
cm^3	cubic centimeter
mm^3	cubic milimetre
mm/min	milimetre per minute

Perincian dan Sifat – sifat Terhadap Keupayaan Degradasi oleh Campuran Linear Polietilena Berketumpatan Rendah / Tepung Kulit Rambutan Biokomposit

ABSTRAK

Pada masa kini, perkembangan plastik dari polimer terbiodegradasi dan pengisi semulajdi telah menarik minat besar dalam bidang sains dan penyelidikan. Polimer terbiodegradasi boleh membenarkan degradasi lengkap di dalam tanah dan tidak mengeluarkan mana-mana komponen toksik atau berbahaya. Oleh itu, dalam kajian ini, percubaan telah dibuat dengan menggabungkan tepung kulit rambutan (RPF) ke dalam matriks linear polietilena berketumpatan rendah (LLDPE). Kajian ini menyiasat pengaruh asid adipik sebagai pengserasi pada sifat-sifat komposit menggabungkan linear polietilena ketumpatan rendah dengan kandungan tepung kulit rambutan variasikan dari 5-25% kandungan. Kobalt stearat sebagai pro-oksidan dengan berat 0.2% telah ditambah ke dalam komposit LLDPE/RPF-AA. Pendedahan polimer kepada persekitaran semulajadi dan ditanam ke dalam tanah dijalankan untuk tempoh 9 bulan untuk mengenal pasti tahap potensi polimer terdegradasi dalam persekitaran yang berbeza. Hasilnya, komposit LLDPE/RPF-AA menunjukkan kekuatan tegangan dan pemanjangan pada takat putus yang lebih tinggi berbanding komposit LLDPE/RPF selepas pendedahan kepada persekitaran dan ditanam di dalam tanah. Walaubagaimanapun, selepas penambahan kobalt stearat, kekuatan tegangan dan pemanjangan takat putus komposit LLDPE/RPF-AA menjadi berkurangan. Pengimbas elektron mikroskopi menunjukkan mikrograf pembentukan retak, liang dan koloni kulat pada permukaan komposit LLDPE/RPF dan komposit LLDPE/RPF-AA. Untuk analisis pengimbas pembezaan kalorimeter, komposit LLDPE/RPF-AA menghasilkan penghabluran yang lebih tinggi berbanding dengan komposit LLDPE/RPF. Kestabilan haba bagi setiap komposit menurun daripada 429 °C bagi LLDPE dengan pertambahan sebanyak 25% kandungan tepung kulit rambutan (251 °C) dan tepung kulit rambutan bersama asid adipik (262 °C).

Characterization and Properties on Degradability of Linear Low Density Polyethylene/Rambutan Peel Flour Biocomposites

ABSTRACT

Nowadays, developments of plastics from biodegradable polymers and natural filler have attracted great interests in science and research. Biodegradable polymer could allow complete degradation in soil and does not emit any toxic or noxious components. Therefore, in this research, an attempt was made by incorporating rambutan peel flour (RPF) into LLDPE matrix. This study investigated the influence of adipic acid as compatibilizer on the properties of the composites prepared from LLDPE with different RPF loading varied from 5 to 25 wt%. Cobalt stearate (CS) as a pro-oxidant (0.2 wt%) has been added into LLDPE/RPF-AA composites. Natural weathering 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, LLDPE/RPF-AA composites showed higher tensile strength and elongation at break (E_b) compared to LLDPE/RPF composites after weathering and composting exposure. However, after the addition of CS, the tensile strength and E_b of LLDPE/RPF-AA composites decreased. Scanning electron microscopy (SEM) micrographs showed the formation of cracks, pores and fungus colonization on the LLDPE/RPF composites and LLDPE/RPF-AA composites surface. For differential scanning calorimetry (DSC) analysis, LLDPE/RPF-AA composites presented higher crystallinity compared to the LLDPE/RPF composites. The thermal stability for the composites decreased from 429 °C (LLDPE) to 251 °C for 25 wt% of RPF and 262 °C for 25 wt% of RPF-AA.

CHAPTER 1

INTRODUCTION

1.1 Overview

Nowadays, the disposal of plastic waste has been continuously on the increase and its has been a big problem up to today in Malaysia. Most of the solid waste is contributed by petroleum-based plastics such as polyethyele (PE), polypropylene (PP), polyethylene terephtalate (PET), polivinyl chloride (PVC) and polystyrene (PS). The application of the plastics typically used for packaging purposes but also in non-plastics applications such as textile fibres and coatings (Dewil et al., 2006). Apart from that, 40% of the plastic that used in packaging application is from PE. Table 1.1 illustrates the total waste generated in peninsular Malaysia.

Table 1.1: Generation of total solid waste in Peninsular Malaysia (Johari et al., 2014)

Year	Total amount (Tonnes per day)
2010	23 000
2012	25 000
2020	30 000

The average amount of solid waste generated in Malaysia is 0.5-0.8 kg/person/day (Kathirvale et al., 2003). Figure 1.1 shows the components of solid waste composition in

Peninsular Malaysia. Plastics contributes about 11% from the component of solid waste and indicates the high amount waste disposal based on statistic generation of total solid waste in Peninsular Malaysia.

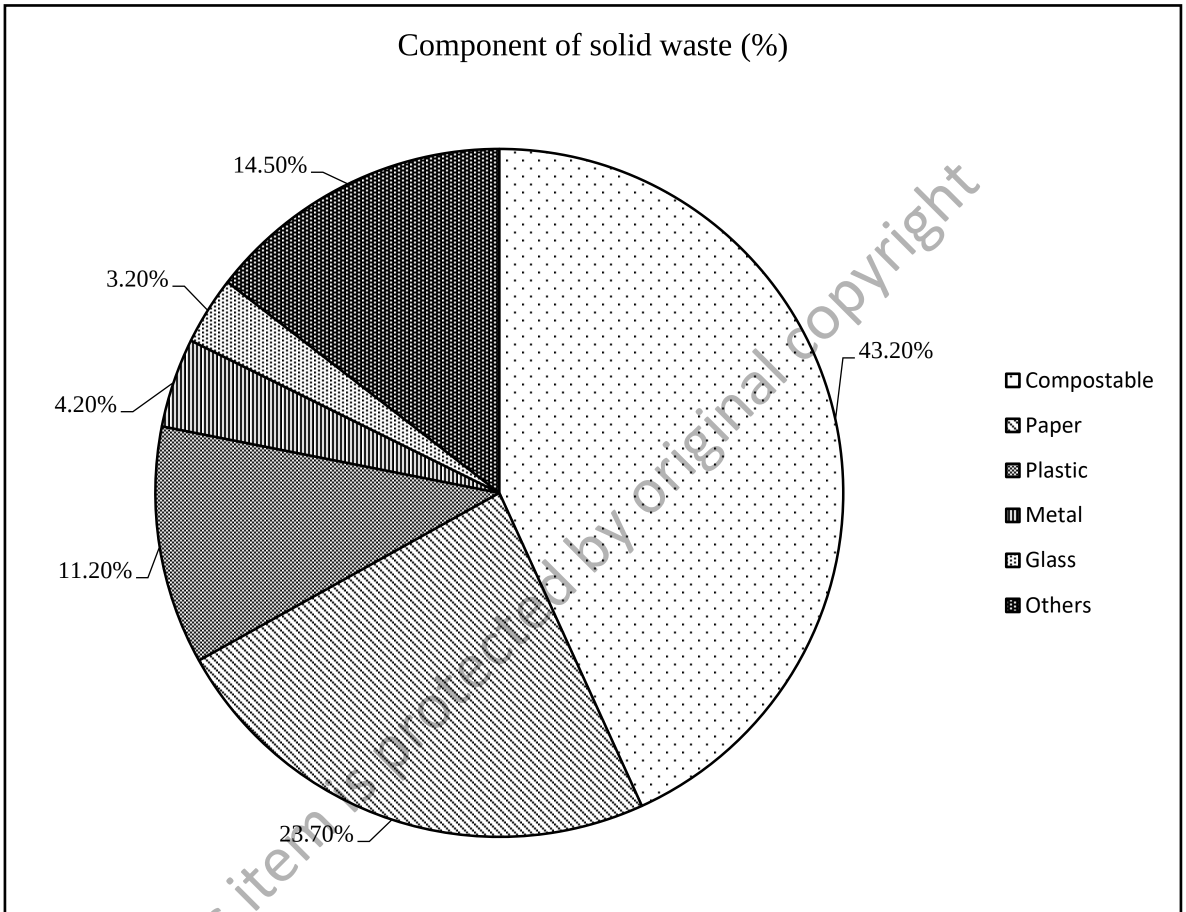

Figure 1.1: Component of solid waste (%) (Pusat Perbadanan dan Pengurusan Sisa Pepejal awam, 2014).

PE is non-degradable polymer and takes hundred years to completely degrade and highly resistant due to its chemical and environmental degradation (Otake et al., 1995). This is due to the properties of PE that has high molecular weight and cannot be degraded since it commprises of many branches that hardly to break down (Kathirvale et al., 2003). One of the alternative accelerates the biodegradation of PE is the incorporation of natural filler into the polymer matrices.

Natural fibres that have been applied in non-degradable matrices are (i) leaf: sisal, pineapple leaf fibre (PALF), and henequen; (ii) bast: flax, ramie, kenaf/mesta, hemp and jute; (iii) seed: cotton; (iv) fruit: coconut husk, i.e., coir (Mohantya et al., 2000). Moreover, natural fibres are lignocellulosic in nature. Lignocellulosic materials are the most abundant renewable biomaterial of photosynthesis on earth. The lignocellulosic materials are widely distributed in the biosphere in the form of trees (wood), plants and crops. In lignocellulosic systems, the amount of cellulose, can vary depending on the species and age of the plant/species. Therefore, all of the natural fibres are hydrophilic in nature; their moisture content reaches 8 to 12.6% (Bledzki et al., 1996). Rambutan peel waste is one type of natural filler and readily abundant but does not have any market value. Therefore, the utilization of rambutan peel waste as natural filler in the polyolefins will provide a new application route to produce a low cost and degradable polymer. Rambutan peel waste as a lignocellulosic natural filler are degraded biologically. Biodegradation by the high molecular weight cellulose weakens the lignocellulosic cell wall and usually photochemical degradation by ultraviolet light occurs when lignocellulosics are exposed to outside exposure (Mohantya et al., 2000). Moreover, the utilization of rambutan peel waste can bring economic benefit and reduced the environmental problem impact. In recent years, the use of natural filler in polyolefins has gained great interest among researchers and industries due to some advantage of natural filler compared to mineral filler (e.g., kaolin, mica, talc, and calcium carbonate) such as low density, biodegradable, ecofriendly and renewable (Chun et al., 2013b; Salmah et al., 2013).

In general, the poor adhesion between the natural filler and the hydrophobic polyolefins is the main drawback to produce biocomposites. However, compatibilizer can be used to modify the hydrophilic natural filler, which can improve filler dispersion, wettability and filler-matrix adhesion. Previously, it was found that the used of used citric acid as a compatibilizer (Ning et al., 2007), glutaaldehyde as a crosslinking agent (Chan et al., 2013) and acryclic acid as chemical modification (Yeng et al., 2013) enhanced the properties of biocomposites. In current study, adipic acid (AA) was used as a compatibilizer. This compatibilizer was first used to compatibilize the polyolefin and rambutan peel. There is a lack of study in the utilization of adipic acid as a compatibilizer in polyolefin.

Apart from incorporating natural filler into non-degradable polymer, another approach to induce biodegradation of polyethylene is adding pro-oxidant into the polyolefin. Pro-oxidants are normally used for initiation of degradation including transition of complexes metal ions that can accelerate the oxidative process, consequently reducing the molecular weight of the polymer on the level that biodegradation takes place. It will act as initiator for the oxidation of the polyolefin. According to Reddy et al. (2009), the smaller segment of polymer chain can become nutrient for microorganism. Moreover, cobalt stearate (CS) has contributed the highest degradability to LDPE compared to the other cobalt carboxylates namely palmite and laurate (Roy et al., 2007). Therefore, cobalt stearate has been applied as pro-oxidant in the present study.

1.2 Problem Statement

In recent years, the disposal of plastics especially those used in packaging, shows a serious challenge to waste management. Many efforts have been done on recycling the polyethylene including mechanical recycling, feedstock recycling and energy recovery. In order to reduce the waste problem of plastic, a replacement is needed. It is well known that polyethylene is highly resistant to biodegradation. One way by which the biodegradation of polyethylene can be accelerated is by the incorporation of a biodegradable filler such as fruit peel waste into the polymer matrix.

The incorporation of polyolefin with rambutan peel waste is necessary to produce a degradable plastic materials and hence resolve the waste problem from non-degradable plastic. However, one of the challenges is the compatibilization of rambutan peel waste and PE. Rambutan peel is hydrophilic material due to the presence of hydroxyl functional group. In contrast, PE is hydrophobic due to its hydrocarbon structure. In order to improve the properties of the biocomposites, compatibilizer is needed to compatibilize both materials.

The degradability of the polyolefin/biocomposites was always an issue among the researches. They claim that polyolefin that can be degraded during the degradation but the non-degradable component is still remain.Therefore, in order to overcome this issue, the potential of cobalt stearate as pro-oxidant in the biocomposites was investigated in the study.

1.3 Objectives of Study

1. To evaluate the effect of rambutan peels flour (RPF) loading on LLDPE/RPF composites properties.
2. To study the effect of adipic acid as compatibilizer on the properties and degradability of LLDPE/RPF composites.
3. To investigate the effect of cobalt stearate as a pro-oxidant on the degradability of LLDPE/RPF-AA composites by natural weathering and soil burial.

1.4 Scope of Study

This study focused on the development of degradable polymers by incorporating RPF into the LLDPE. The addition of adipic acid into RPF filler helps in dispersing RPF homogeneously within the LLDPE matrix. The composites are subjected to tensile, morphological and thermal properties testing. Then, the effect of natural weathering and soil burial test to the composites are investagated to determine their degradability. Other than that, the addition of cobalt stearate is aimed to accelerate the degradation process by accelarating the oxidation of LLDPE.

1.5 Thesis Organization

This thesis contains five chapters with chapter one introduces briefly the scope of the thesis including the introduction about the research background, problem statement and