DEVELOPMENT AND CHARACTERIZATION OF BIODEGRADABLE BLENDS OF LOW DENSITY POLYETHYLENE (LDPE) INCORPERATED WITH THERMOPLASTIC SAGO STARCH

SHAHARUDDIN BIN KORMIN

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Master of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JULY 2012

ABSTRACT

Starch-based polymeric materials offer a renewable, economical alternative to existing petroleum based, non-renewable or costly polymeric materials. The aim of this study is to develop degradable starch-low density polyethylene (LDPE) composites with enhanced mechanical properties. This research studies the effect of different filler loading, effect of compatibilizer and different kind of plasticizer. The compounding of the LDPE with sago starch was performed via a twin screw extruder followed by injection molding. Studies on their physical, mechanical properties and thermal properties of each formulation were carried out by density, melt flow index (MFI), tensile, flexural, impact, Thermogrimetry analyzer (TGA-DTA) and differential scanning calorimetry (DSC). The presence of high starch contents had an adverse effect on the mechanical properties of LDPE/starch blends. However, the addition of compatibilizer or plasticizer improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the blends. Meanwhile, study of degradation of LDPE/SS blend was carried by hydrolysis, fungi exposure, natural weathering and soil burial exposure analysis. The biodegradability of sago starch–filled LDPE blend composites was studied by monitoring its weight loss. Incorporating sago starch with LDPE improved the weight loss. Tensile tests, TGA and SEM imaging were also carried out on the samples before and after degradation. Imaging showed that the increase in starch content from 5% to 20% in the formulations additive increases the biodegradability of the samples. The scanning electron micrographs (SEM) support the findings of biodegradation properties of LDPE/SS blend, compatibilized LDPE/SS and plasticized LDPE/SS blend. In order to increase the compatibility between LDPE and starch, maleic anhydride was used to graft onto the LDPE molecules (compatibilized LDPE/SS). After using the proper composition and processing condition, mechanical properties of compatibilized LDPE/SS blend are significantly higher than those of the LDPE/SS blend with the same starch contents. The second part of the study investigated the effects of different types of plasticizer (sucrose, urea, glycerol and sorbitol) and its content on the structure and properties of the LDPE/SS blend. Plasticized LDPE/SS have higher mechanical properties than unplasticized LDPE/SS blend.

ABSTRACT

Starch-based polymeric materials offer a renewable, economical alternative to existing petroleum based, non-renewable or costly polymeric materials. The aim of this study is to develop degradable starch-low density polyethylene (LDPE) blend with enhanced mechanical properties. This research studies the effect of different filler loading, effect of compatibilizer and different kind of plasticizer. The compounding of the LDPE with sago starch was prepared via a twin screw extruder followed by injection molding. Studies on their physical, mechanical properties and thermal properties of each formulation were carried out by density, melt flow index (MFI), tensile, flexural, impact, thermogravimetry analyzer (TGA-DTA) and differential scanning calorimetry (DSC). The presence of high starch contents had an adverse effect on the mechanical properties of LDPE/starch blends. However, the addition of compatibilizer or plasticizer improved the interfacial adhesion between the two materials, hence, improved the tensile properties of the blends. Meanwhile, study of degradation of sago starch filled-LDPE (LDPE/SS) blend was carried by hydrolysis, fungi exposure, natural weathering and soil burial exposure analysis. The biodegradability of sago starch–filled LDPE blend was studied by monitoring its weight loss. Incorporating sago starch with LDPE improved the weight loss. Tensile tests, TGA and SEM imaging were also carried out on the samples before and after degradation. Imaging showed that the increase in starch content from 5% to 20% in the formulations increases the biodegradability of the samples. The scanning electron micrographs (SEM) support the findings of biodegradation properties of LDPE/SS blend, compatibilized LDPE/SS and plasticized LDPE/SS blend. In order to increase the compatibility between LDPE and starch, malaeic anhydride was used to graft onto the LDPE molecules (compatibilized LDPE/SS). After using the proper composition and processing condition, mechanical properties of compatibilized LDPE/SS blend were found significantly higher than those of the LDPE/SS blend with the same starch contents. The second part of the study investigated the effects of different types of plasticizer (sucrose, urea, glycerol and sorbitol) and its content on the structure and properties of the LDPE/SS blend. Mechanical properties of plasticized LDPE/SS were found higher than unplasticized LDPE/SS blend.

ABSTRAK

Bahan polimer berasaskan kanji menawarkan alternatif yang boleh diperbaharui, menjimatkan petroleum yang sedia ada berasaskan bahan polimer yang tidak boleh diperbaharui atau mahal. Tujuan kajian ini adalah untuk membangunkan degradasi adunan kanji polietilena ketumpatan rendah (LDPE) dengan sifat-sifat mekanikal yang dipertingkatkan. Kajian ini mengkaji kesan pengisian yang berbeza, kesan bahan tambah kompatibilizer dan jenis plastiksizer yang berbeza. Pengadunan LDPE dengan kanji sagu telah disediakan melalui mesin pemutar skru berkembar dan diikuti oleh acuan suntikan untuk menghasilkan spesimen. Kajian ke atas fizikal mereka, sifat mekanik dan sifat haba setiap formulasi telah dijalankan dengan mengkaji ketumpatan, indeks aliran lebur (MFI), tegangan, lenturan, kekuatan hentakan, penganalisis thermogravimetri (TGA) dan pembezaan imbasan kalorimetri (DSC). Kehadiran kandungan kanji yang tinggi mempunyai kesan yang buruk kepada sifat-sifat mekanikal adunan kanji/LDPE. Walau bagaimanapun, penambahan kompatibilizer atau beberapa jenis plastiksizer meningkatkan lekatan antara kedua-dua bahan, secara tidak langsung, meningkatkan sifat-sifat tegangan adunan. Sementara itu, kajian degradasi adunan kanji sagu diisi-LDPE (LDPE/SS) telah diuji dengan ujian hidrolisis, pendedahan pada kulat, pendedahan pada cuaca semula jadi dan penanaman sampel di dalam tanah. Penguraian kanji sagu-diisi LDPE adunan komposit telah dikaji dengan memantau penurunan berat sampel. Adunan kanji sagu dengan LDPE bertambah baik dengan kehilangan berat sampel. Ujian tegangan, analisis TGA dan pengimejan imbasan mikroskop (SEM) juga telah dijalankan ke atas sampel sebelum dan selepas degradasi. Pengimejan menunjukkan peningkatan dalam kandungan kanji daripada 5% kepada 20% dalam formulasi meningkatkan penguraian sampel. Imbasan elektron mikroskop (SEM) menyokong penguraian adunan LDPE/SS, LDPE/SS dengan kompatibilizer dan adunan LDPE/SS dengan pemplastik. Bagi meningkatkan keserasian antara LDPE dan kanji, maleik anhidrida digunakan ke atas molekul LDPE (LDPE/SS dengan kompatibilizer). Selepas menggunakan komposisi dan keadaan pemprosesan yang sesuai, sifat mekanik adunan LDPE/SS didapati jauh lebih tinggi daripada adunan LDPE/SS dengan kandungan kanji yang sama. Bahagian kedua kajian menyiasat kesan jenis plastiksizer (sukrosa, urea, gliserol dan sorbitol) dan kandungan pada struktur dan sifat-sifat adunan LDPE/SS. Sifat mekanikal adunan LDPE/SS dengan pemplastik didapati lebih tinggi daripada adunan LDPE/SS tanpa bahan tambah plastiksizer.

TABLES OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

E_t	Tensile modulus of composite, MPa
E_f	Flexural modulus of composite, MPa
σ_t	Tensile strength of composites, MPa
σ_f	Flexural strength of composite, MPa
σ_i	Impact strength, J/m
ε_p	Elongation at break, %
W_f	Weight percentage, %
W_w	Weight of sample before immersed in water, g
W_c	Weight of sample after immersed in water, g
F_{max}	The maximum peak load, N
A	cross section area, m^2
L_o	Original measured length, m
L	Length of the specimen at its breaking point, m
B	The mean width of the specimen, m
D	The mean thickness of the specimen, m
ΔW	Increment in load, N
ΔS	Increment in deflection
E	Energy in kgf.cm
T	Thickness, mm
X_{com}	Crystallinity of composites, %
X_{LDPE}	Crystallinity of LDPE, %
T_g	Glass transition temperature, ºC
T_m	Melting temperature, ºC
T_d	Decomposition temperature, ºC

LIST OF ABBREVIATIONS

PE	Polyethylene
PP	Polypropylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
LLDPE	Linear low density polyethylene
SS	Sago starch
PS	Potato starch
TS	Tapioca starch
WS	Wheat starch
CS	Corn starch
NaOH	Sodium hydroxide
MA	Malaeic anhydride
MAPE	Maleated anhyride grafted polyethylene
UTPS	Urea thermoplastic starch
STPS	Sorbitol thermoplastic starch
GTPS	Glycerol thermoplastic starch
TPS	Thermoplastics
MFI	Melt flow index
MFR	Melt flow rate
FTIR	Fourier Tranform Infrared Spectroscopy
SEM	Scanning electron Microscope
WLP	Weight loss percentage
DSC	Differential scanning calorimetry

DTA	Differential thermal analysis
DTG	Differential thermogravimetr
TGA	Thermogravimetric Analyzer
XRD	X-ray diffraction
ASTM	American Society for Testing and Materials
CRAUN	Crop Research and Application Unit
LCDA	Land, Custody and Development Authority

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background

A few decades ago, synthetic polymer was used in every field of all human activities. These artificial macromolecular substances are usually developed from petroleum. Synthetic polymers have become technologically significant since the 1940s, and packaging is one industry that has been transformed by oil-based polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and poly(vinyl chloride) (PVC). Each year nearly 78 million tonnes of petrochemicals used to make plastics and polyethylene represents 64% of the produced synthetic plastics. Almost half of that is thrown away within a short time, remaining in waste deposits and landfills for decades (more than 30 years) (Volke-Sepulveda et al., 1999). In recent years, there has been growing concern about the disposal of single-use plastics. There are many biodegradable resins now present on the market. However, most of them are very expensive to compete with the petroleum-based products. Plastics are everywhere in contemporary society. They are found in households and are extensively employed in such many industries.

The most common and significant use of synthetic organic polymers was stimulated by their thermal, mechanical, electrical and optical properties. They occupied and dominate the large and important industries which produce plastics, coatings, textiles, packaging materials, electronic devices, rubbers, adhesives and medical appliances. The justifications behind multiuse of plastics have potential to be manufactured to meet very specific functional needs for users.

Polyethylene is available in many varieties (linear low density, high density, high molecular weight). Low density polyethylene that is used extensively in the rigid packaging industry because of several favorable physical properties. Polyethylene represents 64% of the produced synthetic plastics. Polyethylene is so widely used because of their wide range of physical properties, suitability to most of the commercial thermoplastics fabrication process. In addition, it offer such desirable features as broad range of properties, very good moisture barrier properties, and good chemical resistance and food grades available. The most important properties found in PE resin is because of the cheaper price that can give them a competitive advantage compared to other materials (both polymeric and non polymeric) (Thakore et al., 1999).

1.2 Biodegradable plastic

The petroleum resources are limited, and the use of non-biodegradable polymers cause major environmental problems. In addition, the resistance to natural biodegradation has been becoming more and more problematic, especially where they are used only a short period of time (Vert et al., 2002). Even though there has been a lot of latest technology and approach in recycling and decreasing plastics waste, the amount of these materials is yet growing every year. Recycle of products also has obstacle such as high cost of operation, besides, the technologies of recycling are still under development.

Numerous packaging materials do not provide themselves to recycle because of contamination, and the cleaning indispensable prior to recycling can be very costly. One effective method to address this global inconvenience is the creation of biodegradable plastics, which presently exist in the market. Biodegradable plastics, as new materials, make demands to be environmentally friendly. Biodegradable plastics are plastics that can withstand a degradation process known as biodegradation. Biodegradable plastics refer to degradable polymers that are consumed by microorganisms via polymer chain disintegration and future utilization (Garth and Kowal, 2001). It is also defined as plastics with similar properties to conventional plastics, but it can be decayed after disposal to the environment by the activity of microorganisms to produce end products of CO_2 and H_2O (Tharanathan, 2003).

Naturally occurring biodegradable plastic/biopolymers are derived from four broad feedstock areas (Tharanathan 2003). Animal sources provide collagen and gelatine, while marine sources provide chitin which is processed into chitosan. However, the remaining two feedstock areas are the ones receiving the most attention from scientists, and are the sources thought to be the most promising for future development and expansion. Microbial biopolymer feedstocks are able to produce polylactic acid (PLA) and polyhydroxy alkanoates (PHA). The final category of agricultural feedstocks is the biopolymer source. Starch is an agricultural feedstock hydrocolloid biopolymer found in a variety of plants including (but not limited to) sago, wheat, tapioca, cassava, yam, corn, rice, beans, and potatoes (Salmoral et al., 2000, Martin et al., 2001).

Starch has been used successfully as a polymer in the production of a loose-fill packaging. It has good mechanical properties, readily biodegrades in soil, and sells at competitive prices. Starch is a naturally occurring biodegradable polymer which is cheap, contain hydrosable groups, readily hydrosable, abundant, renewable, and it has been mixed into the thermoplastics/synthetic polymer to increase the biodegradability (as starch is biodegradable and ready be consumed by micoorganism) and reduce the cost of the material (Shah et al., 1994). Examples of synthetic biodegradable polymers are polycaprolactone, poly(lactic acid) and poly(vinyl alcohol). In the degradation of polymers, there are a lot of factors need to be considered. Sunlight, heat, oxygen, humidity, microorganisms are some of the agents that work synergistically towards the degradation of polymers. Native starch will swell when absorbed water with their free hydroxyl groups. As a result, it will become very brittle and it supports the growth of mold. Due to these reasons, native starch alone is not suitable to be used as a packaging material. The introduction of granular starch into plastics via melt-mixing has become the simplest and cheapest way for preparing starch-plastics composites (Danjaji et al., 2002).

Chemical and physical properties of starch have been widely investigated due to its suitability to be converted into a thermoplastic and then to be used in different application as a result of its known biodegradability, availability and economical feasibility (Danjaji et al., 2002). In this works, blending of low density polyethylene (LDPE) with a cheap natural biopolymer such as starch will enhance the biodegradability of this material. Incorporation of starch will accelerate the attack of microorganisms to LDPE. Unfortunately, native starch has poor mechanical properties and is predominantly water soluble and cannot be processed by melt-based routes without being degraded. The most significant problem with the starch-based loose-fill packaging material is that it collapses when it is in contact with water or in an atmosphere with high relative humidity. In order to compete with non-degradable plastics,