SYNTHESIS AND CHARACTERIZATION OF POLY (LACTIC ACID) PLASTICIZED PALM OIL PHOSPHATE ESTER

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ABSTRACT

This study focusing on the synthesis of epoxidized palm oil (EPO) containing flame retardant group, palm oil phosphate ester (POPE) into poly (lactic acid) (PLA) by using melt blending technique. POPE was synthesized by reacting EPO and diethyl phosphate as flame retardant catalyzed by triphenyl phosphine. The effect on variation of catalyst concentration, time and temperature on the yield of synthesized POPE were studied. Triphenyl phosphine acted as a catalyst was varied at the amount of 0.1, 0.2, 0.3 and 0.4 g while temperature ranging from 70, 80, 90 and 100 °C and 1 to 5 h for time variation. Then, PLA was mixed at various amount of POPE. The optimum formulation on POPE was determined by varying the content of POPE from 1 to 5 wt% into the PLA to produce good mechanical and flame retardant properties. Characterizations of POPE and PLA/POPE blends were conducted by using Fourier transform infrared spectroscopy. The samples of PLA/POPE were studied by using tensile test, flexural test and impact test to determine their mechanical properties. While thermogravimetric analysis and differential scanning calorimetry were performed to analyze thermal characteristics of the blends. Limiting oxygen index (LOI) test was conducted to determine the flammability properties of PLA/POPE blends. Finally, the surface of PLA/POPE samples before and after LOI test were investigated by using scanning electron microscopy for morphological study. The optimal reaction for POPE was achieved at 0.2 g catalyst, 80 °C temperature for the reaction time of 4 h. In general, the addition of POPE into PLA reduced the mechanical properties such as stiffness and tensile strength. On the other hand, it increased an elongation at break. Moreover it was observed that the thermal stability of PLA/POPE blend increased by incorporating POPE. Besides that, the incorporation of POPE into PLA improved the flammability properties of the PLA/POPE blend with LOI value of 30. The morphological studies revealed that the maximum amount of POPE which could be well dispersed was at 1 wt% of POPE. Based on the results obtained, the optimum loading in terms of mechanical and flammability properties for POPE incorporating with PLA was at 1 wt%.

ABSTRAK

Kajian ini memberi tumpuan kepada sintesis minyak kelapa sawit terepoksi (EPO) yang mengandungi kumpulan bahan perencat nyalaan, minyak kelapa sawit fosfat ester (POPE) dalam poli (laktik asid) (PLA) dengan menggunakan teknik adunan leburan. POPE telah disintesiskan dengan menindak balas EPO dan dietil fosfat sebagai bahan perencat nyalaan bermangkinkan trifenil fosfina. Kesan daripada variasi kepekatan pemangkin, masa dan suhu sintesis terhadap penghasilan POPE telah dikaji. Trifenil fosfina bertindak sebagai pemangkin dibezakan di antara 0.1, 0.2, 0.3, dan 0.4 g manakala suhu di antara 70, 80, 90, dan 100 ℃ dan 1 hingga 5 jam bagi variasi masa. Kemudian, PLA telah dicampurkan dengan jumlah POPE yang berbeza. Formulasi optimum POPE ditentukan dengan mengubah kandungan POPE dari 1 hingga 5% berat ke dalam PLA untuk menghasilkan sifat mekanikal dan bahan perencat nyalaan yang baik. Pencirian POPE dan adunan PLA/POPE dijalankan dengan menggunakan spektroskopi jelmaan inframerah Fourier. Sampel PLA/POPE telah dikaji menggunakan ujian regangan, lenturan dan kekuatan hentaman untuk menentukan sifat-sifat mekanikalnya. Manakala, analisis bagi ciri-ciri terma adunan PLA/POPE telah dilakukan menggunakan analisis termogravimetrik dan kalorimetri pengimbasan pembezaan. Sifat kemudahbakaran adunan PLA/POPE pula ditentukan dengan menggunakan ujian indeks oksigen penghad (LOI). Permukaan sampel PLA/POPE sebelum dan selepas ujian LOI dikaji menggunakan pengimbasan mikroskop elektron untuk kajian morfologi. Tindak balas optimum bagi POPE dicapai dengan mangkin sebanyak 0.2 g, suhu 80 ℃ pada masa tindak balas selama 4 jam. Secara umumnya, penambahan POPE ke dalam PLA mengurangkan sifat-sifat mekanikal seperti kekakuan dan kekuatan regangan. Walau bagaimanapun, ia meningkatkan pemanjangan pada takat putus. Tambahan pula, diperhatikan kestabilan terma adunan PLA/POPE meningkat dengan pertambahan POPE. Di samping itu, gabungan POPE ke dalam PLA meningkatkan sifat-sifat kebolehbakaran adunan PLA/POPE dengan nilai LOI sebanyak 30. Kajian morfologi menunjukkan nilai maksimum bagi POPE untuk disebarkan dengan baik adalah sebanyak 1% berat POPE. Berdasarkan keputusan dari ujikaji pencirian, kandungan muatan optimum berdasarkan sifat-sifat mekanikal dan sifat kebolehbakaran bagi gabungan POPE dengan PLA adalah sebanyak 1% berat.

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LIST OF ABBREVIATIONS

AMG	-	Acetylated monoglycerides
APP	-	Ammonium polyphosphate
ASTM	-	American society for testing and materials
CONE	-	Cone calorimeter
CPSO	-	Chlorinated phosphate soybean oil
DP	-	Direct polycondensation
DBP	-	Dibutyl phthalate
DBS	-	Dibutyl sebacate
DEP	-	Diethyl phthalate
DOP	-	Dioctyl phthalate
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermograms
DMA	-	Dynamic mechanical analysis
EPO	-	Epoxidized palm oil
ESO	-	Epoxidized soybean oil
EVO	-	Epoxidized vegetable oils
ESOPE	-	Epoxidized soybean oil polyol ester
FTIR	-	Fourier transform Infrared
FRPLA	-	Flame retardant PLA
LOI	-	Limiting oxygen index
N_2	-	Nitrogen gas
O_2	-	Oxygen
PE	-	Polyethylene
PP	-	Polypropylene
PCL	-	Polycapro lactone
PDS	-	Polydioxanone
PEG	-	Poly (ethylene glycol)
PGA	-	Poly (glycolic acid)
PLA	-	Poly (lactic acid)
POPE	-	Palm oil phosphate ester

PPG	-	Poly (propylene glycol)
PVC	-	Poly (vinyl chloride)
PHBV	-	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)
PLLA	-	Poly (L-lactic acid)
POPE	-	Palm oil phosphate ester
PVOH	-	Poly (vinyl alcohol)
SO	-	Soybean oil
SEM	-	Scanning electron microscopy
SOPE	-	Soybean oil polyol ester
TA	-	Glycerol triacetate
TGA	-	Thermogravimetric analysis
MPP	-	Melamine polyphosphate
ZnPi	-	Zinc bis-diethyl phosphinate
MCAPP	-	Microencapsulated ammonium polyphosphate
EPSO	-	Epoxidized palm and soybean oil
TAG	-	Triacylglycerol
PS	-	Polystyrene

LIST OF SYMBOLS

℃	-	Degree celcius
wt %	-	Weight percent
g	-	Gram
cm	-	Centimetre
s	-	Second
kV	-	Kilo volt
min	-	Minute
µm	-	Micrometer
h	-	Hour

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biodegradable polyesters have attracted much attention due to their biodegradability and biocompatibility which offer clear advantages for both customers and the environment. Poly (lactic acid) (PLA), poly (caprolactone) (PCL), poly (butylene succinate), modified poly (ethylene terephthalate) are examples of biodegradable polyester. PLA is the most promising candidate for polymer used as an alternative for petrochemical polymers because it is biodegradable and produced from renewable resources such as corn and starch (Sin et al., 2012).

PLA has been used in many applications such as in medical (Lasprilla et al., 2012), packaging (Arrieta et al., 2013), textile (Cheng et al., 2015) and automotive industries (Imre et al., 2013) which makes it a good candidate for use in disposable packaging due to its good processability. However, PLA has some restrictions on properties that are required for applications due to its high brittleness, low elongation at break and low toughness (Raquez et al., 2013). To overcome these problems, the common practice to improve the properties of PLA is by incorporating plasticizer. The action of plasticizer itself is to increase the free volume and to decrease the polymer chain interactions which induce higher chain mobility at lower temperatures resulted in decreasing in glass transition temperature (T_g) (Kulinski et al., 2005). Many researchers investigated to enhance the mechanical properties and flexibility of PLA by blending with plasticizers such as poly (ethylene glycol) (PEG), poly (propylene glycol) (PPG), citrate esters (Al-Mulla, 2011) and epoxidized soybean oil (ESO) (Ali et al., 2009).

In response to concerns about the environment, plasticizers from natural products are currently being employed in biodegradable polymers, as a replacement for the highly toxic petroleum-based phthalates (Fenollar et al., 2009). Epoxidized vegetable oils (EVO) are a favorable option as biodegradable plasticizer because of availability, low toxicity and cheap (Lathi et al., 2007).

EVO is one of the effective additives that has been used for industrial applications that require properties such as good flexibility, good solvency for fluid additives, good lubricity and low volatility. Many researchers have been using EVO such as palm oil, soybean oil, and castor oil mostly as a plasticizer, additives and stabilizer (Al-Mulla et al., 2010; Ali et al., 2009). Therefore, it is thought that the addition of EVO can improve the toughness and flexibility of the PLA. Chieng et al. (2014) revealed that by adding 5 wt% of EVO, the tensile property of PLA has improved due to the plasticizing effect of EVO that imparted better interfacial adhesion and miscibility. Ali et al. (2009) reported that ESO can be used as a plasticizer to decrease the T_g of PLA by using a melt blending technique. Due to the sustainability and availability of palm oil in Malaysia, epoxidized palm oil (EPO) that was developed from palm oil derivatives has been investigated by many researchers as a plasticizer in PLA.

Many researchers have reported improved flexibility and toughness of PLA by adding EPO. Al-Mulla et al. (2010) reported that PLA/EPO blends showed significant improvement of mechanical properties and high thermal stability. The highest elongation at break was about 210 % at the 80/20 ratio. The mechanical properties of PLA/ EPO are dependent on its morphology. The EPO has good compatibility with PLA due to good molecular interaction between PLA and EPO (Tee et al., 2014). Meanwhile, Silverajah et al. (2012) have found better improvement in tensile, impact and flexural properties of PLA by varying the amount of EPO at 5 wt%, 6 wt%, and 10 wt%, respectively. The effect of EPO on PLA–PCL–EPO blends was studied by Al-Mulla et al. (2014). The formation of hydrogen bonding between the hydroxyl terminal of PLA–PCL blend and the oxirane ring (C-O-C) of EPO was responsible for the increase of elongation at break from 260 % to 390 % at 10 wt% of EPO content. Apart from its biodegradability and processability like other polymers such as polyethylene (PE) and poly (vinyl chloride) (PVC), the application of PLA is restricted to the higher flammability. Therefore, to widen the range of applications flammability characteristics and fire retardance of PLA, more research and improvement are needed.

Flame retardant is normally added to expand the range of application of PLA. Flame retardant is the material that is less ignitable and has slow flame combustion. There are many types of flame retardants such as phosphorus-based, halogen-based, silicon-based, nanometric particles and mineral additives. Phosphorus-based flame retardant has been most widely used because of its organic behavior which can easily biodegrade (Gao et al., 2014). Concerned about environmental issue, phosphorus-based flame retardant release less of smoke and the toxic gases produced is fewer than the other type of flame retardant. The effect of the phosphorus-based flame retardant group towards the PLA was investigated by Song et al. (2011). PLA, PEG6000 and ammonium polyphosphate (APP) were mixed together by using melt blending technique with 5 wt%, 7 wt%, 10 wt% and 15 wt% of APP. The addition of APP as phosphorus-based flame retardant has successfully improved the retardancy of the system with increasing limiting oxygen index (LOI) value from 19 % for the untreated PLA to 31.5 % with phosphorus containing PLA. From all the findings, it is important to use both plasticizer and flame retardant in order to improve the mechanical and flammability properties of PLA. In this research, a novel bio-based plasticizer from palm oil incorporating with phosphorus-based flame retardant was synthesized. With this approach, the product obtained would be able to simultaneously solve the problem of flexibility and flammability of PLA.

1.2 Problem Statement

PLA is an environmental-friendly polymer that possesses excellent mechanical properties. However, PLA also has some limitations because of its brittleness, low flexibility, and low tensile elongation. Thus, attempts have been made to overcome these disadvantages of PLA through the incorporation of plasticizer. EPO is an effective plasticizer to improve the flexibility and stability of PLA (Al-Mulla et al., 2014) instead of using petroleum-based plasticizer, phthalates which are very high in toxicity.

The use of plasticizer in PLA system cannot be avoided in order to improve its poor extensionability properties and environment concern. However, the bio-based nature of PLA and EPO, contributes to high flammability. Previous studies showed that phosphorus-based flame retardant is an effective agent to enhance the flame retardancy of PLA. Thus, research has been conducted on combining plasticizer and flame retardant into PLA (Zhang et al., 2019). However, the addition of phosphorus-based flame retardant with plasticizer into PLA has reduced the elongation at break (Song et al., 2011). One way to improve the elongation at break is by synthesizing EPO with flame retardant first. In recent years, the preparation of EVO such as soybean oil with flame retardant has been reported in several researchers (Jia et al., 2015; Feng et al., 2015). Nevertheless, the use of EPO with flame retardant has not been published in any literature. Thus, the effect of synthesized EPO and flame retardant on variation of catalyst concentration, time and temperature on the yield would be an interest. Many researchers reported the potential to synthesize plasticizer and phosphorus-based flame retardant group to improve the brittleness and delay the production of flames for polymers such as PVC (Wang et al., 2018 ; Jia et al., 2015).

Thus, it is the objective of this research to synthesis EPO including phosphorus based flame retardant (POPE) and later melt blended with PLA via melt blending technique at various POPE contents. Questions that need to be answered during this research include:

1) How does the temperature, time and catalyst affect the yield of synthesized EPO containing phosphorus-based flame retardant (POPE)?
2) How will be the chemical structure of synthesized POPE be obtained?
3) How do the compositions of PLA/POPE affect the mechanical, thermal, morphologies and flame retardant properties of the blends?

1.3 Objectives of the Study

The objectives of this research are as follows:

1) To investigate the effect of various temperatures, time and catalyst concentration on the yield of synthesized POPE.
2) To investigate the effect of PLA/POPE blend ratios on mechanical, thermal, morphological and flame retardant properties.

1.4 Scopes of Study

To achieve the objectives of the research, the following activities were performed:

i. Synthesis of POPE blends by varying the amount of triphenylphosphine as catalyst (0.1, 0.2, 0.3 and 0.4 g), temperature (70, 80, 90 and 100 ℃) and time (1, 2, 3, 4 and 5 h).

ii. Preparation of PLA/POPE blends at various amounts of POPE (1 to 5 wt%) by using a melt blending technique using a twin-screw extruder. After melt blending, the dumbbell-shaped samples were prepared using the injection molding machine.

iii. Characterizations of synthesized POPE by Fourier transform infrared (FTIR) spectroscopy.

iv. Determination of thermal properties using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), flame retardancy analysis by using LOI, investigation of morphology by using scanning electron microscopy (SEM) and mechanical properties by using tensile testing according to ASTM D638.

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