The Effect of Filler Content and Chemical Modification On Properties of Polylactic Acid/Recycled Low Density Polyethylene/*Nypa Fruticans* Husk Biocomposites

by

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LIST OF ABBREVIATIONS

3-APE	3-aminoproplytriethoxysilane
ASTM	American society testing method
ATR	Attenuated total reflectance
CO_2	Carbon dioxide
DP	Degree polymerization
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared
HDPE	High density polyethylene
LDPE	Low density polyethylene
MMA	Methyl methacrylate
NFH	*Nypa Fruticans* husk
PEMA	Polyethylene grafted Maleic Anhydride
php	Part per hundred polymer
PLA	Polylactic acid
rLDPE	Recycled low density polyethylene
SEM	Scanning electron microscopy
T_c	Crystallization temperature
T_g	Glass transition temperature
TGA	Thermogravimetry analysis
T_m	Melting temperature
X_c	Degree of crystallization
ΔH_f	Heat fusion of polymer biocomposites
ΔH_f°	Heat fusion of 100% crystalline matrix

Kesan Kandungan Pengisi dan Modifikasi Kimia Keatas Sifat-Sifat Polilaktik Asid/Polietilena Ketumpatan Rendah Kitar Semula/Serat Nipa Fruktikan Biokomposit

ABSTRAK

Biokomposit serat *Nipa fruktikan* (SNF) terisi polilaktik asid (PLA)/polietilena ketumpatan rendah kitar semula (PKRKS) telah disediakan menggunakan Brabender Plastikorder EC PLUS pada suhu 180 ˚C dan kelajuan rotor 50 rpm. Kesan kandungan SNF dan jenis-jenis modifikasi-modifikasi kimia yang berbeza ke atas sifat-sifat tensil, morfologi, sifat-sifat terma dan biorosotan biokomposit PLA/PKRKS telah dikaji. Pelbagai jenis-jenis modifikasi-modifikasi kimia seperti polietilena dicantum maleik anhidrida (PEMA), 3-aminopropiltriektoksisilana (3-APE), asid metil metakrilat (AMM), asid etilenadiaminatetraasetik garam-2-hidrat (AEDT), dan enzim telah digunakan, berturut-turut. Keputusan menunjukkan bahawa penambahan SNF kedalam PLA/PKRKS telah mengurangkan kekuatan tensil, pemanjangan pada takat putus, dan darjah penghabluran (X_c), dimana modulus Young dan kestabilan terma meningkat. Kesan α-amilase terhadap biorosotan biokomposit PLA/PKRKS/SNF menunjukkan dengan peningkatan kandungan SNF, meningkatkan kadar biorosotan biokomposit. Morfologi permukaan patahan tensil telah menunjukkan bahawa interaksi yang lemah terjadi diantara SNF dengan matrik PLA/rLDPE. Modifikasi-modifikasi kimia menghasilkan kesan positif ke atas sifat-sifat tensil dan terma biokomposit PLA/PKTKS/SNF. Kehadiran PEMA, 3-APE, AMM, AEDT, AEDT/Enzim dan 3-APE/Enzim telah meningkatkan kekuatan tensil, modulus Young, darjah penghabluran dan kestabilan terma biokomposit. Biokomposit terawat PLA/PKRKS/SNF dengan 3-APE/Enzim mempunyai kekuatan tensil, modulus Young, dan kestabilan terma yang paling tinggi berbanding biokomposit dengan modifikasi-modifikasi kimia yang lain. Walaubagaimana, biokomposit PLA/PKRKS/SNF terawat dengan AMM mempunyai darjah penghabluran yang tertinggi. Sementara, biokomposit PLA/PKRKS/SNF terawat dengan AEDT menunjukan kadar biorosotan yang paling tinggi. Interaksi antara muka yang lebih baik diantara SNF yang terawat dan matrik PLA/PKRKS telah dibuktikan melalui kajian SEM. FTIR spektra menunjukkan bahawa perubahan-perubahan kumpulan berfungsi biokomposit yang terawat.

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ABSTRACT

Nypa fruticans husk (NFH) filled polylactic acid (PLA)/recycled low density polyethylene (rLDPE) biocomposites had been prepared using Brabender Plasticoder EC PLUS at temperature 180˚C and rotor speed 50 rpm. The effect of NFH content and different types of chemical modifications on tensile properties, morphology, thermal properties and biodegradation of PLA/rLDPE/NFH biocomposites were studied. The various types of chemical modifications such as Polyethylene grafted maleic anhydride (PEMA), 3-Aminopropyltriethoxysilane (3-APE), Methyl methacrylate acid (MMA), Ethylenediaminetetraacetic acid disodium salt-2-hydrate (EDTA), and enzyme were used, respectively. The results showed that the addition of NFH reduced the tensile strength, elongation at break and degree of crystallinity (X_c), whereas the Young's modulus and thermal stability of biocomposites increased. The effects of α-amylase on the enzyme biodegradation of PLA/rLDPE/NFH biocomposites showed that the increased of NFH content has increased the biodegradation rate of the biocomposites. The morphology tensile fracture surface of PLA/rLDPE/NFH biocomposites indicates that poor interaction occurred between NFH and PLA/rLDPE matrix. The chemical modifications of NFH resulted positive effect on tensile and thermal properties of PLA/rLDPE/NFH biocomposites. The presence of PEMA, 3-APE, MMA, EDTA, EDTA/Enzyme and 3-APE/Enzyme have increased the tensile strength, Young's modulus, degree of crystallinity and thermal stability of biocomposites, whereas the elongation at break decreased. The treated PLA/rLDPE/NFH biocomposites with 3-APE/Enzyme have highest tensile strength, Young's modulus, and thermal stability compared to other chemical modifications of biocomposites. However, PLA/rLDPE/NFH biocomposites treated with MMA has highest degree of crystallinity. Meanwhile PLA/rLDPE/NFH biocomposites treated with EDTA exhibited highest rate of biodegradation. The better interfacial interaction between treated NFH and PLA/rLDPE matrix was proven by SEM study. The spectra FTIR indicated that the changes of functional group of treated biocomposites.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The growing environmental concern and increasing scarcity of fossil fuel resources have proven an intensive demand for biomass with controllable properties, with the desire to reduce petroleum consumption and mitigate pollution (Lu & Oza, 2013; Zhang & Sun, 2004). Biodegradable polymers have received much attention recently with growing pressure on the world resources as well as concern about disposal of plastics and commercial activity. Biodegradability, greenhouse, gas emission and renewability are the environmental benefits offered by biopolymer (Rajesh & Prasad, 2014).

Poly (lactic acid) (PLA) made from renewable agriculture raw materials which are fermented to lactic acid, has been considered to be a type of commercial available and fully biodegradable polymers (Duhovic et al., 2009; Koronis et al., 2013; Lu et al., 2014; Qu et al., 2010). PLA is now one of the most promising biodegradable polymers for industrial plastic application, which served as an alternative to conventional synthetic polymer (Pantani & Sorrentino, 2013). Because of the demand of biodegradable based products in recent years, PLA based products are manufactured commercially in many countries. Their application include film, food packaging, textiles, disposal bottle and table ware (Auras et al., 2004; Jia et al., 2014). In order to make them appropriate in many technical applications, the mechanical properties of PLA can be improved by using reinforcement (A et al., 2015; Akbari et al., 2015; Iwata, 2015; Shukor et al., 2014).

Nowadays, natural fibers exhibit many advantages over the synthetic fibers such as low density, low cost , high strength, high specific modulus and especially their recyclability (Salleh et al., 2014; Yu et al., 2014). The reinforcement of PLA with natural fibers seems to be a logical alternative in order to increase their mechanical performance as well as keeping the final material environmentally friendly. Some researchers have reported the natural fibers or fillers as reinforcement of PLA as shown in Table 1.1.

Table 1.1 : Natural Fibers as filler in PLA.

Natural Fiber	Reported by researcher
Kenaf	Huda et al., 2008; Ochi, 2008
Hemp	Baghaei et al., 2013; Oza et al., 2014; Sawpan et al., 2011
Ramie	Chen et al., 2015; Yu et al., 2010; Zhou et al., 2012
Rice straw	Qin et al., 2011; Zhao et al., 2011
Abaca	Bledzki et al., 2009; Reddy & Yang, 2015
Jute	Arao et al., 2015; Ma & Joo, 2011; Memon & Nakai, 2013; Rajesh & Prasad, 2014
Bamboo	Kumar et al., 2013; Lu et al., 2014; Young et al., 2014
Oil palm	Jaffar Al-Mulla et al., 2013; Koutsomitopoulou et al., 2014
Flax	Manshor et al., 2014; Nassiopoulos & Njuguna, 2015; Zhu et al., 2013
Cordenka	Bax & Müssig, 2008
Wood	Csizmadia et al., 2013; Peltola et al., 2014
Lignin	Spiridon et al., 2015

Nypa fruticans is a monoecious palm with special characteristics. Contrast to usual palms like coconut and oil palm, it thrives in river estuaries and brackish water environment in which salt and fresh water mingle. *Nypa fruticans* are a major source which are extensively used as thatching materials but most parts of the *Nypa fruticans* are left to decompose at its habitat (Rahman, 2000). Therefore, *Nypa fruticans* is an abundance resource that can be found throughout the year. *Nypa fruticans* consisting of frond, shell, husk and leaf. The total chemical composition showed that the cellulose and hemicellulose contents were in the range of 28.9–45.6 wt% and 21.8–26.4 wt%, respectively. The lignin content was 19.4–33.8 wt% with the highest lignin content found in leaf. Besides the main chemical components, starch, protein and extractives were also present in significant amounts from 2 to 8 wt%. Additionally, the ash content was high from 5.1 to 11.7 wt% (Tamunaidu & Saka, 2011). In overall, each part of the *Nypa fruticans* has its individual superior characteristics and could be exploited as lignocellulosic resources for biocomposites.

On the other hand, PLA was chosen for its high biocompatibility and biodegradability. It has become an alternative to traditional commodity plastics for everyday applications as an environmental friendly polymer due to its some unique properties such as high strength, high stiffness and resistance to fats and oil (Hamad et al., 2011b). However, brittleness and other properties such as low viscosity, low thermal stability, high moisture sensitivity, medium gas barrier properties, high cost (comparing with PE, PP, PS, etc) and low solvents resistance (e.g., against water) are often insufficient for many applications . Therefore, blending can aid in the development of new biocomposite products with better performance (Akbari et al., 2015; Ebadi-Dehaghani et al., 2015; Hamad et al., 2011b; Ouchiar et al., 2015; Yu et al., 2006; Zhou et al., 2015).

The properties of PLA can be modified by polymer blending techniques, where it was blended with several synthetic and biopolymers in efforts to enhance its properties and also to obtain novel materials as shown in Table 1.2. PLA have been blended with different polymers to obtain materials with lower cost and improved properties.