PREPARATION AND CHARACTERIZATION ON RICE HUSK ASH FILLED TAPIOCA STARCH COMPOSITES

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ABSTRACT

This research presents the production of tapioca starch as biopolymer and rice husk ash (RHA) as the filler material. Tapioca starch films prepared using casting method and optimizing with different thermal treatment temperature (0°C, 40 °C, 60°C and 80 °C) which was determine chemically and mechanically. Meanwhile the fabrication of rice husk ash (RHA) filled with tapioca starch (TPS) composites was successfully developed whereas composites were prepared using two different technique with simple casting; first, the mixture of TPS films (glycerol, water, and tapioca starch) were added with RHA powder and second, the mixture of TPS films (glycerol, water and tapioca starch) were added with homogenous dispersion of RHA in water. Rice husk ash was produced from hydrolysis treatment by 2M HCl followed by calcinations at 700°C for 24 hour. The effects of thermal treatment and the size of the filler with varying content of rice husk ash (0, 1, 2, and 3 wt%) on biodegradability, thermal, physical and mechanical properties of tapioca starch composite were evaluated in order to characterize the composites. From optimizing result, it was found that different thermal temperature TPS films showed same spectra pattern as shown in FTIR result. For tensile strength result, tensile strength of TPS increased by 240% at 40 °C, 400% at 60 °C and 600% at 80 °C respectively. Meanwhile, for TPS/RHA results shows have shown a significant decrease in biodegradability, density, water absorption and mechanical properties with the increase of rice husk ash content. However, after thermal treatment of the biopolymer at temperature 80°C for 24 hours, all composite showed an increase in tensile strength. From method A, the result has shown that the tensile strength increases of TPS/RHA matrix was 13.04% for TPS/RHA 0, 124.78% for TPS/RHA 1, 340.25% for TPS/RHA 2, and 310.64% for TPS/RHA 3, after thermal treatment at 80°C for 24 hours. Meanwhile, TPS/RHA with smaller particle of filler size with presence of thermal treatment showed that tensile strength increase was 150.72% for TPS/RHA 1, 371.69% for TPS/RHA 2, and 693.62% for TPS/RHA 3. From method B, the result has shown similar pattern, in which the tensile strength increase of TPS/RHA matrix was 13.04% for TPS/RHA 0, 145.08% for TPS/RHA 1, 199.91% for TPS/RHA 2, and 480% for TPS/RHA 3 after thermal treatment. Meanwhile, TPS/RHA with smaller particle of filler size with presence of thermal treatment showed that tensile strength increase was 257.51% for TPS/RHA 1, 69.21% for TPS/RHA 2, and 420% for TPS/RHA 3. The addition of rice husk ash as filler do not affect the chemical properties of composites as shown in FTIR results, in which all composites have shown the same pattern. Thermogravimetric Analysis (TGA) has proven that rice husk ash increases the thermal stability of composites. Meanwhile, SEM has shown the fracture of the composite which explained the observed mechanical properties. Thus, rice husk ash can act as a filler in the development of green biocomposites. This may help in reducing air pollution by the burning of rice husk, and offer a better solution in producing renewable biocomposites.

ABSTRAK

PENYEDIAN DAN PENCIRIAN TERHADAP SERBUK ABU SEKAM PADI SEBAGAI BAHAN PENGISI DENGAN KOMPOSIT KANJI UBI KAYU

Kajian ini berkenaan penghasilan biopolimer daripada kanji ubi kayu (TPS) sebagai bahan asas dan abu sekam padi sebagai bahan pengisi.TPS filem dihasilkan menggunakan kaedah acuan pada suhu rawatan haba yang berbeza ($0^{o}C$, $40^{o}C$, $60^{o}C$ and $80^{o}C$) telah dikaji dari segi kimia dan mekanikal. Daripada kajian ini, TPS filem pada suhu rawatan haba yang berbeza mempunyai corak spectra yang sama seperti yang ditunjukkan dalam keputusan FTIR. Dari segi kekuatan mekanikal, kekuatan TPS meningkat 240% pada 40 ^{o}C, 400% pada $60^{o}C$ and 600% pada 80. Fabrikasi serbuk abu sekam padi ditambahkan kedalam TPS filem telah berjaya dihasilkan; yang mana TPS filem telah dihasilkan melalui dua kaedah iaitu, yang pertama, serbuk abu sekam padi ditambahkan kedalam campuran TPS filem (gliserol, air, dan kanji ubikayu) dan yang kedua, dengan menambah abu sekam padi yang telah dicampur sebati dengan air kedalam campuran TPS filem (gliserol, air, dan kanji ubikayu). Abu sekam padi telah dihasilkan melalui rawatan larut lesap dengan menggunakan 2M HCl diikuti dengan pembakaran dengan suhu $700^{o}C$ selama 24 jam. Kesan rawatan haba dan saiz serta pelbagai jumlah kandungan abu sekam padi digunakan iaitu 0, 1, 2, and 3 (peratus berat) terhadap sifat-sifat kebolehuraian, haba, fizikal dan mekanikal bagi komposit kanji ubikayu telah dinilai untuk tujuan pencirian komposit. Keputusan menunjukkan bahawa peningkatan jumlah peratus abu sekam padi memberi kesan penurunan yang ketara terhadap sifat kebolehuraian, ketumpatan, penyerapan air dan mekanikal komposit. Namun, semua komposit menunjukkan peningkatan dari segi kekuatan tegangan selepas rawatan haba diperkenalkan iaitu pada suhu $80^{o}C$ selama 24 jam. Dari kaedah pertama, hasilnya menunjukkan peningkatan kekuatan tegangan matriks TPS/RHA ialah 13.04% untuk TPS/RHA 0, 124.78% untuk TPS/RHA 1, 340.25% untuk TPS/RHA 2 dan 310.64% untuk TPS/RHA 3, selepas rawatan haba. Sementara itu, bagi TPS/RHA dengan saiz serbuk abu sekam padi yang lebih kecil dan rawatan haba menunjukkan peningkatan kekuatan tegangan yang lebih tinggi iaitu 150.72% untuk TPS/RHA 1, 371.69% untuk TPS/RHA 2, dan 693.62% untuk TPS/RHA 3. Daripada kaedah kedua, hasil kajian menunjukkan corak yang sama, dengan peningkatan kekuatan tegangan matriks komposit iaitu 13.04% untuk TPS/RHA 0, 145.08% untuk TPS/RHA 1, 199.91% untuk TPS/RHA 2, dan 480% RHA 3 selepas rawatan haba. Bagi TPS/RHA dengan saiz serbuk abu sekam yang lebih kecil dengan kehadiran rawatan haba menunjukkan peningkatan kekuatan tegangan adalah 257.51% untuk TPS/RHA 1, 69.21% untuk TPS/RHA 2, dan 420% untuk TPS/RHA 3. Penambahan serbuk abu sekam padi tidak mempengaruhi sifat kimia komposit seperti yang ditunjukan dalam keputusan FTIR di mana kesemua komposit menunjukka paten yang sama. 'Thermogravimetric' analisis (TGA) membuktikan bahawa abu sekam padi meningkatkan kestabilan haba komposit. Sementara itu, 'SEM' menunjukkan keratan komposit yang akan menerangkan kajian sifat mekanikal. Oleh itu, abu sekam padi boleh berfungsi sebagai bahan pengisi dalam menghasilkan biokomposit mesra alam. Ini juga membantu mengurangkan pembakaran sekam padi secara terbuka, serta mengurangkan pencemaran udara dan menyumbang kepada jalan penghasilan biokomposit boleh diperbaharui.

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Al_2O_3	Aluminium oxide
ASTM	American society for Testing and Material
CaO	Calcium oxide
$C_2H_2O_4$	Oxalic
$C_6H_8O_7$	Citric acids
DCP	Dicumly peroxide
DP	Degree of polymerization
E.g.	Example
EPDM	Ethylene-propylene-diene monomer
Fe_2O_3	Iron oxide
FTIR	Fourier transform infrared
HDPE	High density polyethylene
HCl	Hydrochloric acid
IUPAC	International Union of Pure and Applied Chemistry
H_2SO_4	Sulphuric acid
K_2O	Potassium oxide
LLDPE	Linear low density polyethylene
MA	Maleic anhydride
MgO	Magnesium oxide
NaOH	Sodium hydroxide
Na_2O	Sodium oxide
NR	Natural rubber
PHAs	Polyhydroxyalkanoates
PP	Polypropylene
PPEAA	Poly(propylene-ethylene-acrylic acid
PLA	Poly lactic acid
RH	Rice husk
RHA	Rice husk ash
SEM	Scanning electron microscope
SiO	Silica oxide
TGA	Thermogravimetric analysis
TPS	Thermoplastic Starch

TPS	Tapioca starch
TPS/RHA	Rice husk ash filled tapioca starch
TTL	Tea tree leaf
TTB	Tea tree branches
TTT	Tea tree trunk
TTL/TS	Tea tree leaf reinforced tapioca starch composite
TTB/TS	Tea tree branch reinforced tapioca starch composite
TTT/TS	Tea tree trunk reinforced tapioca starch composite
WRHA	White rice husk ash

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

Synthetic polymers are commonly being used in the production of packaging products, construction materials, household items, and agricultural crops. Most commonly used synthetic polymers are non-biodegradable. The limited usage of petroleum in oil industry has progressed to the point in which the usage of these non-biodegradable polymers is causing destructive impact on the ecosystem. The inability of microorganisms to naturally break down these non-biodegradable polymers has cause such heavy waste and toxic accumulation. A better solution which is to produce biodegradable polymers is currently the subject of attention in both academic and industrial applications. Hence, researchers are focusing more on the utilization of natural biodegradable polymers such as such as polyhydroxyalkanoates (PHAs), poly lactic acid (PLA) and starch from plants, as replacement materials (Mortazavi *et al.,* 2013).

Starch is considered as one of the promising raw materials that can be long-term sustained. Besides of its low cost production, starch can biodegrade completely, and highly available in terms of renewability and abundancy. Starch as the subject matter, has been gaining interest since 1970s. Accordingly, numerous efforts have been applied to produce starch-based polymers which in return, can help to reduce the dependency on using petrochemical resources, lower the negative impacts of environmental issues and to explore other possible applications (Lu *et al.,* 2009). Generally, the most common starches used to produce biopolymer are derived from cassava, corn, potato, sago and rice. It can be mixed with plasticizer in high condition and modified into thermoplastic material.

Currently, the most popular rice supplying countries which are likely to remain strong in the next decades are situated across Asia and Africa (Timmer *et al.*, 2010). This fact is supported by a report by Food and Agricultural organization (FAO), which stated that the world rice production in 2014 were approximately 741.3 million tons and might estimate to 749.8 million tons in 2015 (FAO, 2015). Raw rice husk provided from rice milling process contain 35% cellulose, 25% hemicellulose, 20% lignin, 17% ash (94% silica) and about 3% by weight of moisture (Chaudhary *et al.*, 2002). There are also some handful researches that focused on rice husk as reinforcement filler for thermoplastic composites (Park *et al.*, 2004). Sarvanan and Kumar (2013) have stated that rice husk; a popular, common agriculture waste product is suitable to be used as reinforcement filler.

Moreover, rice husk and RHA as filler in thermoplastic polymer composites has been notable lately. It has been considered as a good source of silica and silicon compound due to its high content of silica, which is about 90-98% after undergoing calcination process. Depending upon the calcination condition, two type of ashes will be produced which are white rice husk ash (WRHA) and black rice husk ash (BRHA). But in the following section RHA, refers to specifically white rice husk ash. The presence of hydroxyl group on silica ash particle is advantageous in the case of polymers containing polar group (Ayswarya *et al.*, 2012). The use of RHA as a filler in thermoplastic starch also has twofold advantages of reducing the pollution potential of RHA and modifying the properties of thermoplastic starch by a cost effective and reliable method.

This research focused on utilizing by-products from paddy trees. Its purpose was to convert the by-products into value-added product such as biocomposites. In this study, the effect of thermal treatment on physical, thermo-chemical and mechanical properties of thermoplastic starch (TPS) based on tapioca starch with various amount of rice husk ash (RHA) as filler material has been observed.

1.2 Problem statement

With growing concerns over climate change, increasing pollution rate and inability of petroleum-based plastic to biodegrade and recycled have increases the solid waste production. This problem is just some of the threatening challenges faced by the plastics manufactures. Besides, the qualities of lives are improved due to the availability of plastic such as plastic bags, bottle, plates, cup and others, which are derived from petroleum.

Compare to the traditional materials such as ceramic, metal, leather and wood, plastic is chosen due to its ease of convenience. Having petroleum as the major mineral resources, its gradual depletion may cause a significant shortage of supply in the years to come. Thus, concerning all sides of parties. As industries attempt to decrease the dependency on petroleum based fuels and products, there is an increasing need to find out more solutions of combination of environmentally friendly and sustainable bio-based materials. Therefore, biopolymers such as polyhydroxyalkanoates (PHAs), polylactic acid (PLA) and starch from plants are good candidates as replacement materials for petroleum-based plastic.

Detailed descriptions of biopolymers can be found in numerous review paper and books (Sorrentino and Vittoria, 2007). In the following, we will refer to the common bio-based polymer of potential interest for packaging industry. Several applications of bio-based packaging as well as edible films and coating are reported in literature. However, producers of materials and manufactures of food product have not yet demonstrated their interest because of the problem related with the application of these materials (Krochta and De Mulder-Johnston, 1997).

The problems associated with biodegradable polymers are threefold: performance, processing and cost. Although these factors are somewhat interrelated, problem due to "performance and processing" are common to all biodegradable polymers in spite of their origin (Scott, 2000). To be more specific such as; brittleness, low heat distortion temperature, high gas and vapour permeability, poor resistance to protracted processing operations have strongly limited their application. Example, starch biocomposites have shown poor mechanical properties and poor resistance to humidity. Therefore in order to solve this problem, few approaches were taken such as by adding water and glycerol as plasticizers, which help to enhance the mechanical properties of starch composites. Much of the researches were done using glycerol, water, urea, and sorbitol as plasticizer. Another approaches taken was by adding other material such as synthetic polymer (Averous and Fringant, 2001), crosslinking agent or through esterification (Reddy and Yang, 2010; Averous, 2004), lignin (Baumberg *et al.*, 1998), cellulosic microfibrils (Dufresne and Vignon, 1998), commercial regenerated cellulose fibres (Funke *et al.*, 1998) natural fibres (Wollerdorfer and Bader, 1998) and inorganic filler material (Kompositi and Ani, 2013).

ice is a major food crop in Malaysia, generating large amount of waste which is orm of rice husk and has a potential as a renewable energy. However, the llable rice husk burning in open air or used as a fuel in the rice paddy milling has create a major problem for agriculture waste management. Currently, the tion of rice husk ash wastes as filler in composite materials has been gaining among researchers and industries owing to today's ecological issues and c factors. Apparently, the potential of combination of rice husk ash as inorganic d polymer composite such as tapioca starch can reduce the usage of petroleum hetic fibre.

esearch objectives

eral aim of this study is to determine the effect of thermal treatment on cal properties of rice husk ash filled tapioca starch composites.
cific objectives of this research are:

o characterize RHA filler using XRD and to analyse the effect of thermal reatment on FTIR and tensile properties of TPS composites. .
o analyse the effect of the presence of thermal treatment and effect of a size of HA filler with varying content of RHA filler on mechanical property (tensile trength, elongation at break and young modulus) of TPS/RHA composites.
o analyse the physical properties (density, biodegaradbility, water absorption, nd SEM) and thermo-chemical properties (TGA, and FTIR) of TPS/RHA omposites.

cope and limitation of study

dy is focusing on optimizing the temperature (0, 40, 60 and 80°C) of thermal t that subjected towards tapioca starch composites. The optimizing composites lysed using FTIR, and mechanical testing. The obtained rice husk ash by heated for 24 hours was analysed using XRD. The mechanical testing such as tensile performed in order to determine the mechanical properties of the rice husk ash ioca starch composites. This testing were carried out in accordance to ASTM 996). The measurement of density, water absorption test and biodegradability conducted according to method Rodney *et al.*, (2015) and Sahari *et al.*, (2014) tly modification. Fourier transform infrared (FTIR) spectroscopy was used in order to detect the presence of functional groups in the composites. Thermogravimetric analysis (TGA) was carried out to measure the changes in mass and in thermal decomposition and thermal stability of the materials. Finally, the observation on the surface morphology of the fractured surface of composites failure test specimen completed using scanning electron microscope (SEM).

1.5 Structure of thesis

Chapter 1 presents the background of study, problem statements, objectives, significance of study, and scope of the study and structure of thesis. A literature review on previous research work in various areas which is relevant to this research is presented in chapter 2. The chapter started with a comprehensive literature survey on the natural fibre and rice husk. Review of the chemical and mechanical properties of fibres and its composites are also included in this chapter. The methodology of the study is described in chapter 3. This chapter also include the techniques for preparation of composites and the determination of mechanical properties of rice husk ash reinforced tapioca starch composites. Chapter 4 presents the results and discussion of the mechanical properties of rice husk ash reinforced tapioca starch composites. Surface morphology of fractured specimen was also evaluated in this chapter using Scanning electron microscope (SEM). Meanwhile, thermal decomposition and thermal stability of material were evaluated through Thermogravimetric analysis (TGA). Finally, chapter 5 presents the conclusion and recommendations for future works.