UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF ANTIOXIDANT PACKAGING MATERIAL BASED ON OPTIMIZED POLY(LACTIC ACID) AND CELLULOSE FROM DURIAN RIND BIOCOMPOSITES

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DEVELOPMENT OF ANTIOXIDANT PACKAGING MATERIAL BASED ON OPTIMIZED POLY(LACTIC ACID) AND CELLULOSE FROM DURIAN RIND BIOCOMPOSITES

By

PATPEN PENJUMRAS

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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Durian rinds are the plant waste of durian fruit consumption. Only one-third of a durian is edible, whereas the seeds and the shell become waste. With regards to environmental impact, the waste can be converted into value-added products, such as cellulose, to be used as reinforcement material in biocomposites. Cellulose is extracted from ground durian rind using delignification with acidic sodium chlorite, followed by mercerization with sodium hydroxide. The diameter and aspect ratio of cellulose fibers are in the range of 100-150 µm and the aspect ratio is in the range of 20-25, which is higher than the minimum aspect ratio value for good strength transmission for any reinforcement. A central composite design was employed to determine the optimum preparation condition of the biocomposites to obtain the highest tensile strength and impact strength. The selected optimum condition was 35 wt.% cellulose loading at 165°C and 15 minutes of mixing, leading to a desirability of 94.6%. Under the optimum condition, the tensile strength and impact strength of the biocomposites were 46.21 MPa and 2.93 kJ/m², respectively. The coupling agent 3-aminopropyltrimethoxysilane (APS) was used to modify the surface of cellulose. The result found that silane-treated, cellulose-reinforced biocomposites offered superior mechanical properties compared with neat PLA and untreated cellulose-reinforced biocomposites. The adhesion of cellulose and the PLA matrix was improved by modifying the cellulose surface, which led to less water absorption into biocomposites. An antioxidant packaging material was developed using silane-treated durian rind cellulose reinforced poly(lactic acid) (PLA) biocomposites. The release of BHT and α-tocopherol with 3 wt.% from neat PLA and biocomposites into two food simulants (50% and 95% ethanol in water) at two temperatures (27°C and 37°C) were monitored. The result found that BHT had a higher release rate
than α-tocopherol. At higher temperatures, the resulting release rate increased. Antioxidant was released from neat PLA faster than biocomposites. BHT released faster into 95% ethanol, while α-tocopherol released faster into 50% ethanol. The faster release of antioxidant from each condition contributed to the inhibition of lipid oxidation, which was indicated by the decrease of peroxide value (PV) and thiobarbituric acid reactive substance (TBARS). It can be summarized that BHT had higher effectiveness as an antioxidant in active packaging application for edible oil. This study concluded that durian rind cellulose can be successfully used as a reinforcing material for poly(lactic acid) biocomposites. Its application, with the addition of antioxidants was seen to be an effective active packaging for the protection of edible oil from oxidation.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN BAHAN PEMBUNGKUSAN ANTIOKSIDA BIOKOMPOSIT BERASASKAN CAMPURAN POLI (ASID LAKTIK) DAN SELULOSA DARIAPDA KULIT DURIAN YANG DIOPTIMUMKAN

Oleh

PATPEN PENJUMRAS

Januari 2018

Pengerusi : Profesor Russly A. Rahman, PhD
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Kulit durian merupakan sisa buangan berasaskan tumbuhan. Hanya satu pertiga bahagian daripada buah durian yang boleh dimakan, manakala biji dan kulitnya adalah sisa. Berhubungan kesan terhadap alam sekitar, sisa daripada durian telah diubah kepada produk yang bernilai seperti selulosa yang digunakan sebagai bahan pengukuh dalam biokomposit. Selulosa diekstrak daripada serbuk kulit durian dengan pembuangan lignin menggunakan natrium klorida berasid dan diikuti ‘mercerization’ menggunakan natrium hidroksida. Diameter bagi serat selulosa ialah dalam lingkungan 100–150 μm manakala, nisbah aspek ialah di antara 20 dan 25, yang mana ianya lebih tinggi daripada nisbah aspek minimum bagi bahan pengukuh. ‘Central Composite Design’ (CCD) digunakan bagi menentukan penyediaan yang optimum bagi menghasilkan biokomposit yang berdaya tegangan dan impak yang tinggi. Penyediaan optimum yang dipilih ialah dengan mencampurkan 35% selulosa pada 165 °C selama 15 min, yang meghasilkan 94.6% ‘desirability’. Pada penyediaan yang optimum, daya tegangan dan daya impak biokomposit masing-masing ialah 46.21 MPa dan 2.93 kJ/m². ‘Coupling agent’ yang digunakan adalah 3-aminopropyltriethoxysilane (APS) untuk mengubah suai permukaan selulosa. Keputusan kajian ini menunjukkan, selulosa yang bertindak balas dengan ‘silane’ menghasilkan biokomposit yang daya tegangannya kuku dan kuat, berbanding PLA dan selulosa yang tidak bertindak balas. Keleakatan selulosa dan matriks PLA dipertingkatkan dengan pengubahsuaian permukaan selulosa yang mengurangkan penyerapan air oleh biokomposit. Bahan pembungkusan antioksidan telah dihasilkan menggunakan biokomposit poli (asid laktik) (PLA) yang diperkuatkan dengan selulosa kulit durian yang bertindak balas dengan ‘saline’. Kadar pembebasan 3% BHT dan 3% α-tokoferol dalam PLA dan biokomposit secara berasingan
telah dikaji dalam dua larutan (50% dan 95% etanol dalam air) dan pada dua suhu (27 dan 37 °C) yang berbeza. Keputusan kajian mendapati, BHT mempunyai kadar pembebasan yang lebih tinggi daripada α-tokoferol. Kadar pembebasan telah meningkat pada suhu yang lebih tinggi. Pembebasan bahan antioksida daripada PLA adalah lebih cepat berbanding biokomposit. Pembebasan BHT lebih cepat di dalam 95% etanol, manakala pembebasan α-tokoferol lebih cepat di dalam 50% etanol. Pembebasan bahan antioksida yang cepat dapat meghalang pengoksidaan lemak berlaku yang dapat dilihat daripada penurunan nilai peroksida (PV) dan bahan reaktif asid thiobarbituric (TBARS). Dari kajian ini dapat disimpulkan bahawa, BHT mempunyai keberkesanan yang lebih tinggi untuk menjadi antioksidan dalam aplikasi pembungkusan aktif bagi minyak makanan. Rumusan dari kajian ini mendapati selulos dari kulit durian toleh dapat digunakan dengan jayanya sebagai bahan penguat bagi biokomposit asid polilaktik. Penggunaannya telah terbukti sebagai pembungkus aktif yang efektif bagi perlindungan minyak makan dari oksidasi apabila antioksidan dimasukkan kapada bahan biokomposit.
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I certify that a Thesis Examination Committee has met on 4 January 2018 to conduct the final examination of Patpen Penjumras on her thesis entitled "Development of Antioxidant Packaging Material Based on Optimized Poly(Lactic Acid) and Cellulose from Durian Rind Biocomposites" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>Wt.%</td>
<td>Percentage by weight</td>
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<tr>
<td>°C</td>
<td>Degree celsius</td>
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<tr>
<td>cm</td>
<td>Centimeter</td>
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<tr>
<td>cm²</td>
<td>Square centimeter</td>
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<tr>
<td>CCD</td>
<td>Central composite design</td>
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<td>RSM</td>
<td>Response surface methodology</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>et al.</td>
<td>And friends</td>
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<tr>
<td>h</td>
<td>Hour</td>
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<tr>
<td>psig</td>
<td>Pound (force) per square inch guage</td>
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<tr>
<td>kV</td>
<td>Kilovoltage</td>
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<tr>
<td>MPa</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>kJ/m²</td>
<td>Kilojules per square meter</td>
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<tr>
<td>L</td>
<td>Liter</td>
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<tr>
<td>mL</td>
<td>Milli liter</td>
</tr>
<tr>
<td>MARDI</td>
<td>Malaysian Agricultural Research and Development Institue</td>
</tr>
<tr>
<td>m²</td>
<td>Square meter</td>
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<tr>
<td>T_g</td>
<td>Glass transition temperature</td>
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<td>T_m</td>
<td>Melting temperature</td>
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<td>T_c</td>
<td>Crytallization temperature</td>
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<td>PLA</td>
<td>Poly(lactic acid)</td>
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<td>TPS</td>
<td>Thermoplastic starch</td>
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</table>
$p$ Probability

$C_p$ Specific heat capacity

$APS$ 3-aminopropylriethoxysilane

$BHT$ Butylated hydroxytoluene

$pH$ Measurement of Acidity/Alkalinity

$rpm$ Revolutions per minute

$ASTM$ American Society of Testing Method

$nm$ Nanometer

$AT$ $\alpha$-tocopherol

$Std.Dev$ Standard deviation

$USA$ United States of America

$N$ Normality

$J/g$ Jule per gram

$Eth$ Ethanol

$PET$ Polyethylene terephthalate

$PV$ Peroxide value

$TBARS$ Thiobarbituric acid reactive substances analysis
CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Durian (*Durio zibethinus* Murray) is one of the most popular fruits in Southeast Asia, particularly Thailand, Malaysia, Indonesia, and the Philippines (Booncherm and Siriphanich, 1991). It is well known as the “king of fruits” and its uses have been vigorously widened and entrenched into multidisciplinary food processing industries. Only one-third of a durian is edible, whereas the seeds and rinds become waste (Amid and Mirhosseini, 2012). Normally, durian wastes are sent to landfills without good management, affecting the surrounding environment. To avoid pollution that results from dumping or filling landfills, these wastes can be applied as non-wood raw material. Durian rinds have been found to be a good source of cellulose (Rachtanapun *et al*., 2012).

In recent years, there has been increasing interest in cellulose-based materials due to increasing interest in renewable resources and growing environmental awareness (Mohanty *et al*., 2005). Therefore, natural fibers have been studied to reinforce biodegradable polymers to produce biocomposite materials. Generally, commodity plastics are widely used for many applications, such as packaging material. However, plastic takes a very long time for environmental decomposition, creating a serious problem with the disposal of plastic waste. Substituting non-biodegradable polymers with biodegradable ones leads to fully renewable and degradable composites (Frone *et al*., 2011). Among the many biodegradable polymers, poly(lactic acid) (PLA) is considered to be one of the most promising renewable resource-based biopolymer matrices due to its high mechanical properties and easy processability compared with other biopolymers (Suryanegara *et al*., 2009). Although natural fiber provides many advantages in composites – low density, harmlessness, high toughness, renewable and biodegradable (Santiagoo *et al*., 2011) – a major limitation of natural fiber is the difference in the surface between the fiber and the matrix. Therefore, improvement of interfacial between cellulose and the polymer matrix is needed.

In recent years, consumers have increasingly demanded minimally-processed foods with better, fresh-like qualities. Therefore, the innovative concept of active packaging has gained attention. Its interaction with the package, the food and the environment can extend shelf life of foods by providing higher protection of flavors. It can preserve food by lowering the use of additives and preservatives in food formulations while maintaining the quality of the product. The culmination of this recent work is antioxidant packaging material based on optimized poly(lactic acid) and cellulose from durian rind biocomposites.
1.2 Research Hypotheses and Assumptions

To develop the antioxidant packaging material, the hypotheses of project are;

1. The cellulose extracted from durian rind can achieve a minimum value of aspect ratio for use as reinforcement material in composites.
2. Preparation of biocomposite materials at different levels of cellulose loading, mixing temperature and mixing time has an effect on the mechanical properties of biocomposites based on poly(lactic acid) and cellulose from durian rind.
3. The addition of polyethylene glycol as a plasticizer at different levels affect the mechanical properties of biocomposites.
4. Treating cellulose surfaces with a silane coupling agent can improve adhesion between the surface of the poly(lactic acid) and cellulose.
5. The type of packaging material, type of antioxidant, type of simulant and storage temperature affects the release rate of antioxidants.
6. Active packaging incorporated with antioxidants can delay an oxidation reaction, which is the cause of deterioration of lipid foods.

To simplify the problem, assumptions consist of the following:

1. There is no effect of non-uniform diameter and length of cellulose.
2. For release test of antioxidants:
   1) Initial concentration of antioxidants in food simulant is zero; and,
   2) Interaction between food simulants and packaging materials are not considered.
3. For lipid oxidation testing:
   1) Light has no effect during storage.

1.3 Research Aim and Objectives

The aim of his study is to develop biodegradable antioxidant packaging material based on poly(lactic acid) and cellulose extracted from durian rinds. This can then be used as antioxidant active packaging in lipid food products to prolong its shelf life. To achieve this aim, the objectives of this study are as follows:
1. To characterize the chemical and physical properties of cellulose extracted from durian rinds for use as reinforcement material in biocomposites.
2. To optimize the conditions for the preparation of biocomposites based on poly(lactic acid) and cellulose from durian rinds using a central composite design.
3. To determine the effects of additives, including plasticizer and coupling agents, on the property of biocomposites based on poly(lactic acid) and cellulose from durian rinds.
4. To evaluate the development of antioxidant packaging material based on optimized poly(lactic acid) and cellulose biocomposites and its application.

1.4 Scope of Study

Durian rind D159 Monthong was collected from Phatthalung province. The two-step process of extraction consisting of chlorination and mercerization was used for cellulose extraction. Poly(lactic acid) (PLA2003D food packaging-grade) was used as a matrix in this study. Preparation of biocomposites was optimized. Three independent variables including cellulose loading, mixing temperature and mixing time were employed. Polyethylene glycol was used as a compatibilizer and 3-aminopropyltriethoxysilane (APS) were used as a compatibilizer and coupling agent. For a soil burial test, polyethylene terephthalate (PET) was used as a representative of synthetic polymer, and soil in Rongkwang district, Phrae province, Thailand, was used for this study. Antioxidant release was conducted using α-tocopherol as a representative of natural antioxidants and butylated hydroxyanisole (BHT) as a representative of synthetic antioxidants.

1.5 Thesis Outline

The thesis consists of seven chapters. Chapter 1 introduces a basic understanding related to the study, which includes the problem statement, research hypotheses, research aim and objectives, and scope of study.

Chapter 2 provides the literature review on durian, composites, poly(lactic acid), plasticizer, coupling agent, water absorption and antioxidant active packaging, and mechanism of oxidation. The previous findings related to biocomposites in terms of chemical, physical, thermal and morphological properties and its area are elaborated on and reviewed. In addition, previous research on the release of antioxidants and their efficiency at preventing oxidation is also included here.

Chapters 3 to 6 are experimental chapters in which methodologies, results and discussions are conveyed according to the objectives as reported in Section 1.3.
Finally, Chapter 7 presents the overall conclusion of the research and recommendations for future work.
REFERENCES


