UNIVERSITI TEKNIKAL MALAYSIA MELAKA

THE POTENTIAL OF EPOXIDIZED NATURAL RUBBER AS HYDROPHOBIC CONTRIBUTOR IN BIODEGRDABLE UREA FERTILIZER

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka (UTeM) as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material). The member of the supervisory committee is as follow:

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ABSTRAK

Objektif kajian ini adalah untuk menyiasat potensi ENR dalam penghasilan baja terbiodegradasi urea berasaskan kitosan. Dalam kajian ini, campuran kitosan dan getah asli terepoksida (ENR) digunakan sebagai pengikat untuk memanfaatkan sifat biodegradasi dan ciri hidrofobik masing-masing. Kesan formulasi terhadap sifat baja yang terhasil dikaji secara terperinci di dalam kajian ini. Terlebih dahulu, kitosan dan ENR dicairkan di dalam cecair toluena dengan kehadiran bentonit sebagai pengisi. Setelah pengelatinan, serbuk urea dicampurkan dan dikacau sehingga homogen dalam jangka masa 20 minit kemudian dituang ke dalam piring petri untuk dikeringkan di dalam ketuhar pada suhu ~60°C semalaman. Acuan digunakan untuk memadatkan campuran dengan menggunakan penekan hidraulik untuk mendapatkan saiz dan bentuk yang dikehendaki. Selepas pemprosesan, sifat fizik dan mekanik baja diuji melalui penentuan ketumpatan, ujian biodegredasi, ujian penyerapan air, ujian pengekalan air, ujian kekerasan dan ujian mampatan. Akhirnya, baja dianalisis untuk sifat terma, sifat kimia dan morfologi dengan menggunakan permeteran kalori pengimbasan kebezaan (DSC), pembelauan sinar-X (XRD), spektroskopi penjelmaan Fourier infra-merah (FTIR), serakan tenaga sinar-X (EDX) dan kemikroskopan elektron imbasan (SEM). Diakhir ujikaji ini, didapati peningkatan amaun ENR dapat mengurangkan kadar penyerapan air ke dalam baja melalui pemampasan sifat hidrofilik kitosan. Campuran 10pph ENR didalam kitasan berasaskan baja urea menghasilkan baja urea terbiodegradasi yang mempunyai ketumpatan sebanyak1.128g/cm^3, manakala penyerapan air adalah sebanyak -7.73% dan pengekalan air sebanyak 95.9%. Kekuatan mampatan dan kekerasan urea-ENR10 juga adalah paling rendah dengan masing-masing hanya0.559MPadan 39.53 Shore D. Akhir skali,dengan kehadiran ENR tahap biodegradasi baja urea yanglebih perlahan dapat dihasilkan. Ia diramal dapat meningkatkan prestasi pembebasan nitogen ke persekitaran untuk baja pembebasan perlahan pada masa akan datang.

ABSTRACT

The objective of this research is to investigate the potential of ENR in preparation of chitosan based urea fertilizer. In this research, mixture of chitosan and epoxidized natural rubber (ENR) was used as binder to take advantage of their biodegradable and hydrophobic characteristics, respectively. The effect of mixing formulation to the properties of fertilizer was studied in detail. Firstly, the chitosan and ENR was diluted in toluene with the presence of bentonite as filler. After gelatinization, the urea powder was mixed and stirred until homogenous for 20 minutes. Then, the gelatin was poured into a petri dish and left to dry in an oven at 60°C overnight. Then, it is put in a mold and compressed using a hydraulic presser to obtain the desired size and shape. After processing, the physical and mechanical properties of the fertilizer was determined through density measurement, biodegradability test, water absorption test, water retention test, hardness test and compression test. Finally, the fertilizer was analyzed for thermal, chemical and morphological properties by using differential scanning calorimetry (DSC), X-ray Powder Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Energy Dispersive X-ray (EDX) and scanning electron microscopy (SEM). At the end of this research, it has been found the incorporation of ENR in biodegradable chitosan based urea fertilizer has imparted the properties biodegradable properties to the ENR/chitosan based urea fertilizer. A mixture of 10pph ENR in chitosan based urea fertilizer produced biodegradable urea fertilizer with density low density of 1.23g/cm^3 where as water absorption and water retention was -7.73 % and 95.9% respectively. The compressivestrength and hardness of this sample werethe lowestwith only 0.559 MPa and 39.53 Shore D, respectively. Finally, with the presence of ENR slower biodegradability level of urea fertilizer was produced. It ispredictedto improve the performance of nitrogen release to surrounding for future slow release fertilizer.

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LIST OF ABBREVIATIONS

ENR	-	Epoxidised natural rubber
N	-	Nitrogen
P	-	Phosphorus
K	-	Potassium
C	-	Carbon
O	-	Oxygen
H	-	Hydrogen
Ca	-	Calcium
Mg	-	Magnesium
S	-	Sulphur
DSC	-	Differential scanning calorimetry
T_g	-	Glass transition temperature
FTIR	-	Fourier transform infrared
SEM	-	Scanning Electron Microscopy
SRF	-	Slow-release fertilizer
CRF	-	Control release fertilizer
IBDU	-	Isobutydine diurea
CO_2	-	Carbon dioxide
UF	-	Urea formaldehyde
PUFs	-	Polyurethane foams
$(NH_4)_2SO_4$		Ammonium sulphate
ASTM		The American Society for Testing of Materials
ISO	-	The International Standards Organization
NR	-	Natural rubber
AM	-	Acrylamide

LIST OF SYMBOL

ms^{-1}	-	Meter per second
%	-	Percentage
kW	-	Kilo Watt
min	-	Minute
kg	-	Kilogram
mm	-	Millimeter
μm	-	Micrometer
kN	-	Kilo Newton
MPa	-	Megapascal

CHAPTER 1
INTRODUCTION

1.1 Background

Fertilizers are chemical compounds applied to promote plant and fruit growth (Bahera *et al.*., 2009). According to Akelah *et al.* (1996), fertilizers are one of the most important products of the agrochemical industry. They are added to the soil to release nutrients necessary for plant growth. Artificial fertilizers are inorganic fertilizers formulated in appropriate concentrations and the combinations supply three main nutrients: nitrogen, phosphorus and potassium (N, P and K) for various crops and growing conditions. N (nitrogen) promotes leaf growth and forms proteins and chlorophyll. P (phosphorus) contributes to root, flower and fruit development. K (potassium) contributes to stem and root growth and the synthesis of proteins (Mandal *et al.* and Gu *et al.* 2009).

El- Rafie *et al.* and Byung *et al.* (1996) has found method of reducing nutrient losses involves the use of controlled-release fertilizers. These fertilizers can be physically prepared from the granules of the soluble fertilizers by coating them with materials, which reduce their dissolution rate. Meanwhile, slow release fertilizers are made to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. These fertilizers can be physically prepared by degradability coating granules of conventional fertilizers with various materials that reduce their dissolution rate (Ge *et al*. 2002).

Therefore, this project is intended to study the potential of epoxidized natural rubber (ENR) as hydrophobic contributor in biodegradable urea fertilizer. The formaldehyde was replaced with the mixture of ENR and chitosan as hydrophobic and biodegradable contributor, respectively. A fertilizer granule was produced through compaction and drying process. Then, the granule was characterized for physical, mechanical, thermal, chemical, phase and morphological properties.

1.2 Problem Statement

In urea fertilizer, some percentage of nutrients consist of nitrogen (N), phosphorus (P) and potassium (K) is lost to the environment and cannot be absorbed by plants, causing not only substantial economic and resource losses but also very serious environmental pollution. The losses are due to leaching, decomposition and ammonium volatilization in soil, handling and storage (Trenkel *at al*. (1997) and Saigusa *et al*. (2007).

Recently, the use of slow release fertilizers has become a new trend to save fertilizer consumption and to minimize environmental pollution (Wu *et al*., 2008 and Guo *et al*., 2005). Due to its polymeric cationic, biodegradable, bioabsorbable, and bactericidal characteristics, chitosan (CS) nanoparticle is an interesting material for use in controlled release systems. However, there are limited to explore the potential of chitosan nanoparticles as slow and control release for NPK fertilizers. This brings out the idea of developing biodegradable fertilizer base chitosan as binder and hydrophilicty controller.

Over the last years, there has been research and increasing interest in the use of polymers combining with starch as binder and coating material as a potential biodegradable fertilizer. According to Liu *et al*. (2007), there is a research in improving properties of fertilizer with controlled release and water retention by using chitosan-coated fertilizer polyacrylic-co-acrylamide (P (AA-co-AM) with controlled release and water retention which possessed three layer structure of fertilizer. Therefore, although the control release property has been improved, but after the coating layer is dissolved, the nutrient fertilizer

in its core will degrade. Hence, due to increase in water absorbency, the degradation of fertilizer will become faster after the coated layer dissolve completely. According to Riyajan *et al*. (2012), natural rubber (NR) has potential for controlling urea release. The hydrophobic group of encapsulation of urea fertilizer by NR can control releasing nutrient from capsule and easily degrade to soil. Epoxidized Natural Rubber (ENR) is chemically modified from NR to improve hydrophilicity of NR. However, there is no study in incorporated this ENR in urea fertilizer as control and slow release fertilizer.

In addition, formaldehyde is the material that gives reaction when the elevated level is reached. The dangerous chemical will emit into the air. This can causes watery eyes, nose irritations, wheezing and coughing, fatigue, skin rash, severe allergic reactions, burning sensations in the eyes and throat, nausea, and difficulty in breathing in some humans. In this research, formaldehyde is widely found use in agricultural technology as non-biodegradable binder. Recently, due to many reports of formaldehyde affect to health and environment there are only few studies focuses on the effect of formaldehyde based on urea fertilizer in agriculture; especially in Malaysia. Controlled studies have suggested that tolerance to formaldehydes odour and irritating effects can occur over a prolonged exposure (Meriat *et al.*, 2008). By replacing formaldehyde with biodegradable and free chemical reaction is purposely suggested.

In this research, the incorporation of ENR in biodegradable chitosan based urea fertilizer is hypothesized to impart the biodegradable properties to the ENR/chitosan based urea fertilizer. The introduction of epoxirane ring with existing double bonds in the ENR will act as hydrophobic contributor and chitosan as hydrophilic controller to accelerate the degradation process at a certain time that accomplices with nutrient needed by plant. In principle, the slow and control release with hydrophobicity properties could be significantly improve. To increase the binding energy ENR and chitosan was incorporated in the mixture. ENR is well known as an ideal material for biodegradable type which important to increase the reaction between chitosan and urea. As a result, this research is hoped can formulate and develop into new potential products besides it capable reducing level of formaldehyde releasing to the environment.

1.3 Objective

The aim of this research is to understand the specific cause and effect of formaldehyde based urea fertilizer characteristics and able to understand the properties, structure and effect of biodegradable urea fertilizer on water, soil and air. The objectives of this research are:

i. To incorporate ENR in biodegradable chitosan based urea fertilizer through wet mixing and compression molding.

ii. To study the effect of ENR loading on the physical, mechanical, compositional, morphological and thermal properties of chitosan based biodegradable urea fertilizer.

iii. To characterize the physical, mechanical, compositional, morphological, and thermal properties of ENR/chitosan based urea fertilizer.

1.4 Scope

The scope of this research is to study the effect of ENR in biodegradable urea fertilizer as hydrophobic contributor. ENR/chitosan based urea fertilizer is produced by wet mixing followed by drying and compaction to desired shape where ENR loading is varied in the formulation composition of urea fertilizer. Material testing is performed to measure the physical and mechanical properties in term of density, water absorption, water retention, biodegradability, hardness and compression. The properties of urea fertilizer is further characterized by using morphological, thermal and compositional analysis of the sample using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), x-ray diffraction (XRD), and fourier transform infrared spectroscopy (FTIR).

1.5 Chapter Overview

The organization of this report is as follow; Chapter 1 provides the introduction of the research background consist of problem statement, objectives, scopes of research and report organization. Chapter 2 comprise of a literature review of previous research finding on application of, chitosan, epoxidised natural rubber (ENR), slow and control released fertilizer and many more in fertilizer and the preview of testing and analysis that conducted in this research. Chapter 3 covers the methodology of the research including flow chart, raw materials, sample preparation, testing, analysis and Gantt chart where as Chapter 4 presents the comprehensive discussion on the results obtained throughout the study. Conclusion and recommendation experimental of this study is presented in Chapter 5.

CHAPTER 2
LITERATURE REVIEW

2.1 Fertilizer

Fertilizer is a chemical compound containing three elements which are nitrogen (N), phosphorus (P) and potassium (K). It is added to soil to release nutrients which are essential for growth and development of crops. There are various type of fertilizer either organic or inorganic fertilizers (Papangkorn *et al.*, 2008). Cardarelli (2000) has stated that fertilizers are natural or synthetic chemical compound chemical compounds containing nutrients essential for the normal growth and development of plants. As a general rule, all carbon (C) and oxygen (O) necessary to the plants are provided, via photosynthesis, from carbon dioxide and oxygen gases from the atmosphere while rain and ground waters supply all the hydrogen (H) required. All other nutrients which are N, P and K must be transformed from minerals and organic matter, by microorganisms respectively, before becoming available for plants. The most important fertilizers are fertilizer product which also is called as chemical or mineral fertilizers, manures and plant residues. A fertilizer product is a material produced by industrial processes with the specific purpose of being used as a fertilizer. Fertilizers are essential in today's agricultural system to replace the elements extracted from the soil in the form of food and other agricultural products (Rutland *et al*., 1998).

In practice, either industrial minerals or chemicals are currently used as feedstock's for manufacturing fertilizers and hence it is necessary to distinguish two groups which are mineral fertilizers and chemical fertilizers. Mineral fertilizers that consist mainly of

natural or manufactured industrial minerals such as saltpetre, potash, and phosphate rock meanwhile chemical fertilizers that are chemical commodities, such as ammonia and urea, produced as products or by-product by the chemical industry (Cardarelli, 2000). The N-P-K descriptions are presented in Table 2.1.

Table 2.1: N-P-K description (Materials Handbook: A Concise Desktop Reference, 2000)

Nutrients	**Description**
Nitrogen (N)	Plant intake nitrogen compound are converted into proteins by complex biochemical reaction. For improving the nitrogen intake of crops, nitrogen rich feed stocks must be added to soils artificially. Today, the major industrial minerals used as nitrogen rich feedstock such as, saltpetre (KNO_3), soda nitre ($NaNO_3$), urea (NH_2CONH_2), urea formaldehyde ($NH_2CONHCH_2OH$) and many more. Important because it promotes vigorous plant growth, increases top growth, and is a building block for protein.
Phosphorus (P)	The least used major nutrients. The role of phosphorus in cell of plant is to provide chemical energy which is stored within the strong phosphorus chemical bond. The behaviour of phosphorus is unique in soils as it is usually bound to clay minerals and does not move downward with percolating ground waters and hence accumulates in the top soil. The major phosphorus rich materials are synthetic chemicals obtain from chemical treatment of phosphate rock that is mainly apatite by concentrated sulphuric acid. Promotes cell division and stimulates healthy root growth and is essential for seed germination.
Potassium (K)	It is indispensable as a nutrient and it is required in large quantities by most plants. The role of potassium in plants is regulatory and catalytic. Growing plants absorb potassium as potassium cations K^+ but the metabolic route is unclear. The major industrial mineral used as potassium feedstock is sylvinite (KCl) also known as muriate of potash. Potash is an essential nutrient for photosynthesis which also promotes fruit formation and imparts disease resistance and winter hardiness.