



PREPARATION AND CHARACTERIZATION OF NATURAL
RUBBER/CHITOSAN BIODEGRADABLE UREA FOR SLOW
RELEASE FERTILIZER

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MASTER OF SCIENCE
IN MANUFACTURING ENGINEERING

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Faculty of Manufacturing Engineering

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FERTILIZER**

NOR NADIAH BINTI ABDUL HAMID

**A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
in Manufacturing Engineering**

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2016

DECLARATION

I declare that this thesis entitled “Preparation and Characterization of Natural Rubber/Chitosan Biodegradable Urea for Slow Release Fertilizer” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

Name : Nor Nadiah Binti Abdul Hamid

Date : 5th October 2016

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature :

Name : Dr. Noraiham Binti Mohamad

Date : 5th October 2016

ABSTRACT

Chitosan and natural rubber are highly potential materials to be blended together in urea fertilizer for slow release properties due to its gel forming ability and hydrophobicity, respectively. This study investigates the potential of chitosan and natural rubber incorporation to replace formaldehyde in urea fertilizers. On the first stage, the effect of chitosan content and gelatinization temperature on physical properties of chitosan based urea fertilizer were studied. The chitosan content was varied from 0, 3, 5, 7 and 10 pph at two different mixing temperatures (gelatinization temperature) which are 60°C and room temperature of $25 \pm 3^\circ\text{C}$. Chitosan based urea fertilizer was prepared through a direct wet mixing using laboratory set up consist of beaker, magnetic stirrer and hotplate. Subsequently, the mixture was then dried in an oven at 60°C for 8 hours and compacted into pellets form for further testing and analyses. For the first stage, gelatinization process at room temperature was observed to produce samples which exhibited better water absorption and water retention capability than the one gelatinized at 60°C. The results were supported by XRD analyses. In this study, the formulations which showed good balance between water absorption and water retention was chitosan based urea fertilizer filled with 3 to 7 pph chitosan content. Both gelatinization temperatures produced fertilizer with significant crystallinity in its structure. In overall, gelatinization process at room temperature indicates better performance as well as cost effective. The next stage was performed to investigate the potential of natural rubber (NR) as hydrophobicity contributor to the chitosan based urea fertilizer. In this stage, constant chitosan content at 5 pph was used to be incorporated with NR for preparation of binder. The NR content was varied from 0, 3, 5, 7 and 10 pph. In this stage, chitosan and NR were diluted in toluene with the presence of bentonite as filler. Testing for water absorption, water retention, soil burial degradation, hardness and compression test were carried out. The findings were supported by Fourier Transform Infrared analysis, Differential Scanning Calorimetry (DSC) analysis, X-ray Diffraction (XRD) as well as Scanning Electron Microscopy (SEM). Based on ranking method, it was proven that, chitosan based urea fertilizers with the highest content of natural rubber (10phr) shows the highest rank desired for the characteristics needed. Fertilizer with 5 pph chitosan and 10 pph NR exhibited the highest water absorption capability, the highest water retention ability, appreciable compression strength and hardness as well as the slowest rate in soil burial degradation. Uniform distribution of NR-chitosan rich domains in the fertilizers depicted improvement in encapsulation of urea particles for fertilizers with 10 pph NR loading if compared to the fertilizer without NR. This study had proven the potential of chitosan and natural rubber in replacing formaldehyde for agriculture urea fertilizers.

ABSTRAK

Kajian ini mengkaji potensi kitosan dan getah asli untuk menggantikan formaldehid dalam baja urea. Pada peringkat pertama, kesan kandungan kitosan dan suhu penggelatinan terhadap ciri fizik baja urea berasaskan kitosan dikaji. Kandungan kitosan telah diubah dari 0, 3, 5, 7 dan 10 pph pada dua suhu pencampuran berbeza (suhu penggelatinan) iaitu pada 60 °C dan suhu bilik 25 ± 3 °C. Baja urea berasaskan kitosan telah disediakan melalui pencampuran basah langsung menggunakan kelengkapan makmal yang terdiri daripada bikar, pengacau magnet dan plat panas. Selepas itu, campuran itu kemudian dikeringkan dalam oven pada 60 °C selama 8 jam dan dipadatkan menjadi bentuk pelet untuk ujian lanjut dan analisis. Untuk peringkat pertama, proses penggelatinan pada suhu bilik diperhatikan menghasilkan sampel yang mempamerkan keupayaan penyerapan air dan pengekatan air yang lebih baik daripada yang digelatinkan pada 60 °C. Keputusan ini telah disokong oleh XRD analisis. Dalam kajian ini, formula yang menunjukkan keseimbangan yang baik antara penyerapan air dan pengekatan air adalah baja urea berasaskan kitosan yang diisi dengan 3-7 pph kandungan kitosan. Kedua-dua suhu penggelatinan menghasilkan baja dengan tahap penghabluran yang bererti dalam strukturnya. Secara keseluruhannya, proses penggelatinan pada suhu bilik menunjukkan prestasi yang lebih baik dan juga kos efektif. Peringkat seterusnya dijalankan untuk menyelidik potensi getah asli (NR) sebagai penyumbang sifat tidak suka air terhadap baja urea berasaskan kitosan. Pada peringkat ini, kandungan kitosan malar pada 5 pph digunakan untuk digabungkan dengan getah asli untuk penyediaan pengikat. Kandungan getah asli diubah dari 0, 3, 5, 7 dan 10 pph. Pada peringkat ini, kitosan dan getah asli telah dicairkan dalam toluena dengan kehadiran bentonit sebagai pengisi. Ujian untuk penyerapan air, pengekatan air, pereputan melalui pengambusan tanah, kekerasan dan ujian mampatan dijalankan. Hasil kajian tersebut telah disokong oleh analisis Fourier Transform Infrared, analisis Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) dan juga Kemikroskopan Elektron Imbasan (SEM). Berdasarkan kaedah kedudukan, ia telah membuktikan bahawa, baja urea berasaskan kitosan dengan kandungan tertinggi getah asli (10pph) menunjukkan kedudukan tertinggi yang dikehendaki untuk ciri-ciri yang diperlukan. Baja dengan 5 pph kitosan dan 10 pph NR mempamerkan penyerapan air paling tinggi, keupayaan pengekatan air yang paling tinggi, kekuatan mampatan dan kekerasan yang bererti serta kadar pereputan paling perlahan dalam pengambusan tanah. Taburan seragam domain yang kaya dengan NR-kitosan dalam baja menunjukkan peningkatan pengkapsulan zarah urea dalam baja yang mempunyai 10 pph NR jika dibandingkan dengan baja tanpa getah asli. Kajian ini berjaya membuktikan potensi kitosan dan getah asli dalam menggantikan formaldehid untuk baja urea pertanian.

DEDICATION

To my late father, Abdul Hamid Bin Aman, my mother, Jorah Binti Hasim, siblings and friends. Your love is my driving force.

To my supervisor, Dr Noraiham Binti Mohamad, your guidance is enlightenment to me.

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LIST OF ABBREVIATIONS

%	-	percent
°C	-	degree celsius
AM	-	acrylamide
ASTM	-	American Society for Testing and Materials
C	-	carbon
CBUF	-	Chitosan Based Urea Fertilizer
cm	-	centimeter
CRF	-	controlled release fertilizer
DSC	-	Differential Scanning Calorimetry
EDX	-	Energy-Dispersive X-ray Spectroscopy
ENR	-	Epoxidized Natural Rubber
FTIR	-	Fourier Transform Infrared Spectroscopy
g	-	grams
IFA	-	International Fertilizer Industry Association
ISO	-	International Organization for Standardization
K	-	potassium
kBr	-	potassium bromide
mg	-	milligram
ml	-	milliliters
MSDS	-	Material Safety Data Sheet
N	-	Newton
N	-	nitrogen
NO ₃	-	nitrate
NR	-	natural rubber
O	-	oxygen
P	-	phosphorus
pph	-	part per hundred

pphr	-	part per hundred rubber
ppm	-	part per million
PSA	-	Particle Size Analyzer
PUFs	-	polyurethane foams
PVA	-	polyvinyl alcohol
SBR	-	styrene-butadiene rubber
Sec	-	second
SEM	-	Scanning Electron Microscopy
SRF	-	slow release fertilizer
STR5L	-	Standard Thai Rubber
TA	-	Thermal Analysis
T _m	-	melting temperature
WA	-	water absorption
WL	-	weight Loss
WT	-	gelatinization temperature
XRD	-	X-ray Diffraction
XT	-	gelatinization in room temperature
ΔC _p	-	heat capacity
ΔH	-	enthalpy changing
μm	-	micrometer

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CHAPTER 1

INTRODUCTION

1.1 Background

Fertilizers are chemical compounds applied to promote plant and fruit growth. 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 (Thembakazi et. al., 2015).

Reducing nutrient losses involves the use of controlled-release fertilizers (El-Diwani et. al., 2013). 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 (Shaviv, 2001).

Biodegradability becomes a key factor in fertilizer's technology towards a sustainable agriculture. Biodegradation is a natural process by which organic chemicals in

the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles by micro-organisms activity (Chandra and Rustgi, 1998). Biodegradable polymer binder is new promising candidate to be used as replacement of formaldehyde as anti-caking and slow release agent in fertilizers industry. Although there are large numbers of available synthetic biodegradable polymer binders in the market such as polyethylene glycol, polycaprolactam, polyvinyl alcohol, poly(lactide-co-glycolide) and etc however, it is less practical to be used in agriculture products due to expensive prices.

Chitosan is a natural biodegradable based polysaccharide with amine groups. It is a highly deacetylated derivative of chitin, one of the most abundant natural and biodegradable polymers that have been widely applied in the biomedical, pharmaceutical, and agricultural fields. In many of these applications, chitosan is attractive due to its biodegradability, biocompatibility, and non-toxicity (Wu et. al., 2008; El-Sawy et. al., 2010). According to Lubkowski and Grzmil (2007), chitosan is one of unique materials which easily undergo biodegradation in natural environment, highly biocompatible and having unique polycationic properties (Lubkowski and Grzmil, 2007).

Natural rubber has superior and unique mechanical properties. Natural rubber can be used for controlling urea release in fertilizer system. Therefore, this project is intended to study the potential of natural rubber (NR) as hydrophobic contributor in biodegradable urea fertilizer. The formaldehyde was replaced by the mixture of NR and chitosan as hydrophobic and biodegradable contributor, respectively. Fertilizer granules were produced through compaction and drying process. Then, the granules were 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 (Lal et. al., 1994).

Urea formaldehyde are examples of synthetic organic fertilizer compounds and slowly soluble. Urea and formaldehyde was not totally one complete reaction. Mixture of urea and formaldehyde contains combination of unreacted urea, short and long chain methylene polymers, and other trace compounds (Booze-Daniels, 1997). Formaldehyde is a highly reactive one-carbon compound. It has a characteristic odor in air in the 0.1-1.0 ppm concentration range. In the presence of water, formaldehyde will reacts with the active hydrogen of many compounds such as ammonia, amines, amides, thiols, phenols and nitro-alkanes, and condenses with hydrogen chloride in the presence of water to form chloromethyl ether, which is all of these reaction are known as carcinogen in humans and also animals (James, 2004; Hamdi, 2001).

Formaldehyde is known to cause watery eyes, burning sensations in the eyes, nose and throat, nausea, coughing, chest tightness, wheezing, skin rashes and allergic reactions to humans once exposed at certain level. Its presence could affect people differently. Some people are very sensitive and some people may not get any reaction at the same level. It is reported that in the worst case formaldehyde can cause nasal cancer when human exposed to a significant high amount of formaldehyde (James, 2004; Hamdi et. al., 2001). Recently, formaldehyde is widely used in agriculture technology as a non-biodegradable binder. It can dissolve in water and is leach through the soil. Retention of this highly toxic substance

has high potential to kill most of the soil organisms (Hermery, 1980; Committee on Toxicology, 1980)

Formaldehyde is toxic and also used as seed disinfectants to kill most bacteria and fungi in agricultural. Formaldehyde will be leached through the soil and kill most of organisms inside the soil (Hermery, 1980). Furthermore, most of applied fertilizer on the ground would be lost to environment and results to contamination of water. During leaching to groundwater, some nutrient in fertilizer will convert to gas and escape to atmosphere (Hamdi et. al., 2001). One of the element which escapes to the atmosphere is formaldehyde in fertilizer.

Despite many reports of formaldehyde effects on health and environment there are only limited studies focusing on the effect of formaldehyde based on urea fertilizer in agriculture especially in Malaysia.

Biodegradable polymers are a newly emerging field. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have been identified. In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions. As a result, attempts have been made to solve these problems by including biodegradability into polymers in everyday use through slight modifications of structures. Biodegradation is a natural process by which organic chemicals in the environment are converted to simpler compounds, mineralized and redistributed through elemental cycles such as the carbon, nitrogen and sulphur cycles. Biodegradation can only occur within the biosphere as microorganisms play a central role in the biodegradation process (Chandra et. al., 1998).

Recently, the use of slow release fertilizers has become a new trend to save fertilizer consumption and to minimize environmental pollution (Wu et. al., 2008a and Guo et. al., 2005). Due to its polymeric cationic, biodegradable, bio absorbable, and bactericidal

characteristics, chitosan nanoparticle is an interesting material for use in controlled release systems. However, there are no attempts to explore the potential of chitosan nanoparticles as controlled release for NPK fertilizers. This brings out the idea of developing chitosan as binder and hydrophilicity controller in biodegradable fertilizer.

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 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 slow 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.

In this research, the incorporation of NR in biodegradable chitosan based urea fertilizer are hypothesized to impart the biodegradable properties to the NR/chitosan based urea fertilizer. The introduction of isoprene chains in the NR will act as hydrophobic contributor and chitosan as hydrophilic controller to accelerate the degradation process for a certain time that accomplices with nutrient needed by plant. In principle, the slow and control release with hydrophobicity properties could be significantly improve. NR is well known as a good material for biodegradable type which important to increase the reaction between chitosan and urea. As a result, this research is an alternative step to formulate and