การควบคุมการปลดปล่อยปุ๋ยยูเรียโดยการเคลือบสารไบโอพอลิเมอร์

นางสาวสิริมา พิณเพียงจันทร์

วิทยานิพนธ์เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเทคโนโลยีชีวภาพ
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2555

CONTROLLED-RELEASE UREA FERTILIZER BY BIOPOLYMERIC ENCAPSULATION

Sirima Pinpeangchan

A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Science in Biotechnology

Suranaree University of Technology

Academic Year 2012

CONTROLLED-RELEASE UREA FERTILIZER BY BIOPOLYMERIC ENCAPSULATION

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master’s Degree.

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สิริมา พิณเพียงจันทร์ : การควบคุมการปลดปล่อยปุ๋ยยูเรียโดยการเคลือบสารไบโอพอลิเมอร์ (CONTROLLED - RELEASE UREA FERTILIZER BY BIOPOLYMERIC ENCAPSULATION) อาจารย์ที่ปรึกษา : รองศาสตราจารย์ ดร.โชคชัย วนภู, 114 หน้า.

ไนโตรเจนเป็นธาตุที่สำคัญที่สุดสำหรับพืช แต่มากกว่า 60% ของธาตุไนโตรเจนมีการสูญเสียในระหว่างการใช้งานของเกษตรกร การใช้ไบโอพอลิเมอร์มาเป็นวัสดุเคลือบปุ๋ยได้รู้จักแพร่หลายในการศึกษาทางการเกษตรมาเป็นเวลาหลายปี และมีความพยายามที่จะนำมาใช้เป็นสารควบคุมการละลายของปุ๋ย การศึกษาในครั้งนี้มีวัตถุประสงค์เพื่อลดการสูญเสียธาตุไนโตรเจนจากปุ๋ยยูเรียโดยการเคลือบสารไบโอพอลิเมอร์ 2 ชนิดซึ่งแตกต่างกัน คือ สารโพลีไวนิลแอลกอฮอล์ (PVA) และโพลีไวนิลไพโรลิโดน (PVP) การเคลือบสาร PVA และ PVP สามารถทำได้โดยการพ่นสารละลายลงบนเม็ดปุ๋ยยูเรียในเครื่องหมุน จากการศึกษาการปลดปล่อยของปุ๋ยยูเรียหลังการเคลือบ (EUF) โดยใช้กฎของฟิกซ์ ซึ่งเป็นสมการทางคณิตศาสตร์เพื่ออธิบายพฤติกรรมการปลดปล่อยของยูเรีย โดยค่า n มีค่าอยู่ระหว่าง 0.5 ถึง 1.0 หมายถึงการปลดปล่อยเป็นแบบ non-Fickian diffusion วัสดุเคลือบทั้ง PVA และ PVP ถูกนำมาใช้ในอัตราส่วน 2:0 (EUF1), 1:0 (EUF2), 1:0.25 (EUF3), 1:0.5 (EUF4), 1:1 (EUF5), และ 1:2 (EUF6) ตามน้ำหนัก ผลการทดลองพบว่าค่า n มีค่าระหว่าง 0.86-0.98 แสดงถึงเป็นการปลดปล่อยเป็นแบบ strong non-Fickian diffusion ในขณะที่ปุ๋ยยูเรียที่ไม่ถูกเคลือบมีค่า n เท่ากับ 0.70 สรุปได้ว่าปุ๋ยยูเรียเคลือบทุกสูตรมีการปลดปล่อยธาตุอาหารได้เป็นเวลานานกว่าปุ๋ยยูเรียที่ไม่เคลือบ ผลจากการศึกษาลักษณะทางสัณฐานวิทยาโดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด พบว่า ลักษณะของวัสดุที่เคลือบผิวมีมากกว่าหนึ่งแบบ ได้แก่ ลักษณะแผ่น เข็ม และก้อน จากการศึกษาหมู่พันธะเคมีของตัวอย่างปุ๋ยเคลือบโดยใช้เครื่อง FT-IR พบว่าช่วงความยาวคลื่นของปุ๋ยยูเรียที่ถูกเคลือบใกล้เคียงกับปุ๋ยยูเรียที่ไม่ถูกเคลือบ เนื่องมาจากปริมาณของวัสดุเคลือบมีปริมาณน้อยกว่าตัวปุ๋ยยูเรียที่ถูกเคลือบ จากการศึกษาการเสียสภาพของเม็ดปุ๋ยเคลือบเนื่องจากความร้อนโดยวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารด้วยเทคนิค TGA พบว่าตัวอย่างปุ๋ยเคลือบทุกสูตรมีค่าการสูญเสียน้ำหนักโดยสามารถแบ่งงออกเป็น 3 ช่วงอุณหภูมิ ได้แก่ 140-200, 220-340 และ 350-480 องศาเซลเซียส ขั้นแรกของการสูญเสียน้ำหนักเกิดขึ้นในช่วงกว้างเริ่มต้นก่อนจุดหลอมเหลวของยูเรียที่ (132.5 องศาเซลเซียส) ขั้นที่สองเกิดช่วงอุณหภูมิการสลายยูเรียที่เหลือ ช่วงสุดท้ายเกิดการสลายที่อุณหภูมิสูงกว่า 350 องศาเซลเซียส ซึ่งทำให้โครงสร้างไฮดรอกซิลและอินทรีย์สารถูกกำจัด

จากแบบจำลองทางคณิตศาสตร์กฎของฟิกซ์ พบว่า ปุ๋ยเคลือบสูตร EUF2 และ EUF3 แสดงค่า n ที่สูงที่สุด จึงนำมาทดสอบการเจริญเติบโตของพืชโดยเปรียบเทียบกับ EUF6 ซึ่งแสดงค่า n

น้อยที่สุด โดยวางแผนการทดลองปลูกแบบสุ่มอย่างสมบูรณ์ในเรือนปลูกพืช โดยใช้ผักคะน้า (*Brassica alboglabra* Bailey) เป็นพืชทดสอบ ผลสรุปได้ว่า EUF2 และ EUF3 ให้ค่าน้ำหนักต้นสด น้ำหนักรากสด น้ำหนักต้นแห้ง และน้ำหนักรากแห้งสูงกว่าพืชที่ใช้ปุ๋ยยูเรียชนิดไม่เคลือบและชุดควบคุม นอกจากนี้ยังพบว่ามีการสะสมปริมาณไนโตรเจนที่สูงในพืชที่ใส่ปุ๋ยสูตร EUF2, EUF3, EUF6 และยูเรีย ในขณะที่ PVA, PVP และชุดควบคุม มีการสะสมไนโตรเจนปริมาณต่ำกว่า จึงสรุปได้ว่าปุ๋ยเคลือบสูตร EUF2, EUF3 และ EUF6 สามารถพัฒนาผลผลิตทางการเกษตรได้เนื่องจากมีการสะสมปริมาณธาตุไนโตรเจนที่สูงหรือช่วยลดการสูญเสียธาตุไนโตรเจน

สาขาวิชาเทคโนโลยีชีวภาพ ลายมือชื่อนักศึกษา_______________________

ปีการศึกษา 2555 ลายมือชื่ออาจารย์ที่ปรึกษา________________

SIRIMA PINPEANGCHAN : CONTROLLED - RELEASE UREA
FERTILIZER BY BIOPOLYMERIC ENCAPSULATION.
THESIS ADVISOR : ASSOC. PROF. CHOKCHAI WANAPU, Ph.D., 114 PP.

BIOPOLYMER/CONTROLLED RELEASE/ENCAPSULATION/UREA FERTILIZER

Among plant nutrient elements, N is the most important but more than 60% is lost when farmers apply it into soil. Biopolymers have been an emerging field of study in agriculture for many years which are used as fertilizers coating. In this study, biopolymers were used as a nutrient release-controlling material. Urea fertilizer was coated with two different types of biopolymers, which are polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP). These biopolymers can reduce the loss of nitrogen from coated fertilizer. The urea granules were sprayed with PVA and PVP solutions in a rotary drum, by varying the ratios per mass 2:0 (EUF1), 1:0 (EUF2), 1:0.25 (EUF3), 1:0.5 (EUF4), 1:1 (EUF5), and 1:2 (EUF6), respectively. To understand the release of the nutrient in the encapsulated urea fertilizer (EUF), a mathematical model of Fick's law was used to predict the releasing behaviors. The *n* value from 0.5 to 1.0 is a mechanism of nutrient release for non-Fickian diffusion. The results showed that the predicted *n* values of 0.86-0.98 illustrated a strong non-Fickian diffusion while un-coated urea was 0.70. It could be concluded that the high *n* value refers to the longer nutrient release that benefits plant absorption. The morphology of granules was observed by using scanning electron micrographs, which illustrated the characteristics of coating materials. It was found that there were more than one form, including plates, needles, and bundles. Determination of the chemical functional groups in the sample was performed using FT-IR spectroscopy. The spectrum of the blend was similar to the spectrum of urea. This might be because the amount of coating materials was markedly smaller than that of solid pure urea. Thermal stability and degradation steps of samples were analyzed by TGA technique. It was found that all of the samples displayed three major weight loss stages at 140-200, 220-340, and 350-480°C. The first stage was a wide scale weight loss that starts before the melting point (132.5°C). The second stage was fast thermal decomposition for urea residue. In the final stage at above 350°C, the structures of hydroxyl and organic matter were eliminated.

According to the mathematical model of Fick’s law from previous experiment, EUF2 and EUF3 showed the highest *n* value, so they were used to evaluate plant growth parameters as compared with EUF6 which showed the lowest *n* value. Treatments were arranged in a completely randomized design in the greenhouse. The EUF2, EUF3, and EUF6 were used as the fertilizer for Chinese kale (*Brassica alboglabra* Bailey) cultivation. EUF2 and EUF3 showed the highest stem fresh weight, root fresh weight, stem dry weight, and root dry weight over plants with urea and the control. The high N accumulation in plant was found in EUF2, EUF3, EUF6, and urea, whereas PVA, PVP, and the control showed low N accumulation. This indicates that EUF2, EUF3, and EUF6 could improve agricultural yield due to high N accumulation or less N loss.

School of Biotechnology　　Student’s Signature____________________

Academic Year 2012　　Advisor’s Signature____________________

ACKNOWLEDGMENTS

First of all, I would like to express my sincere thanks to my thesis advisor, Assoc. Prof. Dr. Chokchai Wanapu for him invaluable help and constant encouragement throughout the course of this research. I am most grateful for his teaching and advice, not only the research methodologies but also many other methodologies in life and money also. I would not have achieved this far and this thesis would not have been completed without all the support that I have always received from him.

In addition, I am grateful for the teachers of biotechnology: Prof. Dr. Nantakorn Boonkerd, Asst. Prof. Dr. Sodchol Wonprasaid, crop production of technology and others person for suggestions and all their help.

I wish to express my gratitude to officers in F1, F2, F3 and F5 building for their kind. I also thank my colleagues in School of Biotechnology (especially, Dang, Nut, Bom, Rong, Doi, Wha and Guy) and School of Crop Production for help my work (especially, Jom). This project could not complete without help from them.

Finally, thank for destiny, power of heart from my lover and all of my driving force from other people.

Sirima Pinpeangchan

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LIST OF ABBREVATION

°C = degree Celsius

°C/min = degree Celsius per minute

µm = micrometer

ANOVA = Analysis of varience

c = concentration

cm^{-1} = per centimeter

cP = centipoises

D = diffusion coefficient

et al. = Et alia (and other)

EUF = encapsulated urea fertilizer

g = gram

g/kg = gram per kilogram

HCL = hydrochloric acid

IR = infrared

J = flux

K = potassium

K = release factor

kg/rai = kilogram per rai

length^2 time^{-1} = square length per time

M = mass

LIST OF ABBREVATION (Continued)

m = meter

m^2/s = square meter per second

mg = milligram

mg/kg = milligram per kilogram

min = minute

mL = milliliter

mL/min = milliliter per minute

mm = millimeter

mol/m^3 = mole per cubic meter

mS/cm = milli-Siemens per centimeter

n = release exponent

N = nitrogen

nm = nanometer

OM = organic matter

P = phosphorus

s = second

t = time

T_g = glass transition temperature

w = weight

wt% = percent of weight

x = length

ρ = fluid density

CHAPTER I

INTRODUCTION

1.1 Significance of the study

The growth of plant depends on the soil condition, quantity of water, as well as mainly a function of the quantity of fertilizer. Therefore, it is very important to improve the utilization of plant nutrients. Fertilizers are main factors that limit the development of agricultural production, which is very important to improve the utilization of mineral nutrients. Nitrogen is the most vital nutrient for crops. It has been considered the yield limiting one. Among the nitrogen fertilizers, urea is the most widely used in the crops as well as its high nitrogen content (46%) and comparatively low cost for crop production.

However, consider leaching and hydrolyzing, the utilization efficiency or plant uptake of urea is generally less than 50%. About 40-70% of nitrogen of the applied fertilizer escapes to the environment and cannot be absorbed by crops (Dave et al., 1999; Guo et al., 2005; Liu et al., 2007). As a neutral organic molecule, urea cannot be absorbed easily by the charged soil particles before hydrolyzing, resulting in a great quantity of urea running off and serious environmental hazards as only a fraction is really absorbed by plants.

One possible of this problem is the encapsulation of fertilizer beads by membrane to control the diffusion of water, leach, and release of this fertilizer. Recently, the use of slow release fertilizers is new trend to save nutrient consumption and minimize environmental pollution (Akelah, 1996; Jarosiewicz and Tomaszewska, 2003).

Controlled-release fertilizers (CRFs) are made to control the rate of nutrient release as well as control the slow diffusion of nutrient ions through the membrane to the soil (Ahmed et al., 1963; Lunt and Orteli, 1962). CRFs for urea are made by coating some active soluble components materials as the membrane that serve as a diffusion barrier. Then, coating materials should be inexpensive and exhibit a good coating property. CRFs are made to release their nutrient contents gradually with the nutrient requirement of plant. These fertilizers can be physically prepared by coating granules of conventional fertilizers with various materials that reduce their dissolution rate. The releasing and dissolution rates of water-soluble fertilizers depend on the coating materials. At present, coating material’s degradability is an important focus on the research in this field because of the renewed attention towards environmental protection issues (Ge et al., 2002; Shavit et al., 2002).

Polyvinyl alcohol (PVA) has also been approved for using in controlled-release of fertilizer. PVA is valued for its solubility and biodegradability, which contributes to its very low environmental impact. PVA is a kind of excellent membrane material for preparation of a hydrophilic membrane that swells easily and even dissolves in water. One more kind of material, polyvinylpyrrolidone (PVP) using for water transferring through membrane, has been interested as a binder in granules of urea fertilizer for controlling pore size of coating substance. PVP polymer as a hydrophobicizer and stabilizer, can greatly improve membrane oxidative and chemical stabilities (Qiao et al., 2005). It has been extensively utilize and study in these form of its alone or mix for observed mixing behaviors and properties of the blends. Therefore, it seemed worthy of interest to prepare a new type of control release encapsulated urea fertilizer with their polymer.

1.2 Research objectives

The purposes of this study are as follows:

1.2.1 To apply biopolymer (polyvinyl alcohol and polyvinylpyrrolidone) for encapsulate urea fertilizer.

1.2.2 To determine the releasing rate of urea fertilizer by encapsulation technique.

1.2.3 To analyze the structural properties of encapsulated urea fertilizer (EUF).

1.2.4 To determine the efficiency of EUF on plant growth.

1.3 Research hypothesis

1. The hypothesis of this was to find a suitable coating material to control release of urea fertilizer using encapsulation technique.
2. The encapsulation technology could improve the efficiency of plant growth by preventing and decreasing loss of fertilizer.

1.4 Scope and limitation of the study

Biopolymers, polyvinyl alcohol and polyvinylpyrrolidone, were used in various formulations and concentrations for coating urea granules. Also the thickness, temperature, and stirring times of coating were observed. Structure and surface characteristics of the biopolymers of encapsulated urea fertilizer were observed by fourier transform infrared imaging, scanning electron microscopy and thermal gravimetric analysis. Afterward, the encapsulated urea fertilizer was examined the slow release behavior, and then applied them in soil for studying the plant growth.

1.5 Expected results

- Encapsulated urea fertilizer can reduce loss of fertilizer.
- The encapsulation can increase efficiency of urea fertilizer in agricultural field.

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CHAPTER II

LITERATURE REVIEWS

2.1 Controlled-release fertilizer (CRFs)

Fertilizers are generally classified in two groups, i.e. natural organic products and synthetic chemical products. Among the fertilizers widely applied for nitrogen delivery, one of the most interesting from an economic stand point is urea, $CO(NH_2)_2$, which high nitrogen (N) content (46 %) and comparatively low cost of production. Urea belongs to the synthetic group of fertilizers (Ramirez et al., 1997; Ramirez-Cano et al., 2001). Urea was first prepared by Friedrich Wöhler in 1828 by evaporating a solution containing a mixture of potassium isocyanate (CKNO) and ammonium sulphate ($(NH_4)_2SO_4$). Ammonium isocyanate (CH_4N_2O), which is formed first, undergoes molecular rearrangement to give urea, as shown by the following reaction:

$$NH_4NCO \leftrightarrow NH_3 + N–H=C=O \leftrightarrow (NH_2)_2CO$$

Urea may be prepared in the laboratory by interaction of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. In industry, urea is prepared by allowing liquid carbon dioxide and liquid ammonia to interact, and heating the formed ammonium carbamate at 130 ~ 150°C under about 35 atmospheric pressure (Tonn, 1955). The carbamate is decomposed to form urea and water according to the following reaction;

$2NH_3 + CO_2 \leftrightarrow NH2COONH_4$ (ammonium carbamate)

$NH_2COONH_4 \leftrightarrow H_2O + NH_2CONH_2$ (urea)

Urea is a physiologically important plant nutrient, which is transformed to nitrogenous product of protein metabolism. The symmetrical structure of urea is shown in Fig. 1. Urea has a melting point of 132°C, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-urea resin (plastics) (Feldman and Barbalata, 1996), barbiturates (Finar, 1973), and other formulated fertilizers (Rahman et al., 1994; George et al., 1997; Wang and Douglas, 1996; Yerokun, 1997). Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine (Heinig, 1996; Gnewuch and Sosnovsky, 1997; Miyagawa, 1986).

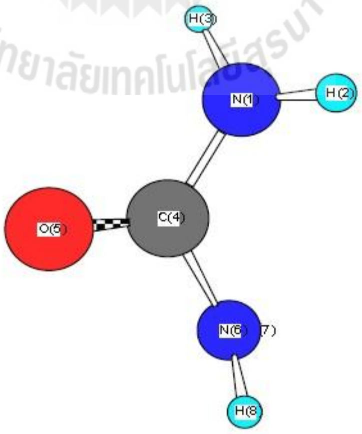

Fig. 1 Structure of urea (Ibrahim et al., 2012).

Urea, when applied to soil, is hydrolyzed by urease to NH_4^+ which is then oxidized to NO_3^- which can be leached or denitrified. To ensure a continuous and optimal supply of N, and to decrease losses, chemicals that retard either urea hydrolysis, or nitrification or both have been interested. Urea is rapidly hydrolyzed to ammonium carbonate through soil by urease activity, and if high concentration usage, the resulting accumulation of ammonium rises in pH which leads to several problems, including damage to germinating seedlings and young plants, nitrite toxicity, and gaseous loss of urea N as ammonia (Gasser, 1964).

One possible way to improve nutrient and particularly nitrogen use efficiency while reducing the environmental hazards is by using controlled release or slow release fertilizers (Hauck, 1985; Shaviv and Mikkelsen, 1993; Peoples et al., 1995; Bockman and Olfs, 1998; Shaviv, 1999). The terms of slow release fertilizers (SRFs) and controlled-release fertilizers (CRFs) are used throughout this review as a general description of fertilizers from which nutrient release into the environment occurs in a more or less slow and controlled manner. The term of CRFs recently became acceptable when applied to fertilizers in which the factors dominating the rate, pattern and duration of release are well-known and controllable during CRFs preparation (Shaviv, 1996). SRFs involve the release of the nutrient in a slower manner than common fertilizers. However, the rate, pattern and duration of release are not well controlled. They may be strongly affected by handling conditions such as storage, transportation and distribution in the field, or by soil conditions such as moisture content, wetting and drying, thawing and freezing, and biological activity (Goertz, 1995; Shaviv, 1996; Raban et al., 1997).

CRFs have been known for a several years. About 40-70 % of nitrogen of the applied normal fertilizer escapes to the environment and cannot be absorbed by crops, which causes not only large economic and resource losses but also very serious environmental pollution (Dave et al., 1999l; Guo et al., 2005; Liu et al., 2007). CRFs keep the nutrient concentration at effective levels in the soil and releases the fertilizer when the plant most needs it. Moreover, controlled-release technology offers a number of advantages in relation to crop production, including sustained correction of a mineral deficiency, decreased application frequency, and thus reduced cost of crop production. Decreased fertilizer loss dues to low leaching with concurrent minimization of environmental hazard (e.g. pollution of water courses), and possible reduction in the total amount of nutrient required because sustained rather than erratic supply was maintained. Additionally, the risk of salt injury to roots of young seedlings may be reduced.

In the following section, a detailed description of preparation methods is provided, with emphasis being placed primarily on the fertilizers that are common in practice such as organic-N compounds and the physically protected (coated forms) of CRFs.

2.1.1 Detailed description of CRFs

2.1.1.1 Organic-N compounds

The condensation of urea with aldehydes (and particularly with formaldehyde) is one of the most common methods for preparing SRFs. Urea formaldehyde (UF) is the most popular organic-N compound used for the slow release of nitrogen, and the most widely used of all SRF/CRFs (Trenkel, 1997; Shaviv, 1999). Typical UF products contain between 37 to 40% nitrogen. UF decomposition is mainly due to microbial action. The release of N from these compounds thus depends strongly on soil properties such as biological activity, clay content, pH, and external conditions such as moisture content, wetting and drying, and temperature (Alexander and Helm, 1990, Goertz, 1991; Aarnio and Martikainen, 1995; Trenkel, 1997).

Other urea-aldehyde and synthetic nitrogen compounds, for example, isobutylidene diurea (IBDU) is a condensate product of urea and isobutyraldehyde. It contains about 31% nitrogen of which 90% is water insoluble. The N release is claimed to be the result of chemical decomposition (hydrolysis), and thus its rate depends strongly (and inversely) on the particle size of the granular material and directly on soil moisture content. The hydrolysis is also pH and temperature dependent. Since the release of N from IBDU has little dependence on microbial activity, it occurs also at low temperatures (Goertz, 1991).

2.1.1.2 Coated Fertilizers

Fertilizers coated with non-organic coatings

Sulphur-coated urea (SCU) has been developed at the TVA (Tennessee Valley Authority) laboratories and manufactured commercially for almost 30 years (Landels, 1994). Its preparation is based on coating preheated urea granules with molten sulphur. Elemental sulphur, a low-cost secondary plant nutrient, was found to be convenient for coating due to its ability to melt at about 156°C, thus enabling spraying molten sulphur over granular urea and possibly on other fertilizers as well. The product contains between 31 to 38% N. After coating the urea with sulphur, a wax sealant is sprayed in order to seal cracks in the coating and reduce the microbial degradation of the sulphur coating (Allen et al., 1971; MaClellan and Scheib, 1973; Oertli, 1974; Jarrell and Boersma, 1980). The release of N from SCU depends on coating quality (Oertli, 1974). A typical population of SCU granules consists of three types of coatings (Jarrell et al., 1979): damaged coatings with cracks, damaged coatings whose cracks were sealed with wax, and perfect and thick coatings. SCU coated with a damaged coating immediately releases the urea when brought in contact with water.

Polymer coating of sulphur-coated fertilizers

Due to the relatively poor performance of the common SCU, several CRF manufacturers introduced a modified product in which the sulphur-coated fertilizer is coated by an additional thin layer of an organic polymer (thermoplastic or resin). A polymer-coated SCU is called a PSCU. According to Goertz (1995), the modified PSCU releases in the same way as common polymer-coated CRFs. The additional polymer layer was also intended to improve the attrition resistance of the coated granules. Indeed, the modified products showed a much better release behavior than the SCU. However, in comparing a PSCU with several polymercoated CRFs, Raban (1994) found that the PSCU had an initial "burst" of more than 20% of its content and a "tailing" of more than 30%.

Fertilizers coated with organic polymers

Resin-coated fertilizers are those whose coatings are commonly prepared by in-situ polymerization resulting in the formation of a cross-linked, hydrophobic polymer, usually classified also as thermosettic one (degrades upon heating). The two main families of common resins in practical use are the alkyd-type resins (e.g., Osmocote®) and polyurethanelike coatings (e.g., Polyon®, Plantacote® and Multicote®) (Trenkel, 1997). The first resin-coated CRFs to be commercially produce was the alkyd-type resin-coated fertilizer, Osmocote®. It was first produced in California in 1967. The alkyd-type resin is a copolymer of dicyclopentadiene with a glycerol ester (Lambie, 1987; Goertz, 1991). The control over nutrient release is achieved by varying the coating composition or thickness. Hauck (1985) described the release from Osmocote® as follows: water penetrates the coating through microscopic pores and increases the osmotic pressure within the coated core, thus stretching the coating. The stretching increases the micro-pores, enabling the release of nutrients through them. The alkyd-type coating provides good control over the resin's composition and thickness, making it possible to control the fertilizer's release rate and pattern. Typical formulations contain urea or compound N-P-K (at various ratios) with or without micro-elements. It can be applied to a large variety of granular or prilled fertilizer products.

The release of nutrients from these products is mainly temperature dependent (Christianson, 1988; Raban, 1994; Moore, 1995), while moisture content in the soil, pH, wetting or drying, and soil microbial activity have little effect on the release (Christianson, 1988; Moore 1995). This, however, is not unique to this type of coating and it is rather common with polymer coatings (resins and thermoplastic polymers).

Thermoplastic polymer-coated fertilizers

The most widespread technology used for coating granular fertilizers with thermoplastic materials such as polyethylene is by dissolving the coating material in a chlorinated hydrocarbon and spraying it on the granules in a fluidized bed reactor (Fujita et al., 1983, Fujita et al., 1989; Shoji and Gandeza, 1992; Fujita, 1995). Control over nutrient release is achieved by blending low-permeability polyethylene with a high-permeability polymer, such as ethylene-vinyl-acetate. Gandeza et al. (1991) claimed that improved control over temperature dependence of the release can be obtained by adding a mineral powder to the coating. It offers excellent control over release rates and patterns obtained by changing the ratio of polyethylene to ethylene-vinyl-acetate and/or the percentage of added mineral powder.

Several other products with thermoplastic polymers or latex coatings are available. One particular product is prepared by coating urea. The latex coating of urea and other granular compounds distinguishes itself from other coatings by being a water-borne process, whereby a suspension of poly-vinylidene chloride is sprayed on the granules, with no need for recycling organic solvents (Kelch and Thompson, 1992; Goertz, 1995).

Moreover, several synthetic chemicals were used such as N-serve (nitrapyrin), dicyandiamide (DCD), carbon disulphide (CS_2), sodium chlorate, benzene hexachloride (BHC) etc. have been examined for inhibition of urea hydrolysis or nitrification or both in soils (Zaman et al., 2008). However, the use of these chemicals has been restricted only for academic experimental studying because of high cost, lack of availability, and adverse effects on soil microflora (Purakayastha, 1997).

Natural starch is a polysaccharide polymer with many hydroxyl groups that make the starch matrix hydrophilic and capable to absorb water and swell dramatically in aqueous solution. Consequently, the matrix provides an effective control over the fertilizer encapsulated in the starch only for a relatively short period of time after rainfall or irrigation, which reduce the survival life in field uses, especially in heavy water environments (Li et al., 2008).

In the past few decades, the environmental and ecological pollution resulted from low fertilizer use efficiency has encouraged great concerns (Elizabeth 2000; Zhu 2000; Paramasivam and Alva 1997). Slow release controlled fertilizer has been developed, and used to improve the efficiency as well as prevent and decrease the environmental pollution from loss of fertilizers. Many studies have been done; but mainly focused on the membrane materials (Du and Zhou 2002; Liao et al, 2001; Sun et al, 2005). The membrane materials can be divided into two main varieties, inorganic minerals and organic polymers. Inorganic minerals are example; silicon, sulfur, gypsum, phosphates, zeolete, bentonite, maifanitum, diatomite, etc. (Xu, 2006; Wu and Liao, 2000; Feng et al, 2005; Pan et al, 2006; Zou et al, 2006).

In the case of organic polymers consist of natural macromolecular materials (e.g., starch, fibrin, natural rubber, etc.), high molecular synthetic materials (e.g., polyethylene, polyvinyl chloride, etc.), and high molecular semi-synthetic material (e.g., ethyl cellulose) (Wu et al., 2002; Hanyuu et al., 1999; Rong et al., 2005). Moreover, inorganic minerals used are easily available with low price. And the membrane remaining in the soil after nutrient release may be decomposed naturally, which can not only supply some minor nutrients but also improve soil structure. However, the concentration of inorganic materials may be not high enough, leading to bad control of nutrients in the soil. In contrast, organic polymer as membrane material has shown good control of nutrients. Nevertheless, the organic polymer membrane requires sophisticated technical process such as some fungi or bacteria was occurred when fertilizer attached moisture.

Another method of regulating plant nutrient release is the application of a coating. Several release mechanisms are possible depending on the type of applied coating. When a hydrophobic coating without pores is used, release only takes places after partly degradation of coating by e.g. micro-organisms. Water soluble coatings usually only slow down fertilizer release. After a certain uptake of water, the coating becomes porous or even breaks and burst release of fertilizer takes place.

The polysulfone coated fertilizer showed the best properties and low porosity. The urea fertilizer was coated with the grafted polymer composite of starch grafted poly-L-lactide (st-g-PLLA) (Li et al., 2008). The stability of the composite films in water increases with increasing graft efficiency of PLLA. Compared to the pure starch/urea composite film, the st-g-PLLA/urea composite films showed improved resistance to water. When the pure starch/urea composite film was immersed in distilled water, it was first swollen, and quickly broken because both starch and urea are sensitive to water and can absorb a quantity of water. In all cases, the presence of PLLA in st-g-PLLA copolymer leads to a significant improvement of the film hydrophobicity (Li et al., 2008).

CRFs coatings materials should be sufficiently hydrophilic to take up water for making fertilizer transport possible, and on the other hand be sufficiently hydrophobic to prevent disruption of the coating wall. When damage occurs to a controlled-release coating, the product loses its controlled-release properties completely or in part, since coating holes, cracks or thin spots allow for rapid access of water in which the fertilizer is soluble. However, controlled-release coating properties are dependent on the type of polymer and molecular weight, which play an important role in urea release (Jintakanon et al., 2008).

The methods of longevity predicting and nutrient release test CRFs have been studied since the early 1950. However, there is not any uniform standard method for the longevity predicting and nutrient release of CRFs. Based on the definition of slow release by Europe Standard Committee, pure water dissolving incubation at 25°C is described the release characteristics (Li et al., 2005).

About 40 years ago, sulfur has been used for coating urea but that sulfur is friable cause easily cracks and the shell is even peeled from particle surface during transportation. Many works have reported the improvement of the coating quality (Goertz et al., 1993; Choi and Meisen, 1997). Wax was usually coated on the outer surface of the sulfur coated urea to seal the flaws to reduce the release rate. However, these have a high cost, and the wax coating made an inconvenient adhesive product.

The polymer coating on fertilizers is an emerging field of study. Hanafi et al. (2000) used PVC, polyacrylamide, natural rubber and polylactic acid as coating compounds on fertilizers. These polymer coated fertilizers are highly stable at high temperature, however, these polymers are non biodegradable. The blending of biodegradable polymer can contribute to the CRFs.

Recently, many reports on introducing starch, cellulose, lignin, inorganic clays, and chitosan into pure polymeric encapsulation in order to improve swelling property, reduce production costs and ensure biodegradability (Farag and Al-Afleq, 2002; Shogren et al., 2009; Zhang et al., 2007). However, the researches on super absorbent polymer based on crops residues are still remaining. In addition, many materials have been reported to be used as coating such as polysulfone (Jarosiewicz and Tomaszewska, 2003) polyvinyl chloride (Hanafi et al., 2000), and polystyrene (Liang and Liu, 2006) were remained the coating materials in the soil. Therefore, the environmentally safe and biodegradable coating materials are expected to be used. Till now, attempting development of controlled-release fertilizer is to design device for preventing nutrient loss and enhancing nutrient utilization efficiency by plants.

In order to reduce the loss of nitrogen (N) from urea, research workers developed different polymer coatings. Among the alternatives reported in the literature, the application of polyvinyl alcohols (PVA) is interesting. PVA is a polyhydroxy polymer that is very commonly used in practical applications because of its easy preparation and biodegradability (Park et al., 2001). Also, PVA has film forming capacity, hydrophilic properties, and a high density of reactive chemical functions that are favorable for cross-linking by thermal or chemicals (Lebrun et al., 2004). Another chemical, Poly(vinylpyrrolidone), PVP as a hydrophobicizer and stabilizer, can greatly improve membrane oxidative stability and chemical stability (Qiao et al., 2005). Based on the consideration of reported in a novel alkaline solid polymer electrolyte membrane composed of KOH dropped PVA/PVP (Jinli et al., 2010).

In order to apply biopolymer with conventional spray technique that easily formed membrane on the urea granule as well as easily to use. Furthermore, the compound materials were used PVA and PVP. There are shown excellent film forming, solubility, and biodegradability. Moreover, both materials are shown very low environmental impact that lead to environmentally safe. The effect of different ratios of PVA/PVP on urea granules were discussed in this thesis. Biopolymers are reviewed in details in the following sections.

2.2 Materials for Encapsulation

2.2.1 Polyvinyl alcohol (PVA)

PVA was firstly prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide. The acetate groups are hydrolyzed by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. The physical characteristics of PVA are dependent on its method of preparation from the above mention. PVA generally classified into two groups, fully hydrolyzed and partially hydrolyzed, are shown in Fig. 2. Partially hydrolyzed PVA is used in the foods.

PVA has a simple chemical structure of vinyl alcohol as monomer unit with pendant hydroxyl groups. PVA is obtained by the vinyl acetate polymerization in alcoholic solutions followed by partial hydrolysis. It is possible that not all acetate groups be substituted by OH radicals (Zhu and Qian, 2007), consequently polymers with different hydrolysis degree will be obtained (Constantin and Claudia, 2006).

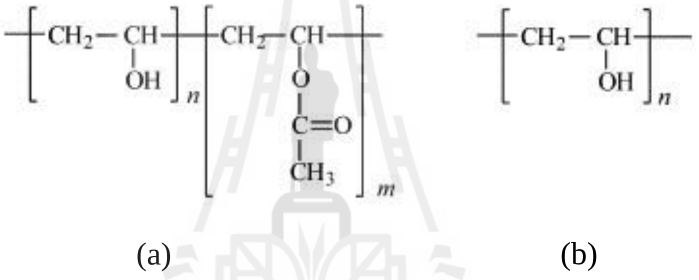

Fig. 2 Chemical structure for PVA: (a) partially hydrolyzed polymer and (b) fully hydrolyzed polymer (Demerlis and Schoneker, 2003).

The PVA melting temperature is 230°C for fully hydrolyzed polymer and melting point between 180 to 190°C for partial hydrolyzed polymer (Judit et al., 2001). The PVA density is 1.26 g/cm^3 for the amorphous phase at 25°C and 1.35 g/cm^3 for the crystalline phase at the same temperature (Saxena, 2004).

PVA is synthetic polymers used since the early 1930s in a wide range of industrial, commercial, medical and food applications including resins, lacquers, surgical threads and food-contact applications. PVA is one of the hydrogels often used in biomedical applications (Aleyamma and Sharma, 1988; Hyon and Ikada, 1986). It is a water-soluble synthetic polymer with excellent film forming, emulsifying and adhesive properties. This polymer has outstanding resistance to oil, grease and solvents (Schellekens and Bastiaansen, 1991). PVA was evaluated for its food use by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in June 2003.

PVA for food use is an odourless and tasteless, translucent, white or cream colored granular powder. It is soluble in water, slightly soluble in ethanol, but insoluble in other organic solvents. Typically a 5% solution of PVA exhibits a pH in the range of 5.0 to 6.5. PVA has a melting point between 180 and 190°C. It has a molecular weight of between 26,300 and 30,000 and a degree of hydrolysis of 86.5 to 89%. PVA may be used in high moisture foods in order to retain the overall satisfactory taste, texture and quality of the foods. Confectionery products may also contain PVA in order to preserve the integrity of the moisture sensitive constituents. Use levels for PVA were developed by application of 2.3 mg PVA/cm^2 in aqueous film coatings. Maximum use levels of PVA were derived for the final foods by selecting products within each food category with the greatest proportion of moisture sensitive components, estimating the surface area of those components, and assuming coating of the entire surface area with PVA.

In the USA, the majority of PVA is used in the textile industries as a sizing and finishing agent. PVA is also widely used in the manufacture of paper products. PVA is used as a thickening agent for latex paint and common household white glue or in other adhesive mixtures and seals, as well as gypsum-based cements such as is used for ceramic tiles. PVA is relatively insoluble in organic solvents and its solubility in aqueous solutions is adaptable to its necessary application.

PVA is approved for using in several medical applications such as transdermal patches, the preparation of jellies that dry rapidly when applied to the skin and in immediate and sustained release tablet formulations. Cross-linked PVA microspheres are also used for controlled release of oral drugs. Ophthalmic solutions, such as synthetic tears, may also contain PVA because it provides good dispersion and coating properties (Wade and Weller, 1994). PVA is valued for its solubility and biodegradability, which contributes to its very low environmental impact. In addition, the intermolecular hydrogen bonds between hydroxyl groups belonging to monomer units of PVA with water molecules assist the dissolution of PVA in water (Gao et al., 2010). PVA is increasingly being used in the field of biomedical applications due to its biocompatibility (Lin et al., 2006; Qi et al., 2004; Yang et al., 2004; Kobayashi et al., 2005).

2.2.2 Polyvinylpyrrolidone (PVP)

PVP belongs to the class of water soluble polymers. From a chemical point of view, PVP is a polymeric lactam with an internal amide bond. Considering the structure of monomer unit (Fig. 3), PVP has amphiphilic character since it contains a highly polar amide group that confers hydrophilic and polar-attracting properties, and also non-polar methylene groups in the backbone and in the ring that confer hydrophobic properties.

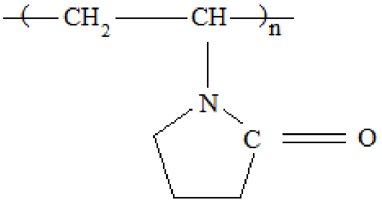

Fig. 3 Chemical structure of PVP (Hassouna et al., 2009).

PVP is used in wide variety of applications. It is also interesting for biological point of view, since it has structural feature similar to those of proteins and has great potential for applications in medical domain. Specifically, PVP is a bio- and hemocompatible polymer with very low toxicity, so that materials can be used as medical devices intended for implanting in the human body as well as coating could be used also (Doneux et al., 1997).

PVP is also interesting for technological applications. Its film forming and adhesive qualities are utilized in aerosol hair sprays, adhesives, and lithographic solutions. As a protective colloid, it is used in drug and detergent formulations, cosmetic preparations, polymerization reactions, and in pigment or dyestuff dispersions (Blecher et al., 1980). Moreover, PVP is miscible with hydroxyl-containing polymers, such as PVA. Since, water-soluble polymers are potential contributors to environmental problems, it is particularly important to determine their fate in conditions of natural weathering. After using, depending on the domains of application, PVP can be discarded into solid waste disposal systems or as a dilute aqueous solution. In biodegradable tests have showed that PVP is recalcitrant fraction (Trimpin et al., 2001).

PVA/PVP interactions have been described in many papers because of interesting properties of the resulting blend, which combines the features of both polymers (Taleb, 2009). Cassu et al. (1979) attributed the good blending of PVA and PVP to hydrogen bonding which may take place between the proton-accepting carbonyl moiety in pyrrolidone rings and the hydroxyl side group of PVA. Hydrogen bonding is also responsible for solubility of both PVA and PVP in water. This present work is aimed at synthesizing copolymeric of blended PVA/PVP in aqueous solution for urea fertilizer coating which used encapsulation technique.

2.3 Encapsulation Technology

Encapsulation is a technique by which one material or a mixture of materials is coated with or entrapped within another material or system (Green and Scheicher, 1995). Encapsulation may be defined as the process of forming a continuous, thin coating around encapsulants (solid particles, droplets of liquids), which are wholly contained within the capsule wall as a core of encapsulated material. On the other hand, entrapment refers to the trapping of encapsulants within or throughout a matrix (e.g., gel, crystal, etc.).

The purpose of encapsulation is often to stabilize an active ingredient, control its release rate. Encapsulates for typical industrial applications can vary from several microns to several millimeters in diameter although there is an increasing interest in preparing nano-encapsulates. Encapsulates are basically particles with a core-shell structure, but some of them can have a more complex structure, e.g. in a form of multiple cores embedded in a matrix. Particles have physical, mechanical and structural properties, including particle size, size distribution, morphology, and wall thickness. Information about the properties of encapsulates is very important to understanding their behaviors in different environments, including their manufacturing processes and end-user applications.

Normally, the material is coated which most often used a liquid form. The coated material is called various names such as core, shell, wall material, carrier, or encapsulant. With some encapsulation techniques, the product can be designed to either release slowly over time or to release at a certain point. The protection provided by encapsulation can be to prevent degradation due to exposure to light or oxygen or to retard evaporation. In addition, encapsulation technology is well developed and accepted within pharmaceutical, chemical, cosmetic, and food industries (Augustin et al., 2001; Heinzen, 2002).

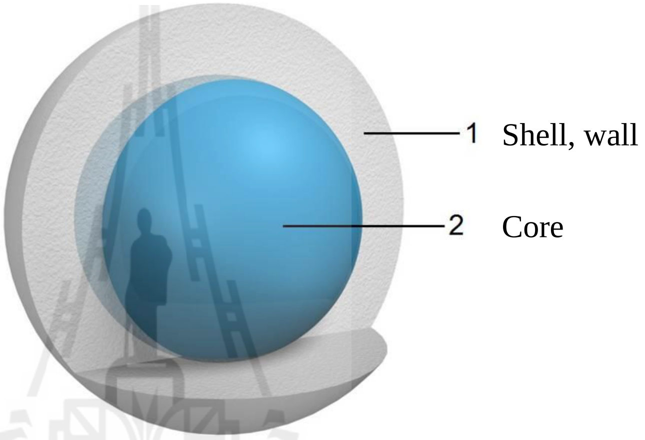

Fig. 4 Scheme of core/shell particle.

Many encapsulation techniques have been developed, such as spray drying, spray chilling, cooling, coacervation and fluidized bed coating (Madene et al., 2006). The widely used wall materials include polysaccharides and proteins, the key components in both natural processed foods (Tolstoguzov and Rivier, 1997). Such polymers have critical impact on the structure and stability (Sanchez and Renard, 2002).

Hydrocolloids, which lists of polymer used for encapsulation are quite extensive used which are synthetic and natural polymers (Bissery et al., 1984). Properties such as permeability, temperature stability, mechanical stability, and stability to various ingredients are critical to successful encapsulation applications. Each hydrocolloid will offer different properties, but even within an individual polymer type, significant variations in these properties may exist. Consequently, control of critical capsule properties is very important.

2.4 Physical characterization techniques of polymer coated fertilizers

2.4.1 Microscopy

Optical and electron microscope have been widely used to provide important information about size, surface topography, shell thickness and sometimes porosity of the shell materials of encapsulation product. The performance and dissolution properties of encapsulates with active ingredients are often related to the physical properties.

Polarizing microscopes are extremely useful for specialized medical and industrial applications, such as identifying crystals or fibers suspended in liquid, identifying minerals in core samples and detecting defects in semiconductors or finding stress points in metal, glass and other materials. A polarizing microscope is a special microscope that uses polarized light for investigating the optical properties of specimens. Although originally called a mineral microscope because of its applications in petrographic and mineralogical research, in recent years it has now come to be used in such diverse fields as biology, medicine, polymer chemistry, liquid crystals, magnetic memory, and state-of-the-art materials.

Scanning Electron Microscopy (SEM) that is capable of resolving structures with smaller dimensions than optical microscopy has often been used. SEM focuses electrons emitted by a heated filament to provide images restricted only by wavelength of electrons. SEM must be operated under high vacuum to prevent collisions of electrons with air molecules, which can cause losses in resolution. SEM has a resolution of approximately 3 nm, which has the feature of simplicity in sample preparation and ease of operation. It has a great advantage because of its capability to analyse samples ranging in size from nano-metre to centimtre scale (Weiss et al., 1995; Shu et al., 2006; Yan-yu et al., 2006; Roueche et al., 2006). The specious chamber and goniometer of scanning electron microscope can accommodate relatively large samples as compared to a transmission electron microscope and provide nearly unlimited points of viewing with the assistance of translational, tilting, and rotary movements. Nonetheless, SEM does not distinguish colours as optical microscopy does and has lower resolution compared to TEM.

2.4.2 Thermal analysis techniques

The structure of encapsulates defines how the molecules in encapsulates are organized. Two parameters are often used to characterize the fine structure of encapsulates: glass transition temperature (T_m) of encapsulates and crystallinity of encapsulate shell materials. Theses parameters may be used in designing encapsulates with desirable mass transfer properties (Meste et al., 2002).

Ricciardi et al. (2004) used differential scanning calorimeter (DSC), x-ray diffractometer (XRD), and nuclear magnetic resonance spectrometer (NMR) to measure the degree of crystallinity of PVA hydrogels, and demonstrated that these three methods had different accuracies, which depended on the complexity of their structure.

DSC is a thermal analysis technique for measuring the energy required to maintain zero temperature difference between a sample and a reference (Hu et al., 2007). A similar technique to DSC is thermal gravimetric analysis (TGA), which is based on measuring weight changes associated with transformations of a material on heating (Foster and Clifford. 1996) and has been used to identify the thermal decompositions of a copolymer (Shukla and Srivastava, 2004).

2.4.3 Fourier transform infrared (FTIR) spectroscopy

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can be accepted a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification (Sherman, 1997).

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy (Sherman, 1997).

2.5 Theoretical modeling based on Fick’s laws models

A serious experimental study of the diffusion of one solution into another was first undertaken by Thomas Graham (1850), who devised a number of experimental techniques for studying the phenomenon and obtained a great deal of qualitative and quantitative data. His achievements in this field have perhaps been overrated and he is more justly remembered for his distinction between crystalloids and colloids in terms of the different rates at which they pass through membranes, and for his description of the process of dialysis. A far more important name in the early literature of the subject is that of Adolf Fick (1829-1901). Fick's laws of diffusion and the Fickian frame of reference are terms which frequently appear in modern papers on transport properties. Virtually all experimental papers on diffusion are concerned, in the first instance, with the determination of diffusion coefficients defined in a manner similar to that proposed by Fick, namely.

Fick's principal paper on diffusion entitled "Ueber Diffusion" appeared in Poggendorff's Annalen in 1856. It was clearly intended to be read by physical scientists. Most of the theoretical studies used to model the diffusion process are based on Fick’s laws. That is the rate of transport through a unit area is proportional to the concentration gradient measured normal to area. The easiest assumption is that the proportionality (diffusion coefficient, D) is constant. A frequently used assumption is that the surface concentration immediately attains its equilibrium value and remains constant through the sorption process.

Numerous investigators have unsuccessfully to develop a unified theoretical framework that could explain and model non-Fickian diffusion and its associated swelling (Aminabhavi et al., 1988; Chan et al., 1885-1889).

Frisch (1966) and Crank (1979) were among the first researchers to attribute non-Fickian transport to time-dependent mechanisms within a polymer. Crank and

Park (1968) proposed a history dependent diffusion coefficient that contained a term that instantaneously changed with concentration to an equilibrium value. That model was able to predict many of the features of non-Fickian diffusion, but did not predict the sharp front. Their approach introduced the concept of differential swelling stresses at the boundary due to expansive and compressive forces of the swollen and non-swollen regions.

Frisch (1964) suggested that a polymer below its grassing temperature value (T_g) must possess history-dependent diffusion coefficients and experience time-dependent changes in surface concentration in order to maintain sorption-equilibrium at its boundaries. These time dependencies are intrinsically related to the relaxation times for molecular rearrangement in the polymer.

Long and Richman (1960) proposed that the concentration of solvent at the polymer surface does not instantaneously reach its equilibrium value. They assumed that the diffusion process can be divided into two states. The first stage “initial state” involves molecular rearrangements that occur almost instantaneously. The second stage is a slower process, leading to a final equilibrium. Thus, the diffusion process consists of two parts: the absorption due to the concentration gradient set by the initial surface concentration and that due to penetrate transport as a result of the time-dependence of the surface concentration. This theory explains some non-Fickian diffusion behaviour, such as the two-stage sorption process. This concept introduced the relaxation idea of rather than a discontinuous jump or change in the diffusion coefficient as expressed previously by Crank.

From modeling of Fick’s laws can be mentioned follows: equations 1 and 2 are frequently used because of its simplicity and mathematical tractability. This is also known as Case I or Fickian diffusion.

$$J = -\rho D \frac{dc}{dx} \tag{1}$$

$$\frac{dc}{dt} = -\frac{dJ}{dx} \tag{2}$$

Fick’s first law (equation 1) assumes that the flux (J) through a unit area of material which is proportional to the concentration (c) gradient of material. The constant of proportionality is known as the diffusion coefficient (D) where ρ is the fluid density. Note that the density is outside the gradient operator (Crank, 1979). Fick’s second law (equation 2) relates the concentration change as a function of time to change in flux with respect to position. The concentration in dimensions of amount of substance (mol/m^3) is represent by C, t is time (s), and D is the diffusion coefficient in dimensions of [length^2 time^{-1}], example (m^2/s) whereas, x is the length (m). A fundamental criterion for Fickian diffusion is that the surface concentration attains its equilibrium value immediately upon a change in conditions and remains constant through the sorption process, i.e., in a resin matrix system the polymer chain segments at the surface must instantaneously reach saturation. Although Fickian diffusion theories have been completely developed, most of the polymer-solvent systems do not obey such a simplified description (Vrentas et al, 1997; Neogi, 1983).

Fickian diffusion is rarely observed for the transport of a liquid through a glassy polymer (Vrentas, 1993; Petropoulos et al., 1999). In the case of non-Fickian diffusion, a sharp front, which separates the dry polymer from the swollen polymer, is assumed to move linearly with time (Alfrey et al., 1966). If the mass uptake M can initially be represented by

$$M = k\ t^{n} \tag{3}$$

Where t is the time and k and n are constants, then Fickian sorption corresponds to $n = 0.5$. Case II sorption associated with $n = 1$. Anomalous sorption is characterized by: $0.5 < n < 1$. Fig. 5 showed different classes of non-Fickian sorption or diffusion (Neogi, 1996). By applying the approach presented in this work, it is possible to control the rate of release for long period of time (from few minute to an estimated the un-dissolved nutrients and fertilizer solution period of several days). It is also possible to design devices with a particular time pattern of the release profile. So, Fickian, non-Fickian, and linear play an important role in controlling the rate of patterns can be obtained.

The release results can be analyzed by using an empirical equation to estimate the value of n and K as follows (Al-Zahrani, 2000; Peng et al., 2006):

$$\log (M_t/M) = \log(K) + n\log(t) \tag{4}$$

Where M_t/M is the release fraction at time t, n is the release exponent, and K is the release factor. From the slope and intercept of the plot of log (M_t/M) versus log (t), kinetic parameters n and K can be calculated.

The n value is an empirical parameter characterizing the release mechanism (Shaviv, 2000). On the basis of the diffusion exponent, n value of 0.5 indicates the nutrient release mechanism approaches to a Fickian diffusion controlled release, whereas n equal to 0.1 indicates the nutrient release mechanism approaches to zero-order release. The n value from 0.5 to 1.0 is a nutrient release mechanism for non-Fickian diffusion or chain relaxation control release.

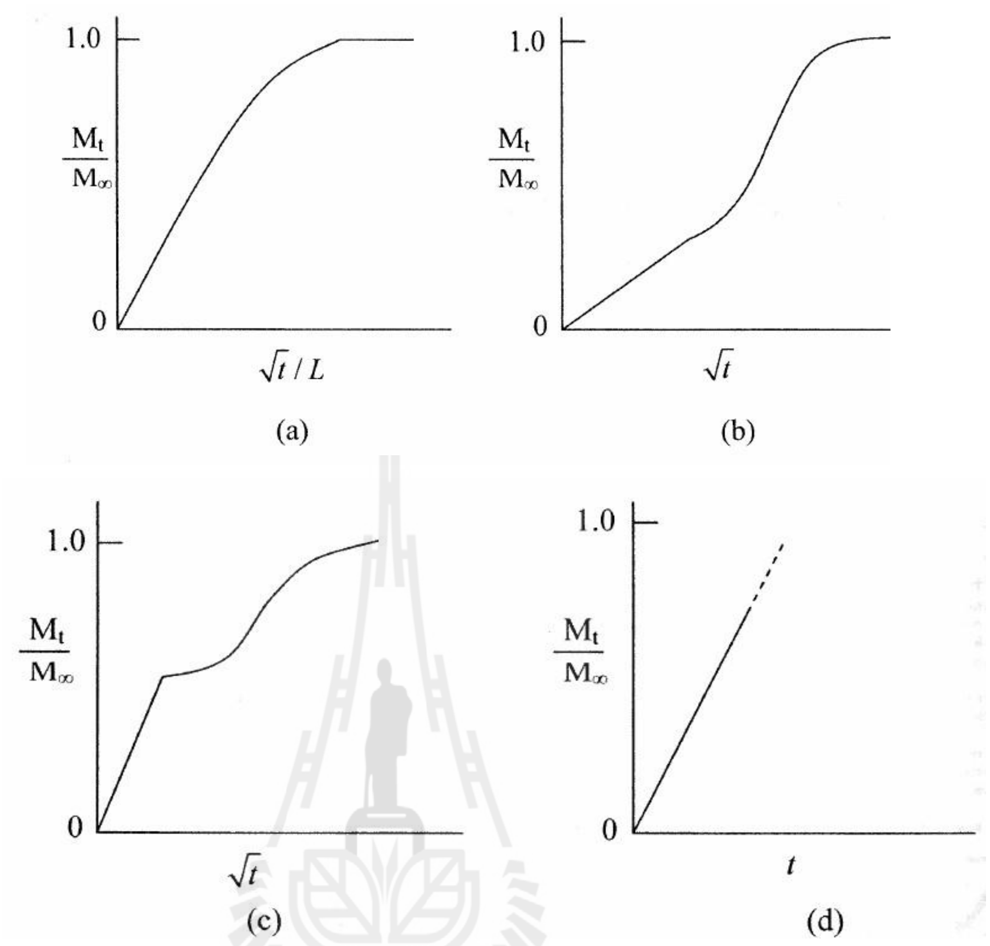

Fig. 5 Different classes of non-Fickian sorption: (a) classical, (b) sigmodial, (c) two-step, and (d) Case II (Kee et al., 2005).

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CHAPTER III

CONTROLLED-RELEASE UREA FERTILIZER BY BIOPOLYMERIC ENCAPSULATION

3.1 Abstract

Biopolymers are currently the most popular controlled-release fertilizers, and offer great advantages over conventional fertilizers. PVA and PVP as the biodegradable polymers were desired for this studying. Experiments of urea granule based on PVA and PVP coating were carried in a rotary drum and polymer solutions were sprayed on the granules. To understand the releasing of encapsulated urea fertilizer (EUF), a mathematical of Fick's law was obtained to predict urea releasing behaviors. The coating material was conducted PVA and PVP in various ratio 2:0 (EUF1), 1:0 (EUF2), 1:0.25 (EUF3), 1:0.5 (EUF4), 1:1 (EUF5), and 1:2 (EUF6) by mass. The results showed that the predicted *n* values of between 0.86-0.98 were strong non-Fickian diffusion while un-coated urea was *n* values of 0.70 which released faster than all EUFs. The PVA coating polymer showed releasing control properties better than PVP. However, results revealed that PVP concentration had some effects on the controlled release. The reduction of PVP ratio was found to increase controlled release properties. Moreover, the ability of their polymer could control both the rate and time pattern of the release through different combinations. Consequently, EUFs could be easily produced with conventional process and had better controlled release

properties. Therefore, the EUF products have widely potential application in agricultural industry as urea encapsulated fertilizer.

Keywords: controlled-release fertilizer, encapsulated urea fertilizer (EUF), non-Fickian diffusion, polymer-coated fertilizer, polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP)

3.2 Introduction

The growth of plant depends on the soil condition, quantity of water, as well as mainly a function of the quantity of fertilizer. Therefore, it is very important to improve the utilization of fertilizer nutrients. Fertilizers are the main factors that limit the development of agricultural production, which is very important to improve the utilization of fertilizer nutrients. Nitrogen is the most vital nutrient for crops, it has been considered the yield limiting one. Among the nitrogen fertilizers, urea is the most widely used in the crops as well as its high nitrogen content (46%) and comparatively low cost of production.

However, consider leaching and vaporization, the utilization efficiency or plant uptake of urea is generally less than 50%. About 40-70% of nitrogen of the applied fertilizer is escaped to the environment and cannot be absorbed by crops (Dave et al., 1999; Guo et al., 2005; Liu et al., 2007). As a neutral organic molecule, urea cannot be absorbed easily by the charged soil particles before hydrolyzing, resulting in a great quantity of urea running off and serious environmental hazards as only a fraction is really absorbed by plants.

One possible of this problem is the encapsulation of fertilizer by membrane to control the diffusion of water, leach, and release of the fertilizer. Recently, the use of slow release fertilizers is a new trend to save fertilizer consumption and minimize environmental pollution (Akelah, 1996; Jarosiewicz and Tomaszewska, 2003).

Controlled-release fertilizers (CRFs) are made to control the rate of nutrient release as well as control the slow diffusion of nutrient ions through the membrane to the soil (Ahmed et al., 1963; Lunt and Orteli, 1962). The CRFs for urea are made by coating the active soluble component as the membrane that serves as a diffusion barrier. Then, coating materials should be inexpensive and exhibited a good coating property. CRFs are made to release their nutrient contents gradually with the nutrient requirement of plant. These fertilizers can be physically prepared by coating the conventional fertilizer granules with various materials that reduce their dissolution rate. The release and dissolution rates of water-soluble fertilizers depend on the coating materials properties. At present, degradability of materials is an important focus on the research in this field because of the renewed attention towards environmental protection issues (Li, 2002; Shavit et al., 2002).

Polyvinyl alcohol (PVA) is a kind of excellent membrane material for preparation of a hydrophilic membrane that swells easily and even dissolves in water. PVA is valued for its solubility and biodegradability, which contributes to its very low environmental impact. PVA has also been approved for using in controlled releasing of fertilizer. Polyvinylpyrrolidone (PVP) has been interested as a binder in granules of urea fertilizer for controlling pore size of coating membrane. PVP polymer as a hydrophobicizer and stabilizer, can greatly improve membrane oxidative stability and chemical stability (Qiao et al., 2005). Moreover, PVP is miscible with hydroxyl-containing polymers, such as PVA. PVP was thus interpenetrated into the PVA network due to increased cross-linking density. It has been extensively utilize and study in these form of its alone or mix for observed mixing behaviors and properties of the blends. Therefore, it seemed worthy of interest to prepare a new type of encapsulated urea fertilizer (EUF) with their polymer.

3.3 Materials and Methods

3.3.1 Materials

Commercial urea fertilizer granules with diameter in the range 2-3 mm were purchased from the C.P. Company, Thailand. Polyvinyl alcohols (PVA) (CAS no. 9002-89-5) are synthetic polymers used in a wide range of industrial, commercial, medical and food applications. It has a molecular weight between 26,300 to 30,000 and a degree of hydrolysis of 86.5 to 89%. PVA was purchased from Aldrich chemicals. Polyvinylpyrrolidone (PVP) was purchased from Acros Organics. Other chemicals and solvents were all of analytical grade. Deionized water was used throughout the experiment. Osmocote® (13-13-13) was purchased from sotus international Co., Ltd.

3.3.2 Methods

3.3.2.1 Preparation of EUF

Urea fertilizer granules were sieved to about 2-3 mm in diameter and were placed into a rotary drum, and 10% (w/v) of biopolymer solutions were sprayed on the granules. The adhesive was applied by spraying at regular time intervals. The urea coated granules were dried to a constant mass at 70°C overnight. The polymeric EUF granules were obtained for further structure and releasing analysis. Six combinations among PVA and PVP were shown in Table 1. A controlled experiment without EUF was also carried out.

Table 1 The combinations among PVA/PVP in different ratio.

Combination	PVA	PVP
EUF 1	2	0
EUF 2	1	0
EUF 3	1	0.25
EUF 4	1	0.5
EUF 5	1	1
EUF 6	1	2

3.3.2.2 Determination of urea

A solution (0.5 ml) containing 4% (w/v) of p-dimethylamino-benzaldehyde and 4% (v/v) sulfuric acid in absolute ethanol was added to 2 ml of a solution of urea. After 10 min of reaction at 25°C the absorbance of the solution was measured at 422 nm against a reagent blank using a spectrophotometer (Spectronic 21, Milton Roy Company). The concentrations of the yellow-coloured compound in the samples were determined by reference to the calibration curve. The absorption spectra were recorded against a reagent blank (Knorst et al., 1996).

3.3.2.3 Controlled-release behavior of EUF

To study the slow releasing behavior of EUF, the following experiment was carried out: Five grams of EUF was kept in a 10 mL syringe and allowed to penetrate with deionized water and incubated at 25°C. Every one minute of incubation period, the deionized water was continuous feeding. The release urea solution of EUF in the containers were obtained and kept at 4°C to determine the content of urea, a spectrophotometer was used. For triplicate experiments were prepared at the same time. The release results were analyzed by using an empirical equation to estimate the value of n and K as follows (Al-Zahrani, 1999; Peng, Zhang and Kennedy, 2006):

$$M_t/M = Kt^n \text{ or } \log (M_t/M) = \log(K) + n\log(t) \qquad (5)$$

Where M_t/M is the release fraction at time t, n is the release exponent value, and K is the release factor. From the slope and intercept of the plot of $\log(M_t/M)$ versus $\log(t)$, the kinetic parameters n and K were calculated.

3.3.2.4 Measurement of the water retention of EUF in sand

Two grams of EUF were well mixed with 200 g of dry sand and kept in a container and then 200 g of deionized water was slowly added into the container and weighed ($W1$). A controlled experiment, i.e., without EUF, was also carried out. The containers were maintained at 25°C and were weighed every 4 days (Wi) over a period of 28 days (Wu & Liu, 2008). The water retention ratio ($WR\%$) of sand was calculated using the following equation:

$$WR\% = (Wi - W1) \times 100 / 200 \qquad (6)$$

3.3.2.5 Morphological analysis of EUF

Morphological investigations of EUF were observed by using scanning electron microscopy (SEM) (Jeol, JSM-5600LV, Japan). The samples were dried at

70°C. Each sample was covered by gold dust in a vacuum in order to fix the sample and to make the detail visible to the SEM. The SEM images have been taken at different magnifications by mounting on metal stubs.

3.3.2.6 Characterization of the outer coating material of EUF by FT-IR

FT-IR spectra of pure PVA, PVP, urea, and urea coated with PVA/PVP in various ratios were recorded at room temperature using a Bruker TENSER 27 spectrometer (Germany) at a resolution of 4 cm^{-1} in the range 4000-400 cm^{-1}. The samples were mounted directly on the sample holder. Data processing was performed by OPUS version 7.0 (Bruker Optic GmbH, Germany).

3.3.2.7 Thermal gravimetric analysis (TGA)

TGA system of type TA Instruments SDT 2960 Simultaneous DTA-TGA (USA) under nitrogen atmosphere (100 mL/min) was used in this study. Sample weights between 5-10 mg were used and placed into alumina pans. The temperature was ranged from ambient to 600°C at heating rate of 10 °C/min. TGA data were recorded using a TA Instruments SDT-2960 DTA-TGA analyzer.

3.3.2.8 Apparent viscosity measurement

The apparent viscosity of PVA and PVP aqueous solution was analyzed with viscometer (Well-Brookfield LVT, series 82198, USA). The determination was carried out at room temperature (25°C). The viscosity of long-term retardant products is normally measured using a #1 spindle for products having a viscosity between 1 and 100 centipoise (cP).

3.3.2.9 Determination the efficiency of EUF on plant growth

3.3.2.9.1 Experiment design

In the experiment, eight different materials coating of urea granules, un-coated urea and osmocote® (13-13-13) were applied, as follows: (1) Unfertilized control (N = 0); (2) un-coated urea (N = 46); (3) EUF2 (N = 46); (4) EUF3 (N = 46); (5) EUF6 (N = 46); (6) Osmocote® (13-13-13) (N = 13); (7) PVP (N = 12.6) and (8) PVA (N = 0). Pots were arranged in a completely randomized design in the greenhouse with five replicates.

3.3.2.9.2 Soil and fertilizer preparation

The soil sample was pre-incubated at imposing place for 7 days to eliminate moisture. Pots diameter were 15 x 13 cm and soil was taken in 40 pots which contained 3 kg of soil per pot. The experiment was conducted in a naturally lit greenhouse, located at the Suranaree University of Technology, Thailand, during October–November 2012, and temperature was between 20-30°C. Chinese kale (*Brassica* species) was grown in free draining pots containing soil. Seeds were first sown in germination pots, and 2 weeks after germination uniform seedlings were transplanted at a rate of one plant per pot. In the experiment, eight different fertilizers were applied at 30kg N/rai. Fertilizer was added into the pot after transplanting for 7 and 14 days. All plants were well watered daily until harvesting stage.

3.3.2.9.3 Observation of plant growth

Forty-five days after seeding, plant growth parameters were investigated as followed; shoot and root length, fresh and dry weight, and element analysis including nitrogen, phosphorus and potassium. The methods for plant element analysis were followed as;

- Nitrogen was analyzed by Kjeldahl method (Abraham and Rajasekharan, 1996). Total Kjeldahl nitrogen is the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion. Calculations:

$$\% \text{ nitrogen} = ((A-B) \times N \times 1.4) / w \qquad (7)$$

A = volume of titration with sample (mL)

B = volume of titration with blank (mL)

N = normality of HCL

w = weight (g)

3.3.2.9.4 Statistical analysis

All data were subjected by analysis of variance (ANOVA) and means were separated by Duncan's multiple range tests (SPSS® software for WINDOW™, Version 13.0; SPSS, Chicago, IL). Significance of differences was established at $P \leq 0.05$.

3.4 Results and Discussion

3.4.1 Controlled-release behavior of EUF

The EUFs were coated by spraying aqueous solution of PVA/PVP (2:0), (EUF1); PVA/PVP (1:0), (EUF2); PVA/PVP (1:0.25), (EUF3); PVA/PVP (1:0.5), (EUF4); PVA/PVP (1:1), (EUF5) and PVA/PVP (1:2), (EUF6) by mass ratios. All EUFs were separated into two groups, urea coated PVA (EUF1 and 2) and urea coated PVA/PVP (EUF3, 4, 5 and 6).

The releasing process of coated urea in water could be described as the following process. Water penetrated through the coating shell and dissolved the urea and then the dissolved urea diffuses into the water medium through the coating shell. Fig. 6 showed the cumulative released quantity versus time from PVA in different coating quantities. The coated urea was released at a constant rate in the first stage (initial state) and then released slowly till the end.

The PVA coated urea particle (EUF1) release was 54% and 93% at 5 min and 10 min, while the EUF2 release was 50% and 90% at 5 min and 10 min, respectively. The un-coated urea release was faster for 85% at 5 min and 100% at 10 min until endpoint (Fig. 6). Both EUF1 and EUF2 have shown strong non-Fickian diffusion behaviors, while un-coated urea was non-Fickian diffusion.

Furthermore, the reduction in urea release of granules with a smaller quantity of PVA was obvious. Probably, PVA increased the hydrophobic and thereby reduced the water-sensitivity of the PVA coating. Therefore, the uptake of water and as a result the release of urea was decreased. Besides the hydrophobicity, also the coating quality had a major influence on the release of urea.

The *n* value is an empirical parameter characterizing the release mechanism. On the basis of the diffusion exponent, an *n* value of 0.5 indicates the nutrient release mechanism approaches to a Fickian diffusion controlled release, whereas *n* equal to 1.0 indicates the nutrient release mechanism approaches to zero-order release. The *n* value from 0.5 to 1.0 is a nutrient release mechanism for non-Fickian diffusion or chain relaxation control release.

From the plot of log (*Mt/M*) versus log (t) (Fig. 7), the release exponent (*n*) and release factor (*K*) had been calculated. Table 3 summarized the values for urea release from EUF. The *n* values of EUF1 and EUF2 were in the range from 0.95-0.98, which were higher than un-coated urea. Therefore, the nutrient release mechanism was strong non-Fickian diffusion by PVA coating bipolymer.

Fig. 8 showed the cumulative released quantity versus time from PVA and PVP in different ratios. The EUF3 was released 45% at 5 min and 84% at 10 min while the EUF4 was released 48% at 5 min and 90% at 10 min. The EUF5 was released 51% at 5 min and 87% at 10 min. The EUF6 was released 56% at 5 min and 94% at 10 min. Similar trends were observed for the concentration dependence, where the PVA/PVP mass ratio ranged from 1:0.25 to 1:2. It depended on the PVP content. It could clearly be seen that the trends of releasing of urea was increased when increasing PVP content. Due to the hydrophilic nature of PVP, the biopolymer would be released well in water.

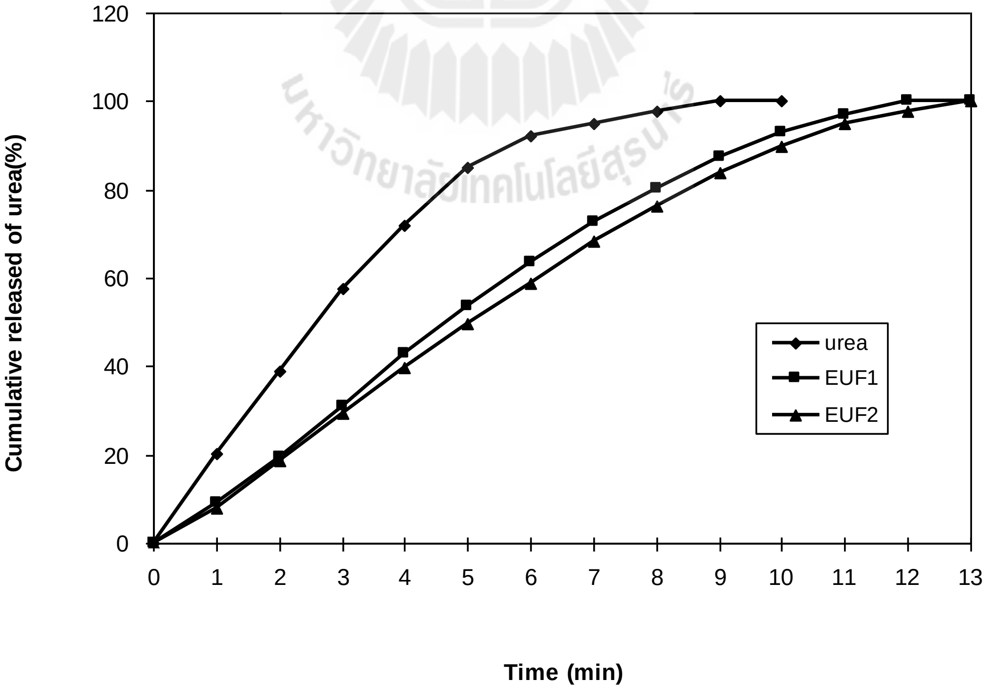

Fig. 6 Release behaviors of urea, EUF1, and EUF2.

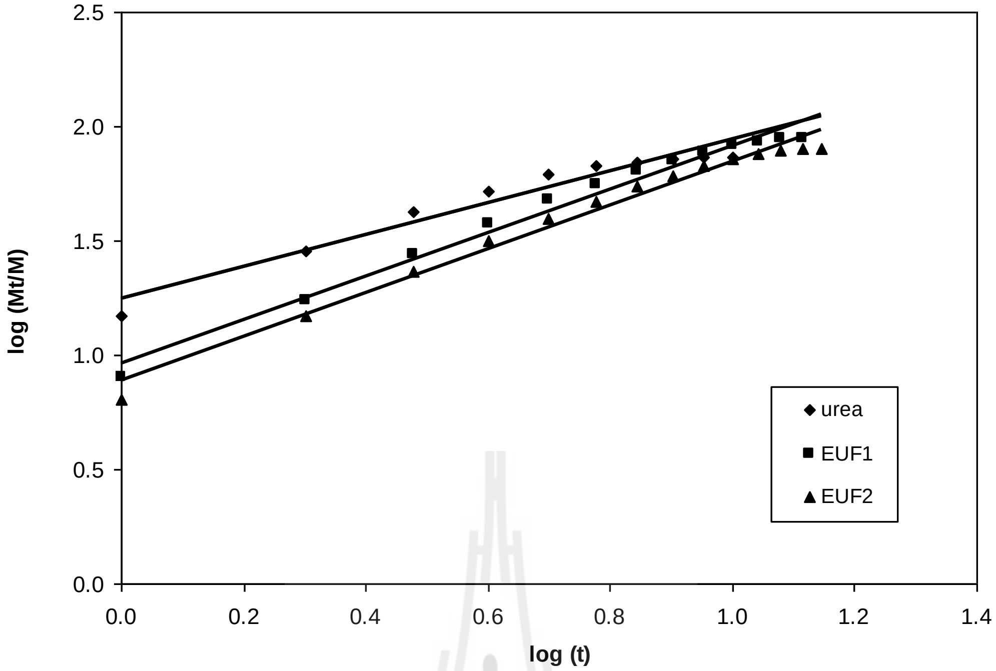

Fig. 7 Plot of release data log (*Mt/M*) versus log (t).

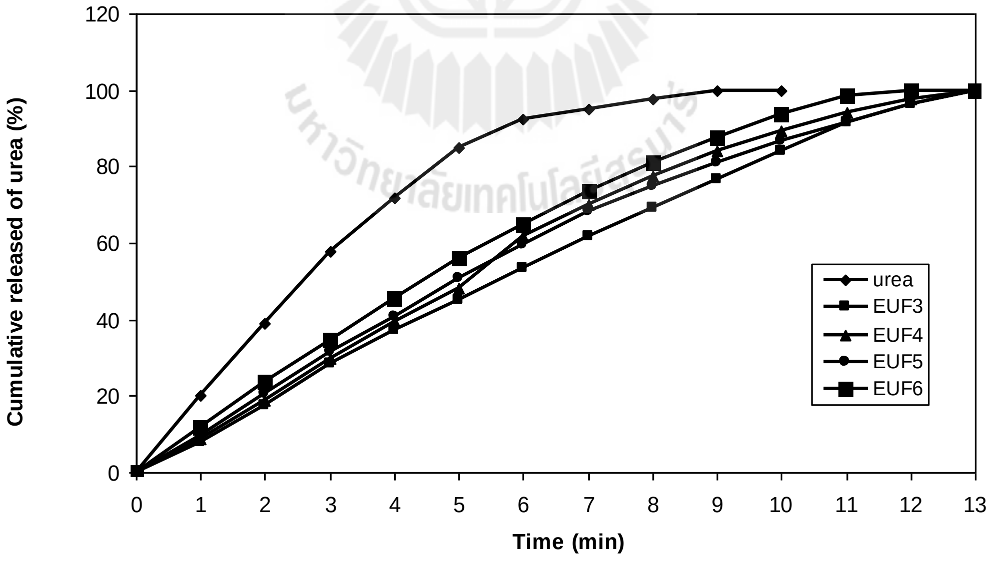

Fig. 8 Release behaviors of urea, EUF3, EUF4, EUF5, and EUF6

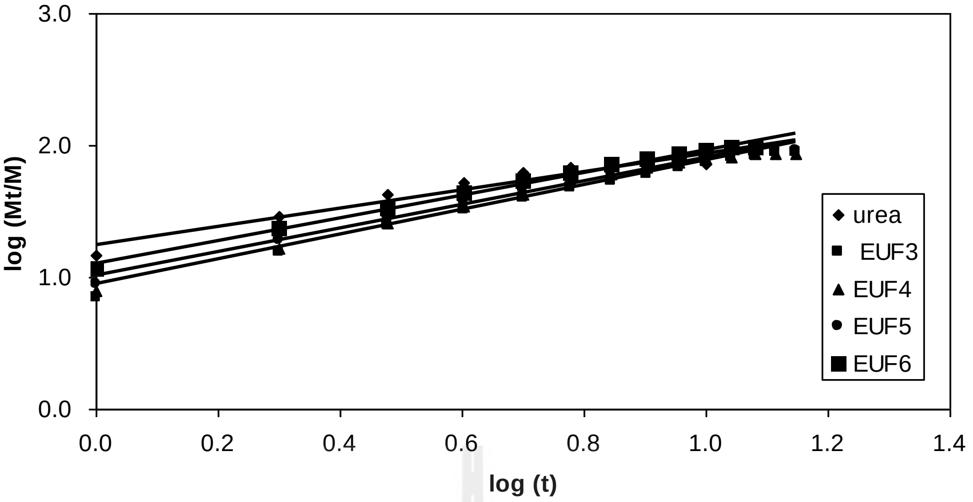

Fig. 9 Plot of release data log (*Mt/M*) versus log (t)

Table 2 The release factors (*K*), release exponents (*n*), and determination coefficients (r^2) following linear regression of release data of urea from EUF.

Sample	*n*	*K*	r^2
urea	0.70	23.97	0.9468
EUF1	0.95	10.44	0.9827
EUF2	0.98	9.37	0.9867
EUF3	0.96	9.14	0.9910
EUF4	0.93	10.22	0.9832
EUF5	0.88	11.24	0.9858
EUF6	0.86	13.05	0.9922

From the plot of log (*Mt/M*) versus log (t) (Fig. 9), the *n* and *K* values have been calculated. Table 2 summarized the values for urea release from EUF. The *n* value was in the ranged from 0.86-0.98. Therefore, the nutrient release mechanisms of all samples were non-Fickian diffusion. Providing the problem of using fertilizer as sufficient N fertilization to crops is critical to achieve high quality and yields. Encapsulated urea fertilizer is needed to control release, maximized N uptake efficiency, and minimized environmental hazards. It can be utilized as a management tool to supply nutrients during an extended period of time while reducing potential nutrient losses to the environment. Urea granules, being used as fertilizer, were coated in rotary drum with PVA/PVP polymer based formulations.

The development of this conventional encapsulation technique on the basis of PVA/PVP blending with spraying polymer solution on the granules, in which PVP served as both a plasticizer and stabilizer on granule. High control releasing rate was obtained at room temperature for PVA/PVP in a mass ratio of 1:0 and 1:0.25 which EUF2 and EUF3. The release of urea through these coating was measured and compared to un-coated urea granules. When PVA was used, the urea release decreased. PVA was found more efficient than PVP in reducing the rate of release. It was also found that mixtures with PVA/PVP induced a non-Fickian release pattern as PVA.

3.4.2 Measurement of the water retention of EUFs in sand

The most of important application of EUFs is for agriculture and horticulture, especially for saving water in dry and desert regions and for expediting plant growth. Therefore, it is necessary to investigate the water-retention ability of EUFs in sand. Fig. 10 showed the water retention ratio versus time from PVA in different coating quantities. The water-retention behaviors of the sand with and without EUFs were showed in Fig. 10-11. The addition of EUFs to sand could obviously increase the water-retention another way the water evaporation was decreased. The water retention ratio of sand without EUFs was remained 32.8 and 14.6 wt% on the 6th and 15th days, respectively, while that of sand with EUF1 was remained 46.7 and 17.5 wt% on the 6th and 15th days, respectively. The water retention ratio of sand with EUF2 was remained 49.0 and 21.0 wt% on the 6th and 15th days, respectively. After 21 days, the water-retention was escaped from the sand both the sand with and without EUFs.

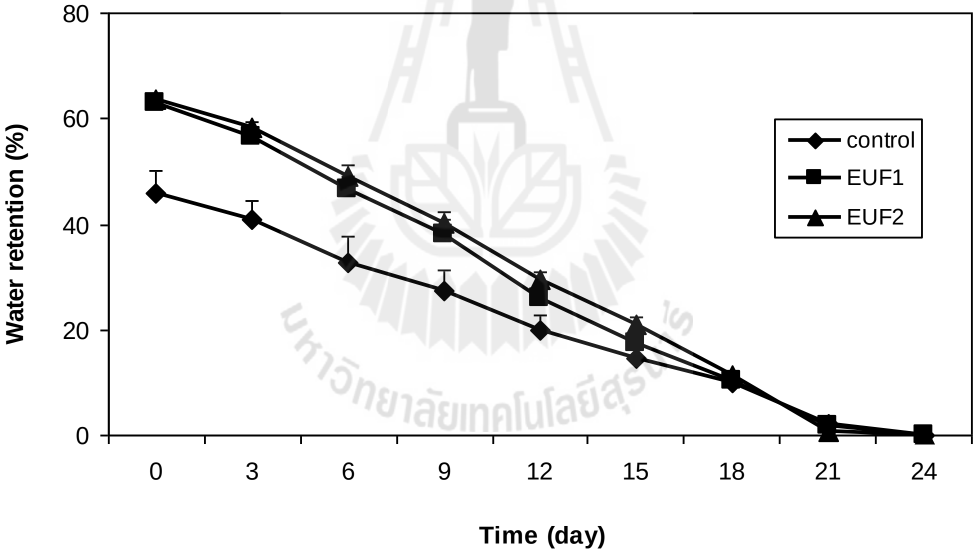

Fig. 10 Water-retention behavior of sand with two formula EUFs (EUF1 and EUF2) and sand without EUF as control.

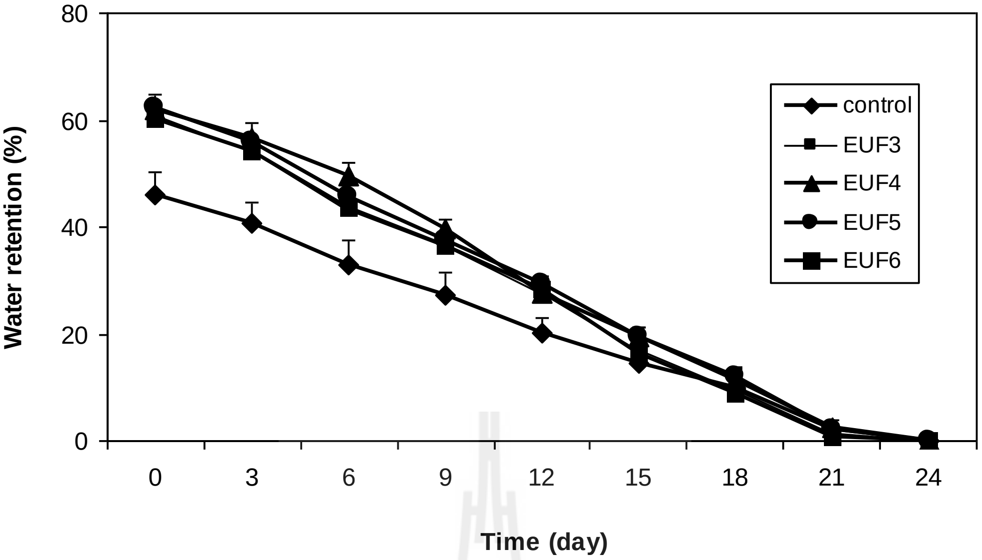

Fig. 11 Water-retention behavior of sand with four formula EUFs (EUF3, EUF4, EUF5, and EUF6) and sand without EUF.

From this study, it was indicated that EUF had good water-retention capacity in sand. The both formula of EUFs could be saved and managed water. In addition, that they could be effectively used for the growth of plant. Similar trends were observed for the concentration dependence, where the PVA/PVP mass ratio ranged from 1:0.25 to 1:2. Fig. 11 showed the water retention ratio of sand with EUF3 was remained 43.4 and 16.9 wt% on the 6th and 15th days, respectively. The water retention ratio of sand with EUF4 was remained 49.4 and 19.6 wt% on the 6th and 15th days, respectively. EUF5 was remained 45.5 and 19.5 wt%, while EUF6 was remained 43.7 and 16.4 wt% on the 6th and 15th days, respectively. After 21 days, the water-retention was also escaped from the sand both the sand with and without EUF.

Addition of EUF to sand, the coated urea had increased water-retention and decreased the water evaporation. In addition, that they could be effectively used for the growth of plant. These were significant advantages over the normal slow release fertilizers which always only had a controlled-release property. The reason was that the outer coating of EUF could absorb and store a large quantity of the water in the sand, and allowed the water absorption in it to be slowly released with the decrease the moisture in the sand. Concurrently, urea could also be released slowly with the water. Therefore, the swollen EUF was adjusted like additional nutrient reservoir for the plant-soil or sand system, and thus could increase the utilization efficiency of water and fertilizer at the same time. Moreover, the coating materials were not harmful to the soil (Wu and Liu, 2008).

3.4.3 Scanning electron micrographs of EUF

Scanning electron micrograph (SEM) of EUF granules and their surface morphologies are depicted in Fig. 12. Urea granules and EUF granules were photographed in shape and characteristic of surface by SEM. The SEM images of all EUF were shown in Fig. 12 which displayed the overall surface of urea coating with PVA and PVP. There were many apertures found on surface, it seems water could be absorbed by the fertilizer granules because of the high specific surface area. Urea showed the surface without coating materials. It cloud be observed that the small hole. At the same time, EUF could be inferred a small plate-like crystals (5-10 μm) with rough surface. PVP component was seen as typical amorphous spherical particles (Fig. 12). PVP particles were appeared as flakes (Kumar et al., 1999).

However, the characteristic of coating materials were showed more than one form of PVA/PVP coated on urea granules such as plates, needles and bundles. These results reveal that the biopolymers (PVA, PVP) are compatible. The surfaces of all images are composed of relatively regular crystal and the crystals have strong tendency to aggregate. Therefore, this experiment was used PVA/PVP for material coating because of its higher strongly than un-coated urea.

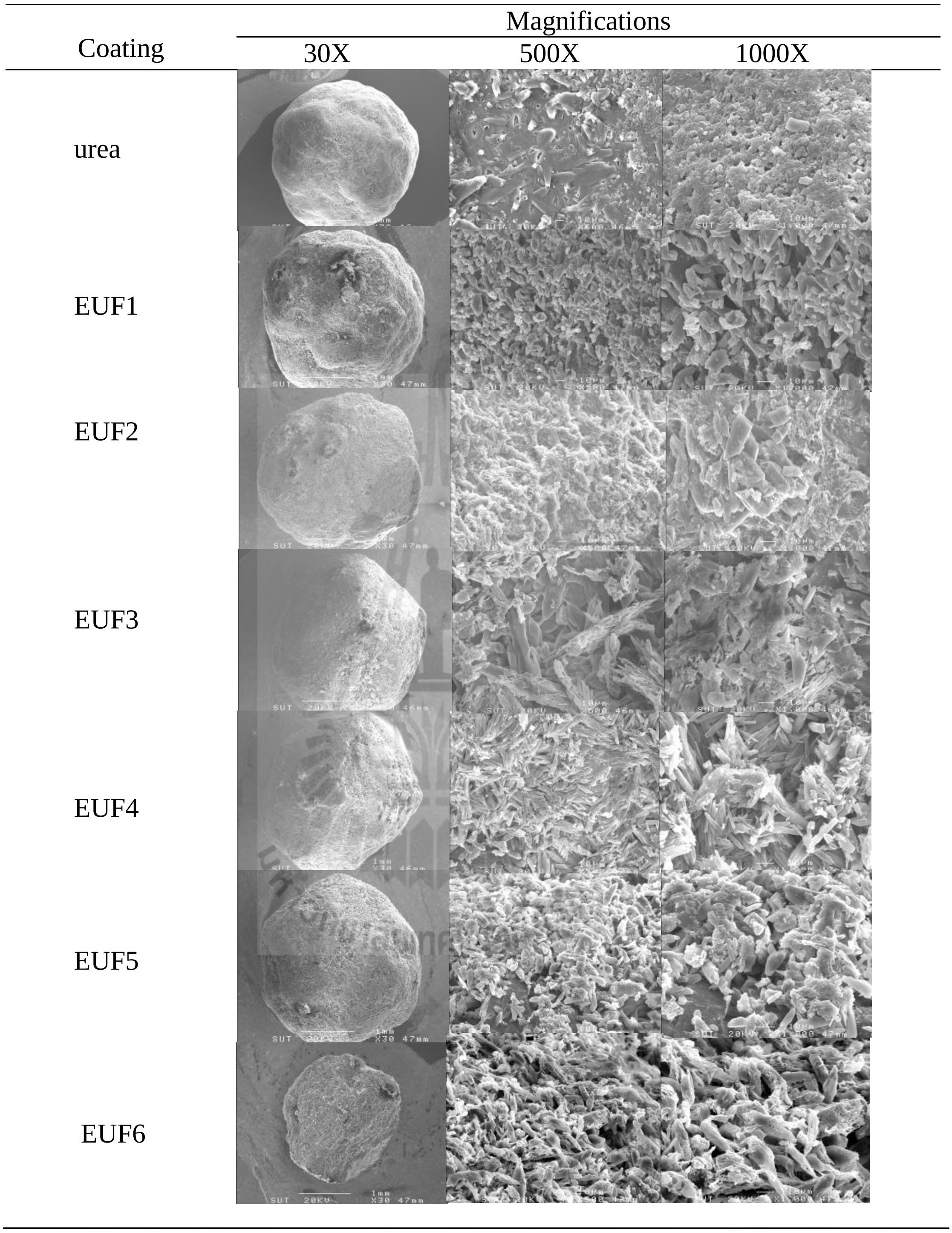

Fig. 12 Scaning electron micrographs of urea, PVA/PVP (2:0), (EUF1); PVA/PVP (1:0), (EUF2); PVA/PVP (1:0.25), (EUF3); PVA/PVP (1:0.5), (EUF4); PVA/PVP (1:1), (EUF5) and PVA/PVP (1:2), (EUF6) surface morphology of magnification x30, x500, and x1000.

3.4.4 Polarized microscopy

The polarization colors seen in the microscope could be correlated with the actual retardation, thickness, and birefringence of the sample (i.e., the optical path difference of the sample) and were reiterated in multiples of 550 nm. This is visible as a color change every 20-30 nm up to 550 nm, and the colors repeat for an additional 550 nm, and so on. The first set of colors is referred to as first order, followed by second order etc. up to seven order. The birefringent colors could be correlated to specimen thickness by a reference scale (Michel-Lévy scale).

The ray is transverse the crystal by different paths, in which one wave will become retarded with respect to the other. The difference between these refractive indices depends on the orientation of the crystal lattice relative to the ray. At one or two positions relative to the light ray was occurred in urea and coating materials (Fig. 13). Image analysis of polarized microscopy methods were obtained spherical particles and differently shaped particles. Normally, 100-300 nm of coating thickness of membrane coating granules was appeared on its, which played a major filtration barrier role (Kanwar et al., 1980) by delaying or preventing the movement of large molecules and also negatively charged molecules (abundant in sulfate and carboxyl groups).

The definitions of coating thickness are many analyses which based on the distances between borders required to be an extension of the radius originating from the centre of gravity of the pellet. However, in this work, these are determined from images obtained using polarized microscopy. A method of making a light polarizing material having excellent polarization characteristic over wavelengths from the visible to the infrared (IR) region is disclosed. IR transmitting materials of EUF was performed on the surface while un-coated urea was not occurred coating material. The resulting polarizer material could be produced in white sheet form on border a granule of EUF. Fig. 13 illustrated a magnified view of the resulting polarizing material showing in cross section. Image analysis was concluded to be the optimal method for narrow size distributions. As a result, the coating granules are spherical of about in range of 350-400 µm in diameter from average calculation.

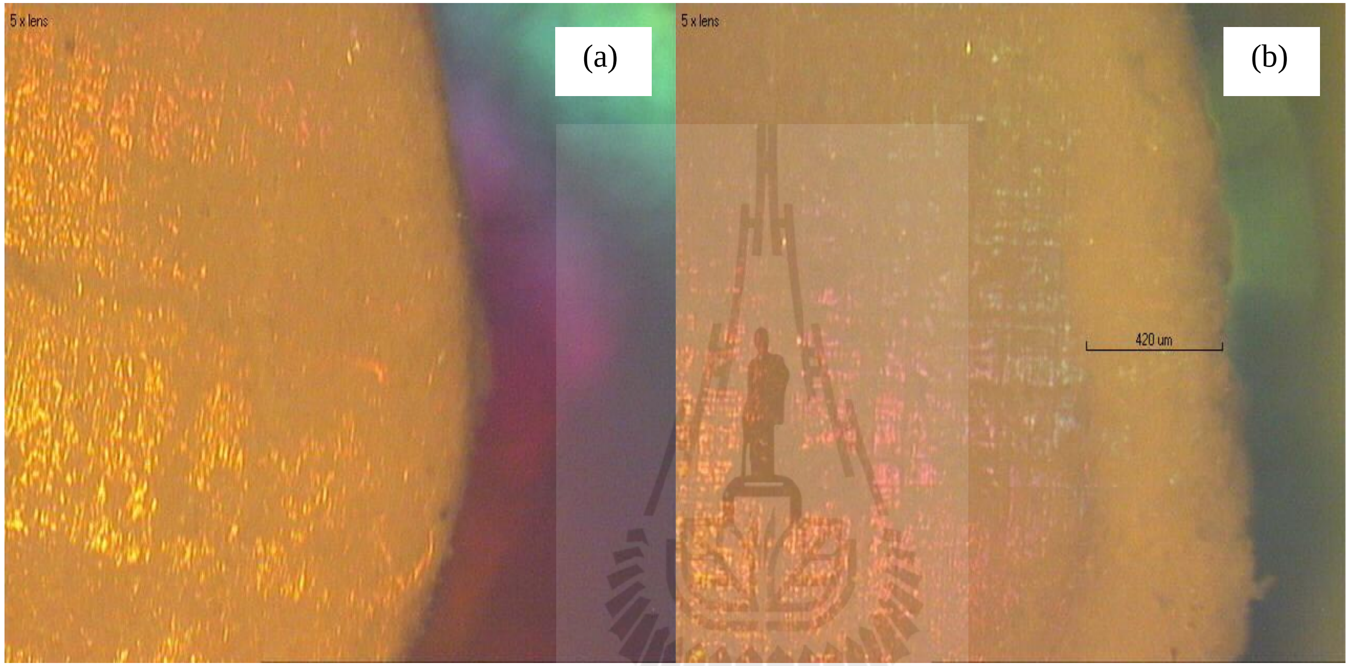

Fig. 13 Cross section of coated urea pellets under polarized microscopy (a) urea uncoated, (b) urea coated or encapsulated PVA/PVP.

3.4.5 FT-IR spectroscopy

FT-IR spectra of urea are appearance on the characteristic NH_2 stretching (ν) band (3500-3100 cm^{-1}) and the CO stretching band (1800-1500 cm^{-1}). The symmetric and asymmetric NH_2 stretching bands due to the intramolecular coupling of equivalent NH bonds of monomeric urea occur at 3548 and 3440 cm^{-1}, respectively (King, 1972; Li et al., 1987). Fig. 14 presented of two bands at 3435 and 3338 cm^{-1}, which assign to the ν(NH) vibrations. The frequency region 1800-1500 cm^{-1} is constituted of the band which assigned to the CO stretching of urea at 1678 cm^{-1}. The comparison among the CO band positions of monomeric urea was occurred (1734 cm^{-1}) (King, 1972). The frequency region 1640-1550 cm^{-1} is constituted of NH bending of urea at 1621 cm^{-1}. Yamaguchi et al. (1957) observed frequencies in the spectra of urea. The two vibrations of the frequencies 1686 cm^{-1} and 1603 cm^{-1}, there are considerable contributions of both CO stretching and NH_2 bending motions, whereas Stewart (1957) found that the 1686 cm^{-1} band of CO stretching vibration and the 1603 cm^{-1} band of NH_2 bending motion. The calculations studied by Yamaguchi et al. (1957) showed that for the band at 1686 cm^{-1} of the NH_2 bending motion is greater than that CO stretching motion. The 1464 cm^{-1} frequency of urea is assigned to the CN stretching vibration.

In case of urea dissolved in a series of halogen derivatives of aliphatic hydrocarbons (1700 cm^{-1}) (Dobrowolski et al., 1994), urea dissolved in acetonitrile (1695 cm^{-1}) (Hadzie et al., 1976), and pure solid urea (1682 cm^{-1}) suggests that the environment is strongly affected by changes of the urea CO group surroundings. In the bulk, urea develops an extended network constituted by infinite chains of molecules linked together by two hydrogen bonds in a head-to-tail manner. Each chain is orthogonal to the neighboring chain (Dong et al., 2000).

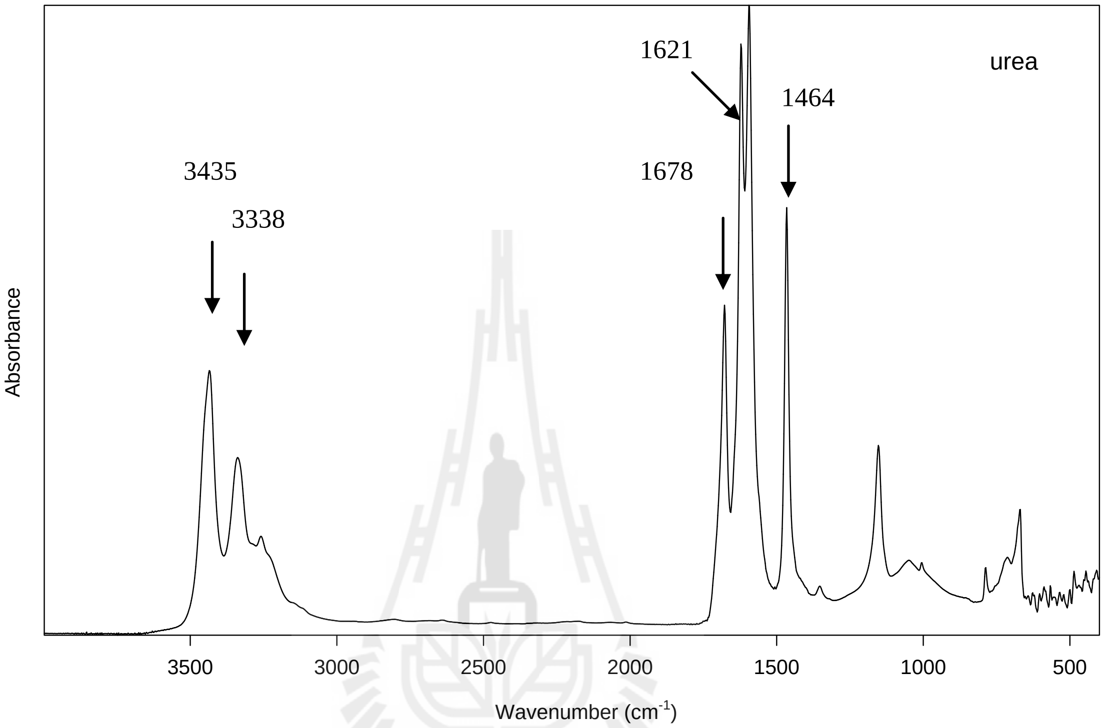

Fig. 14 FT-IR spectra of pure urea in the range of 3500-500 cm^{-1}

From the FT-IR spectra of pure PVA, the wide absorption band at about 3305 cm^{-1} is attributed to OH stretching vibration of hydroxyl group. The band corresponding to CH_2 asymmetric stretching vibration occurs at about 2920 cm^{-1}. The band of 1143 and 1420 cm^{-1} corresponds to C-O stretching of acetyl groups present on the PVA backbone (Fig. 15). The other work presented, the spectra of PVA are showed absorption peaks of PVA at about 3247 cm^{-1} (OH stretching) and about 1082 and 1414 cm^{-1} for the -C-C group (Rodrigues et al., 2007). Where appearing of C=O stretching is due to semicrystalline nature of the blends. The vibrational band at about

1646 cm^{-1} corresponds to C-O symmetric bending of PVA and PVP (Laot et al., 1999; Wu et al., 2001).

All major peaks related to hydroxyl and acetate groups were observed. The large bands observed between 3550 and 3200 cm^{-1} are linked to the stretching O-H from the intermolecular and intramolecular hydrogen bonds. The vibrational band observed between 3000 and 2840 cm^{-1} refers to the stretching C-H from alkyl groups and the peaks between 1750-1735 cm^{-1} are due to the stretching C=O and C-O from acetate group remaining from PVA (Silverstein, 1994; John, 2000; Andrade et al., 2006).

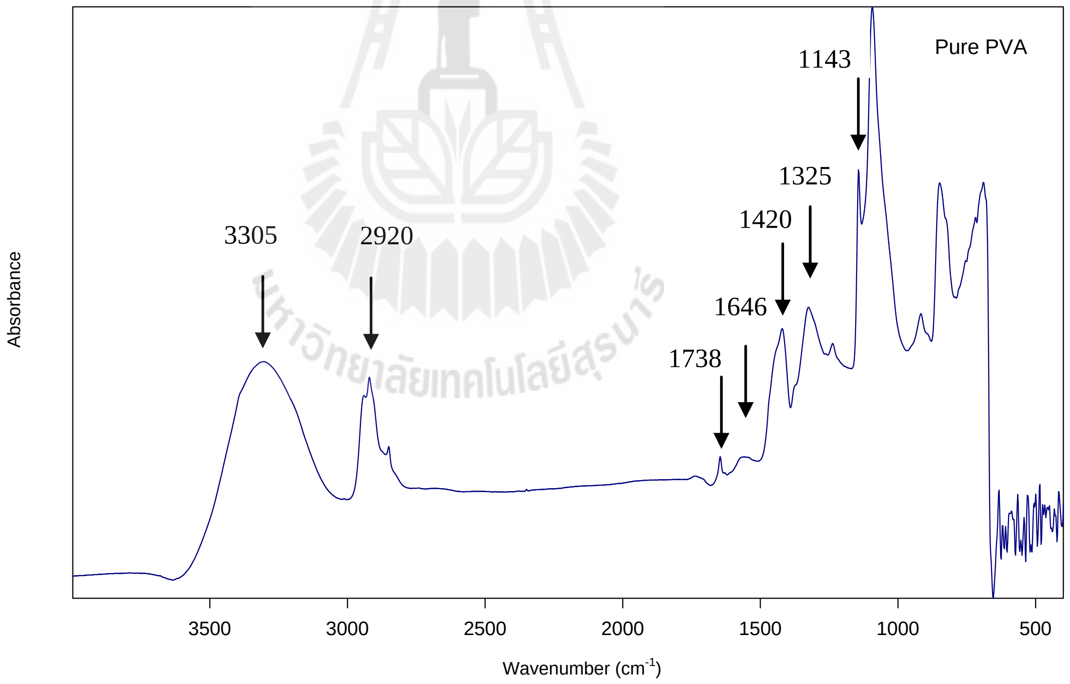

Fig. 15 FT-IR spectra of pure PVA in the range of 3500-500 cm^{-1}

PVP is a highly hygroscopic polymer, an absorption band in the hydroxyl region corresponding to adsorbed water which was observed on the infrared spectra

(Fig. 16). The study vibration of OH groups of PVP was shown at 3405 cm^{-1} which observed an intense band between 3750 and 3100 cm^{-1} vibration of OH groups from bound of water (Qiao et al., 2010).The vibrational band was observed at 2955 cm^{-1} refers to the stretching C-H from alkyl groups. The bands at 2954 and 2894 cm^{-1} arise from the stretching of $-CH_3-$, $-CH_2-$, and CH- groups (Qiao et al., 2010).

Although the stretching absorption band at 1557 cm^{-1} , which is attributed to the ν(C-N) of PVP could not be unambiguously assigned, a sharp peak at 1672 cm^{-1}, which is ascribed to ν(C=O) absorption from PVP, was clearly observed (Qiao et al., 2010). The frequency of 1672 cm^{-1} (keto carbonyl stretching band) these data suggest that complex with hydrogen bonded, but this hydrogen bonding would not be a strong one. The behavior of carbonyl stretching bands of PVP has been observed frequency at 1652 cm^{-1} band is definitely lower in frequency than the corresponding bands.

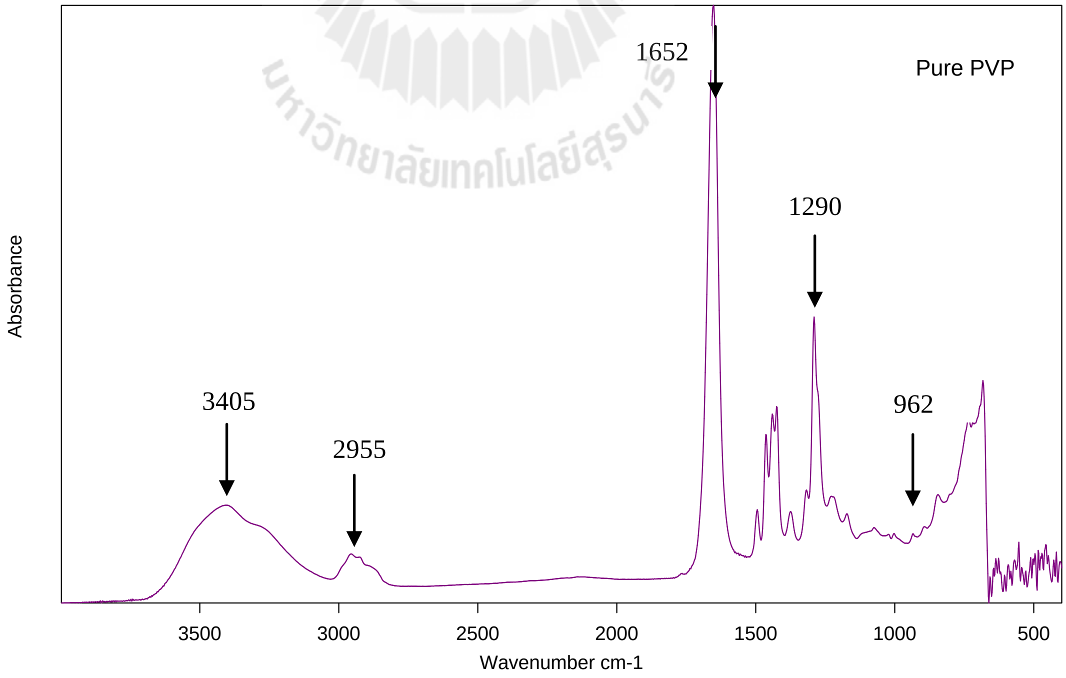

Fig. 16 FT-IR spectra of pure PVP in the range of 3500-500 cm^{-1}

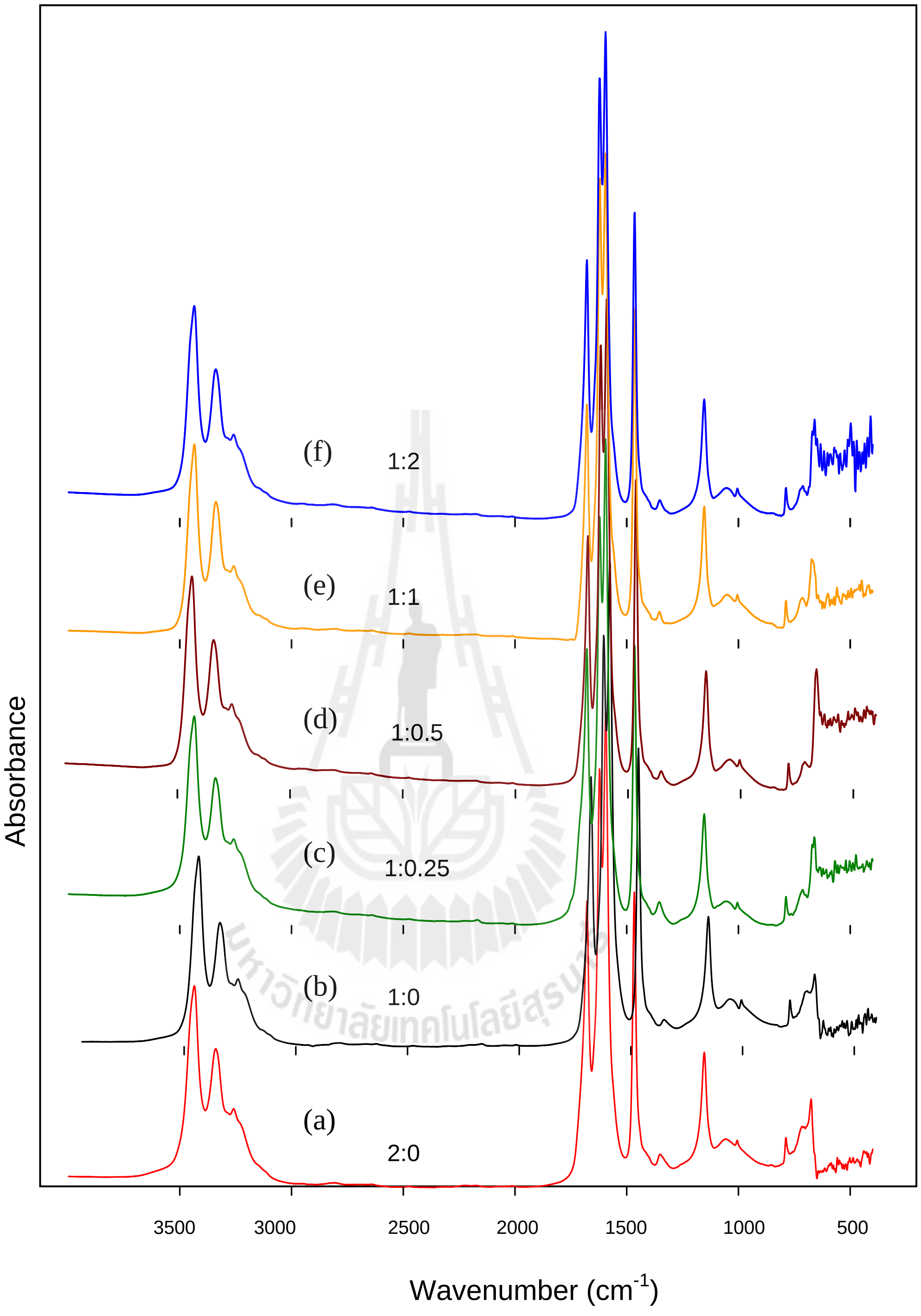

Fig. 17 FT-IR spectra of urea coated with biopolymers (a) PVA/PVP (2:0), (EUF1); (b) PVA/PVP (1:0), (EUF2); (c) PVA/PVP (1:0.25), (EUF3); (d) PVA/PVP (1:0.5), (EUF4); (e) PVA/PVP (1:1),(EUF5) and (f) PVA/PVP (1:2), (EUF6) by mass ratios.

To clarify the conducting mechanisms of PVA/PVP blend composite on urea granule at different ratios, 2:0, 1:0, 1:0.25, 1:0.5, 1:1, and 1:2 by mass (Fig. 17). FT-IR spectra were recorded in the wavenumber region between 3500 and 500 cm^{-1}, which covers the whole range of all of the characteristic IR vibrations. All of the spectra show an intense between 3435 and 3338 cm^{-1}, which were ascribed to the stretching vibration of NH_2 stretching band (3500-3100 cm^{-1}) from urea. Similar behavior was observed by analyzing the urea CO band (Calvaruso et al., 2001). The position bands at CO group of urea (1800-1500 cm^{-1}) is not involved in urea/surfactant interactions but rather in urea/urea interactions, i.e., hydrogen bounded with urea NH_2 groups (Hadzi et al., 1976; Mido, 1973; Huber et al., 1994).

It could be seen clearly from FT-IR spectra for each EUF. The spectrum of the blend was similar to that of spectrum of urea (Fig. 14). It must be pointed out that the amount of materials coating (PVA/PVP) were markedly smaller than that pure solid (urea), whereas the spectra occurring at about 3435 and 3338 cm^{-1}, assigned to the NH_2 symmetric stretching, is markedly larger. Also indicates that urea encapsulation is does not established of specific interactions between PVA/PVP on urea coated.

3.4.6 Thermal degradation process

Thermogravimetric analysis (TGA) is a process in which a material is decomposed by heat, which causes bonds within the molecule to be broken. TGA plays an important role in determining thermal stability of the materials. TGA curves and their derivatives TGA are presented. The thermogravimetric (TG) and derivative thermogravimetric curves (DTG) were shown in Fig. 18. Chen and Isa (1998) applied simultaneous thermogravimetry and mass spectrometry to the investigation of the decomposition of urea and concluded that this compound had a complicated behavior of thermal decomposition. In Fig. 18 (b) the stages of decomposition were observed, which starts before the melting point (132.5°C) until the complete oxidation of the sample. The first stage was a wide scale weight loss that started between 130 to 230°C. The second stage was fast thermal decomposition for urea residue between 300 to 360°C. The initial loss (between 25 and 150°C) was related to dehydration of adsorbed water (nonconstitutional water), interlayer water, and exchangeable cations water. The mass was lost above 350°C corresponds to elimination of structural hydroxyl and organic matter similar as Santos, (1975) and Bayram et al., (2010). There are two main peaks of the DTG curve (weight loss rate) in this stage: the maximum weight loss rate occurred at 226°C, while the temperature at secondary peak is 348°C (Fig. 18b).

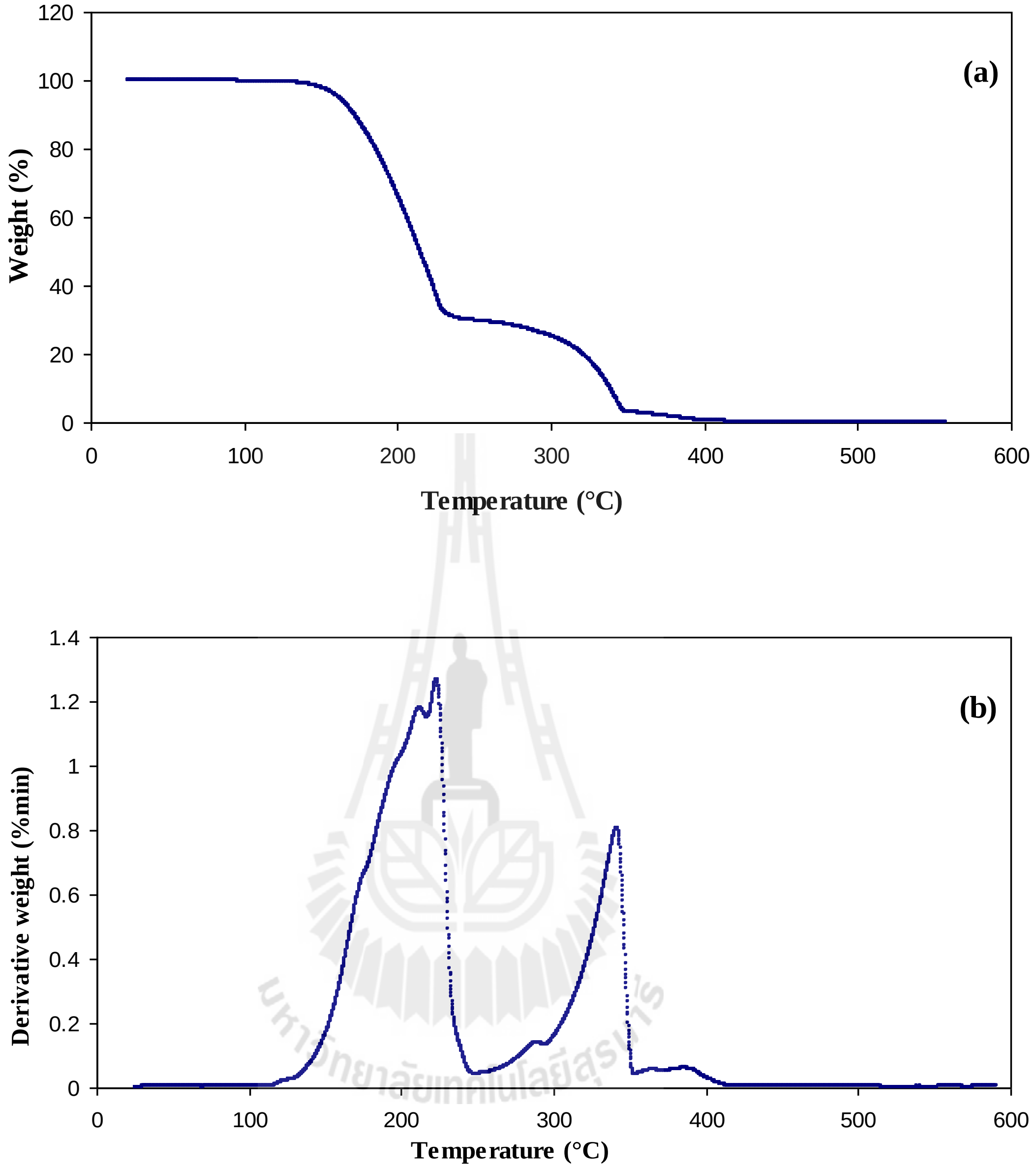

Fig. 18 TG (a) and DTG (b) curves of urea under nitrogen with heating rate 10°C/min.

There are two distinct and well-separated turns (300-400°C and 400-500°C) in the TG curves (Fig. 19a) and two corresponding weight-loss peaks in derivative thermogravimetric (DTG) curves for pure PVA (Fig. 19b). The weight loss of PVA gradually starts at 160°C and thereafter it begins to abruptly decompose at 280°C. Therefore, the peak degradation temperature with maximum weight loss rate was presented. The thermal degradation of PVA can be roughly regarded as a two-step-degradation. Correspondingly, at a given lower temperature the degradation rate is significant (Zheng et al., 2006).

The linear increase of thermal degradation temperatures with heating rate is caused by the heat hysteresis, i.e. the inner part of the samples cannot follow the program temperature when the temperature increases too fast. Theoretically, the slower the heating rate, the more accurate the degradation presents. According to others work (Alexy et al., 2001; Gilman et al., 1994; Zhao et al., 1998) they found that PVA thermally degrades in two steps. At the first degradation step mainly involves the elimination reactions, while the second one is dominated by chain-scission and cyclization reactions.

The weight losses in the first and second stages could be respectively attributed to the expulsion of water molecules from the polymer matrix or the moisture absorbed from the air, the decomposition of hydroxide groups, and the splitting of the main chain of PVA followed by decomposition of the polymer backbone above 450°C (Jinli et al., 2010).

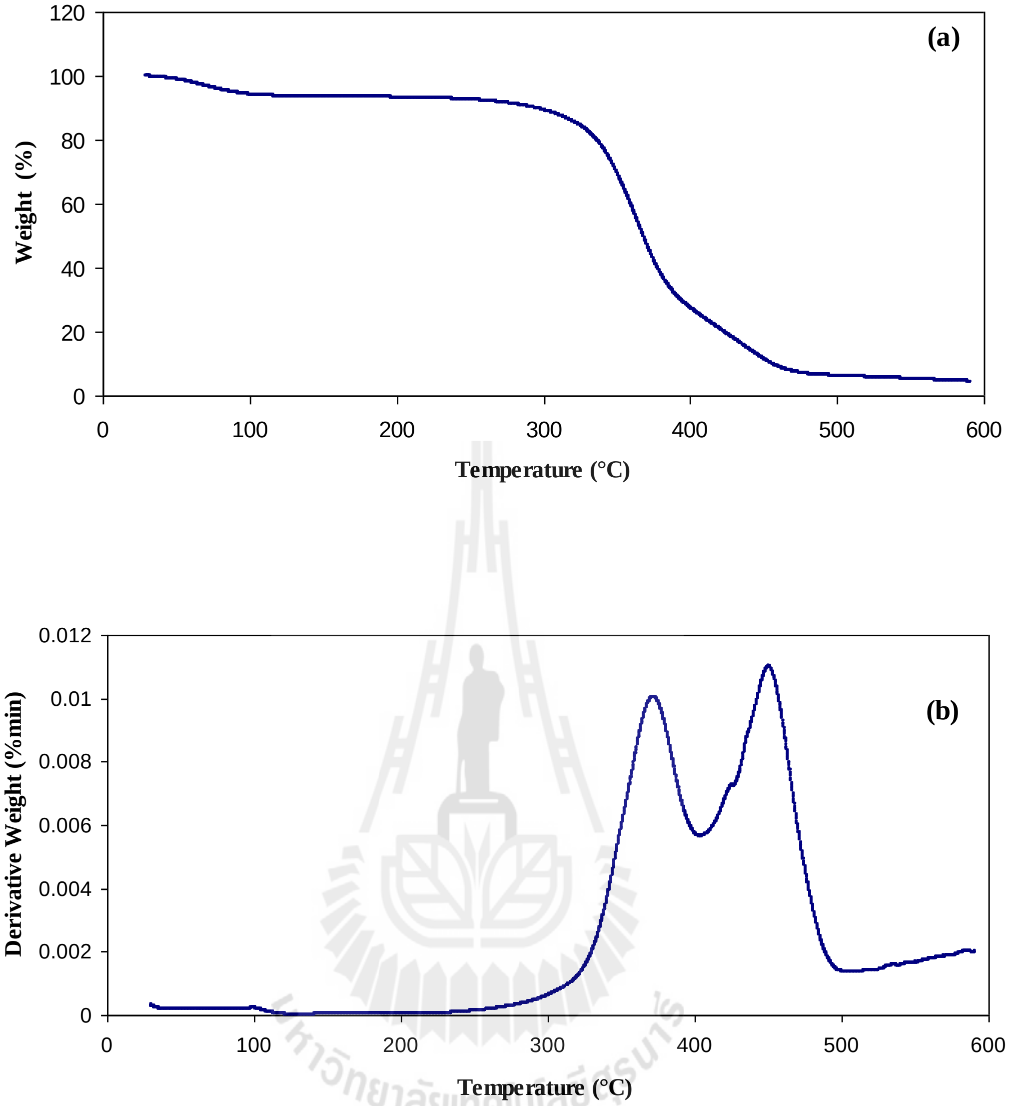

Fig. 19 TGA (a) and DTG (b) curves of PVA under nitrogen at a heating rate 10°C/min.

TG and DTG curves of PVP were shown in Fig. 20. The thermal decomposition of pure PVP was observed initial weight loss at 35-100°C, is due to loss of OH content (Sivaiah et al., 2010). In the DTG curve of PVP in thermal stability that starts to decomposed at 320-480°C. However, the weight loss was also observed at 480-600°C regions under nitrogen which is mainly attributed to thermooxidative degradation of PVP polymer chain (Li, 1999). Other work, pure PVP showed high thermal stability that starts to decompose at 400°C which due to lose of associated water (Cerrai et al., 1994; Cerrai et al., 1996).

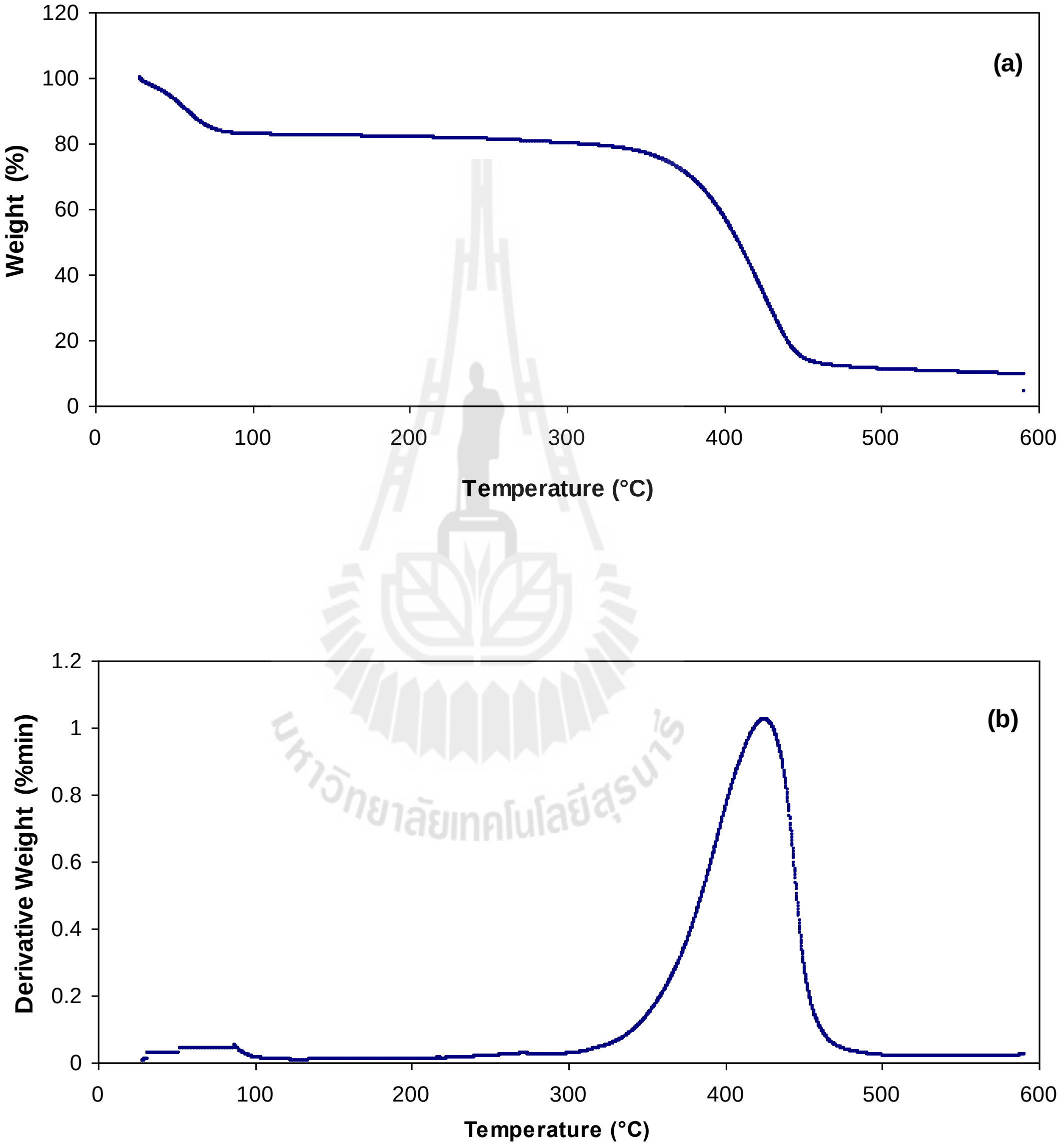

Fig. 20 TG (a) and DTG (b) curves of PVP under nitrogen with heating rate 10°C/min.

After coating, the EUF species dried to evaporate the solvent. The compact film was formed after drying at 70°C for 24 h. In the case of PVA, the polymer chains are very flexible due to either intra or inter molecular associations. This flexibility of the chain in PVA varies monotonically with temperature. Fig 21a showed the influence of PVA/PVP contents ratio on the thermal stability of formulated coating urea. The representative TGA curves were shown the initial decomposition temperature of PVA/PVP blended membranes which coated on urea granule was at about 210-220°C, whereas the initial decomposition was at about 300-400°C for pure PVA membrane as well as the decomposition of pure PVP occurred in a single step starting about at 420°C. The maximum decomposition temperature of PVA/PVP shifted significantly from about 350°C to about 400°C. On analysis of the mixtures, the maximum decomposition temperatures of PVA/PVP blended are lower than that pure PVA or PVP. The weight% loss decreased with increasing the PVP content.

However, the biopolymer mixtures were coated on the surface of urea fertilizer and dried in the oven held at 70°C. The coating of PVA and PVP was carried out by a solvent-evaporation process. Moreover, the quantity of mixtures solution sprayed on it should be not too much due to preventing the water reacting with water and urea fertilizer. All of the samples displayed three major weight loss stages at around 140-200, 220-340, and 350-480°C, followed by the final decomposition of the biopolymer coated on urea granule. For the samples exposed to TG analysis, the weight losses in the first second and third stages were occurred. Further analysis by D-TGA revealed that with increasing PVP content in the urea, the degradation temperature was increased which illustrates the high thermal stability of the PVA network structure (Jinli et al., 2010).

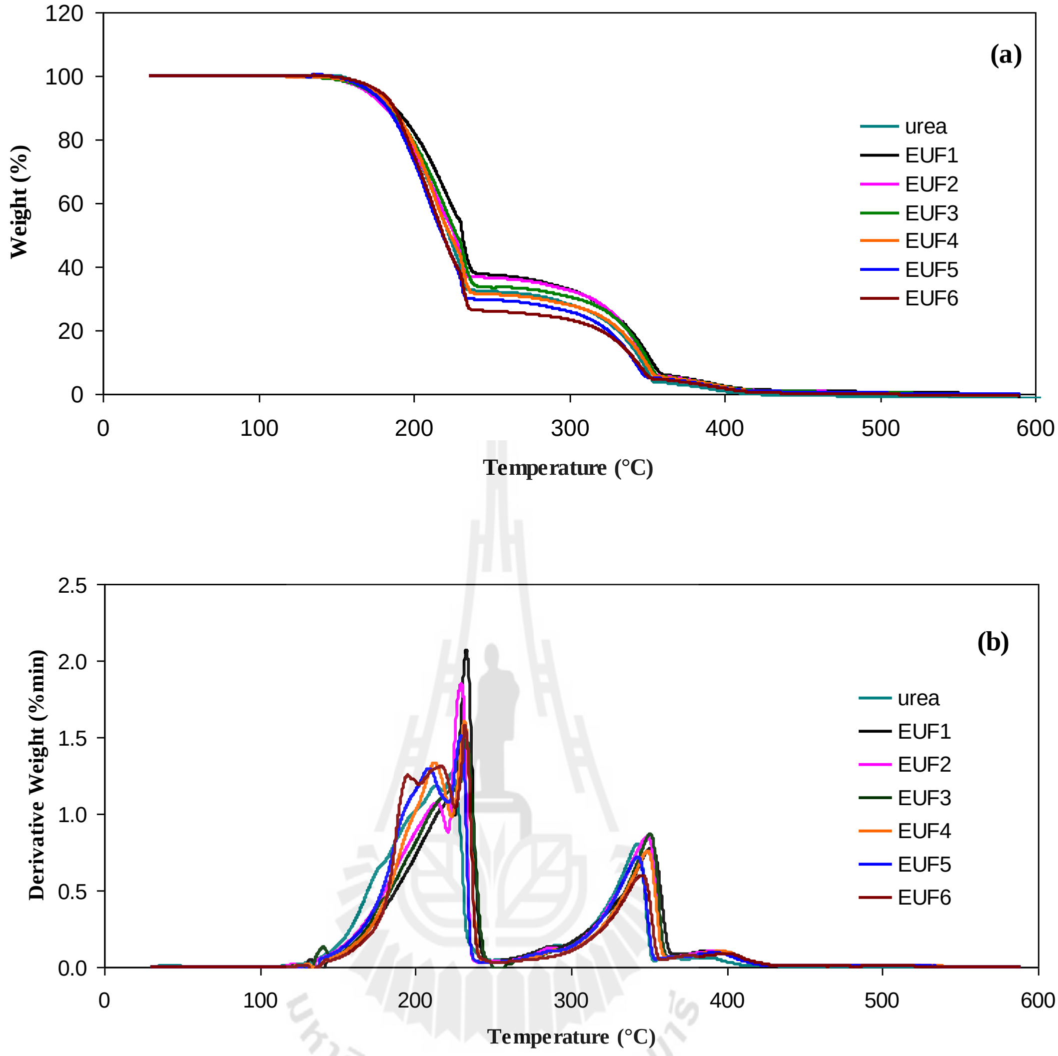

Fig. 21 TG (a) and DTG (b) curves of urea coated with biopolymers (EUF1) PVA/PVP (2:0); (EUF2) PVA/PVP (1:0); (EUF3) PVA/PVP (1:0.25); (EUF4) PVA/PVP (1:0.5); (EUF5) PVA/PVP (1:1); (1:2), and (EUF6) PVA/PVP (1:2) by mass ratios, under nitrogen with heating rate 10°C/min.

3.4.7 Viscosity

The viscosity of PVA and PVP solutions was measured by a Brookfield digital viscometer at 25°C. The viscosity of 10% PVA solution was showed 122.5cP (pH 6.7), while 10% PVP solution was showed 22.0cP (pH 5.9). The temperature of sample was ranged between 32.4-32.9°C. Among all the water-soluble neutral polymers, PVP is an unusually soluble one. Its water solution also has a much lower viscosity compared to other polymer solutions with the same concentration and molecular weight (Mohamadi et al., 2008). The viscosity is very low, e.g., 27 cP for the 4.5% solution and only 3 cP for the 1% solution of PVP (M_r = 1,000,000) as a function of concentration in 1xTBE buffer (Gao and Yeung, 1998).

PVA solutions are generally shear thinning and may exhibit significant thixotropy (Hebeish et al., 1996). Normally, the viscosity of aqueous PVA solutions increases with the molecular weight and concentration which increased because the existence of longer chains or higher molecular weight, and/or more chains or higher concentration enhances the formation of inter and intra molecular hydrogen bonding. The water becomes a poorer solvent and hence the viscosity of the solution increases. The temperature and % hydrolysis have a weaker effect on the solution viscosity because the amount of residual acetic groups or more active molecular mobility does not help as much as molecular weight or concentration on reducing the hydrogen bonding within and between chains (Wiley and Sons, 1971).

Table 3 Viscosity data of PVA and PVP aqueous solution.

Sample	Viscosity (cP)	Temperature (°C)
10% PVA	122.5	32.4
10% PVP	22	32.9

3.4.8 Plant cultivation with urea coated PVA/PVP in greenhouse

Nitrogen (N) is an essential nutrient for plant growth and in the desire to produce more food, farmers apply it intensively, and often in excessive quantities, in the form of nitrogen-based fertilizers. Chinese kale is the main leafy vegetable crops grown in south-east Asia countries, especially in Thailand. This *Brassica* species originated in China, however, different cultivars of them can be grown successfully in a wide range of climatic conditions including cool winters, warm summers and even the hot and humid conditions experienced in the Thailand. Leafy vegetable is expected to grow where there is an adequate water supply and the soil is well drained. Effects of different material coating of urea fertilizer on vegetables growth have attracted considerable attention. These experiments have shown that most leafy vegetables preferred N, and that the application of urea coated with biopolymer usually promoted their growth.

3.4.8.1 Soil characterization

The results were shown in Table 4. The result revealed that at low levels of nitrogen (0.37 mg/kg) was not a serious concern because observing urea could be truly affected on plant. It has long been known that N is one of the elements of which supply is most often limiting growth. Traditionally agricultural research has focused on how to provide the crop with sufficient nitrogen to guarantee optimum yields. If efficiency was taken into account, the reason was usually to maximize financial returns rather than to minimize the danger of leaching.

The propose was to observe the effect of un-coated urea and coated urea with PVA/PVP in the soil-crop system. A soil test was taken from each plot before sowing. In this work was presented of the relevant processes underlying plant response to nitrogen nutrition. Soil was planted with pH 7.75, organic matter content 7.4 % and adequate level of available P and K.

Table 4 Chemical characteristics of the soil before fertilizer applications.

Parameter	Value
pH (water, 1:1)	7.75
OM (%)	7.4
EC (mS/cm)	0.33
Available N (mg/kg)	0.37
Available P (mg/kg)	29.6
Available K (mg/kg)	877.15

3.4.8.2 Application of EUF as N fertilizer for vegetable

The experiment was conducted during October 2012 to November 2012, and temperature was between 20-30°C. The experiment was obtained for 45 days. Nitrogen, as urea (46%), was broadcast into the soil at 30 kg/rai in each pot. In the previous experiment, EUF2 and EUF3 were showed the best Fick’s law value of controlled-release behavior while EUF6 was showed the lowest value. Thus, investigation of the best EUF and the lowest EUF was interested for this study. Eight treatments were applied, as follows: (1) unfertilized control (N = 0); (2) urea (N = 46); (3) EUF2 (N = 46); (4) EUF3 (N = 46); (5) EUF6 (N = 46); (6) osmocote (13-13-13) (N = 13); (7) PVP solution (N = 12.6) and (8) PVA solution (N =0).

All treatments were contained fertilizer or coating solution in the same weight (N calculated from 30kg/rai). Pots were arranged in a completely randomized design in the greenhouse. Fig. 23 showed statistical analyses demonstrated the difference between treatments. Analysis of variance at ($P \leq 0.05$) and showed the F-test was significant, mean separation was done using the Duncan's Multiple Range Test. Each treatment was five replicated. All results of fresh weight and dry weight were summarized in Table 5. Stem length, root length, and leaf area were summarized in Table 6.

From the data of plant growth found that urea coated with biopolymer can be stimulated plant growth higher than control. Kale planted with EUF2 and EUF3 had significantly ($P \leq 0.05$) increased the fresh weight and dry weight compared to plants with urea and control (Table 5). There was significant difference in plant yield between urea fertilizers. Plants with control, osmocote, PVP and PVA resulted in plants with lowest in stem and root dry weight.

Stem length showed a significant different at P value ≤ 0.05 highest in urea, EUF2, EUF3 and EUF6 (Table 6). Root length showed significantly highest in EUF2 treatment. The amounts of leaf per unit area of kale exposed to significantly the high value of leaf area in urea, EUF2, EUF3 and EUF6. Leaf area is important in determining yield through radiation interception (Monteith, 1977) and biomass production (Watson, 1958; Nanda et al., 1995). Application of coated urea was slightly increased leaf area, while control, osmocote, PVA, and PVP was slightly smaller leaf area. Leaf area is depends on biophysical factors such as soil water, nutrient supply, temperature and diseases as they affect leaf size, appearance and persistence (Terry et al., 1983).

The results can be concluded that EUF2 and EUF3 resulted to the highest stem fresh weight, root fresh weight, stem dry weight and root dry weight. The study showed that kale plants have the ability to take up N source and partition into different plant parts. The results were also showed that PVA and PVP coated urea applied (EUF2 and EUF3); kale plants absorbed a maximum of N as seem in dry weight of plant as biomass of plant (Table 5). Kale plants with EUF2 and EUF3 significantly increased kale fresh stem and dry matter accumulation. These suggested that PVA or PVP did not available to kale plants for growth and development.

Table 5 Fresh weight and dry matter weight in stem and root of kale which treated with un-coated and coated urea.

Treatment	Fresh weight (g/plants)		Dry weight (g/plants)	
	Stem	Root	Stem	Root
Control (N = 0)	3.95^{c}	0.36^{d}	0.41^{c}	0.07^{c}
Urea (N = 46)	36.05^{b}	1.82^{bc}	3.64^{b}	0.37^{b}
EUF2 (N = 46)	44.18^{a}	2.86^{a}	4.56^{a}	0.56^{a}
EUF3 (N = 46)	43.84^{a}	2.33^{b}	4.64^{a}	0.52^{a}
EUF6 (N = 46)	39.95^{ab}	1.77^{c}	4.32^{a}	0.42^{b}
Osmocote (N = 13)	6.26^{c}	0.26^{d}	0.55^{c}	0.05^{c}
PVP (N = 12.6)	3.42^{c}	0.18^{d}	0.35^{c}	0.03^{c}
PVA (N = 0)	2.15^{c}	0.16^{d}	0.26^{c}	0.04^{c}
% CV	11.54	24.17	12.75	21.06

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

Table 6 Stem length, root length, and leaf area of kale which treated with un-coated and coated urea.

Treatment	Stem length (cm)	Root length (cm)	Leaf area (cm^2)
Control (N = 0)	20.50^{cd}	9.83^{bc}	74.53^{cd}
Urea (N = 46)	39.67^{a}	15.67^{ab}	455.47^{b}
EUF2 (N = 46)	37.33^{a}	22.33^{a}	569.15^{a}
EUF3 (N = 46)	33.16^{b}	16.00^{ab}	542.77^{a}
EUF6 (N = 46)	37.33^{a}	15.67^{ab}	468.45^{b}
Osmocote (N = 13)	21.83^{c}	12.5^{bc}	109.96^{c}
PVP (N = 12.6)	18.00^{d}	7.33^{c}	61.19^{cd}
PVA (N = 0)	14.66^{e}	12.00^{bc}	39.83^{d}
% CV	6.69	30.36	12.44

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

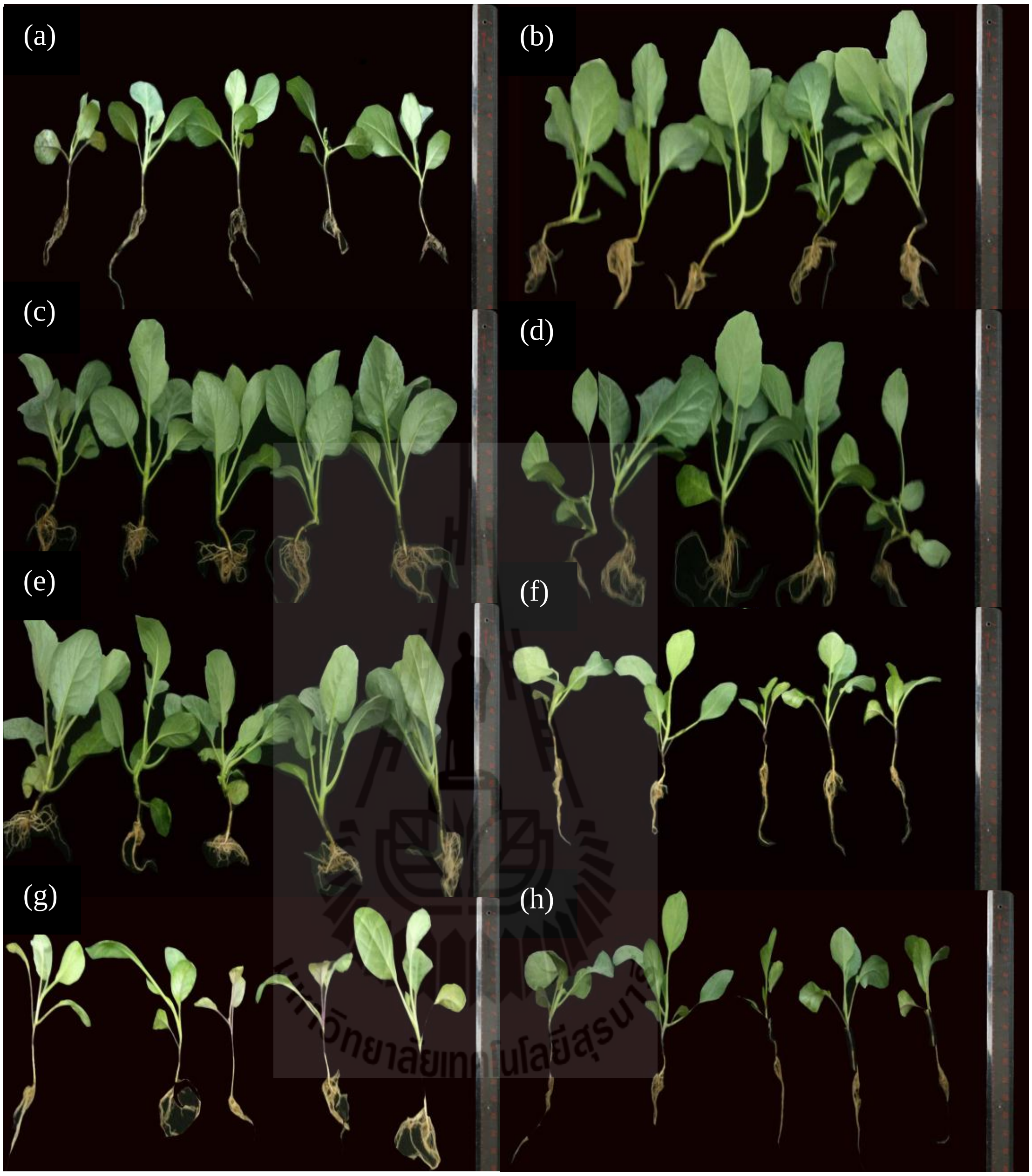

Fig. 22 Kale plant harvesting stage treat with (a) control; (b) urea; (c) EUF2; (d) EUF3; (e) EUF6; (f) Osmocote; (g) PVP and (h) PVA.

According to Wilson et al. (2006), fertilizer management is an important aspect of growing high yielding in brassica crops. The key drivers of soil fertility for crop production in general are nitrogen (N) and phosphorus (P) (Moot et al., 2007) with leafy brassica crops responding strongly. Phosphorus plays regulatory role in plant growth, photosynthesis, energy conservation, carbon metabolism and enzyme function (Akhter et al. 2007; Moot et al. 2007). Nitrogen is necessary for N-biological products production in the plant, for the proper growth of leaves, and for many other critical functions (such as photosynthesis) performed.

Plant element analysis of Chinese kale (*Brassica alboglabra* Bailey) belonging to the *Brassicaceae* family applied with un-coated and coated urea. Osmocote was incorporated into the soil for plants culture which was compared with EUFs as controlled-release fertilizer. Plant growth was used as an indicator of the effectiveness of the treatments. Of all the slowly-release products available, Osmocote has been around the longest. It is available in many different formulations and works from 2 to 6 months, depending on temperature. Normally, use of the controlled-release fertilizer Osmocote for the culture of ornamental plants is desirable practice.

In this study, the content of %N (Kjeldahl method) and total N (biomass) were showed in Table 7. A comparison of the level total N in kale in this treatment showed that coating materials (PVA and PVP) were distinctly lower values (1.05 and 1.36), respectively. Osmocote was found higher total N than control but not significantly due to osmocote (13-13-13) has a slightly longer release period which used to extend the length of time nutrients are available to the plant (2.16 and 1.69), respectively. For inorganic fertilizers (urea) are usually high soluble and are more rapidly available for plant growth. Some inorganic fertilizers (EUF2, EUF3, and EUF6) were coated with biopolymers to slow down the release of nutrients. The highest content of total N was found in EUF2 (24.14), and EUF3 (24.56), which significant higher than uncoated urea (13.29) and control (1.69), respectively.

The percentage of N in leaves of kale was determined by Kjedahl method. Also showed N accumulation ranged from 3.49-5.24%. Chuphutsa, 2010 showed content of %N in kale (*Brassica oleracea*) ranged from 3.00-5.18%. The content of %N in kale varied from 0.54 to 0.74 % in fresh matter (Korus, 2010 and Lisiewska et al., 2008). Lower levels of total N were recorded in such leafy vegetables as New Zealand spinach (Jaworska and Slupski, 2001), lettuce and summer endive (Wills et al., 1986), and among brassicas, in broccoli (Wills, 1987); while in Brussels sprouts the content was higher (Gebczynski, 2002).

Table 7 Element analysis of Kale in the values of nitrogen (%N) by Kjedahl method and total N/plant (from dry matter) which treated with un-coated and coated urea.

Treatment	% N	Total N/plants
Control (N = 0)	4.05^b	1.68^d
Urea (N = 46)	4.04^b	13.29^c
EUF2 (N = 46)	5.24^a	24.14^a
EUF3 (N = 46)	5.12^a	24.56^a
EUF6 (N = 46)	3.62^c	16.63^b
Osmocote (N = 13)	3.56^c	2.16^d
PVP (N = 12.6)	3.49^c	1.36^d
PVA (N = 0)	3.63^c	1.05^d
%CV	3.53	7.08

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

The relation of stem dry weight and stem length were compared with accumulation of N in plant analysis that showed in total N (%). Fig. 23 showed that the level of N was associated with stem dry weight. The research of this work was showed the effects of excess N on various treatment fertilizers. The high value of stem dry weight and stem length were observed on EUF2, EUF3, EUF6, and urea while PVA, PVP, and control were lower value that following with N accumulation. The observation of plant growth is major importance than the level of N accumulation that means efficiency of fertilizer coated urea (EUF2, EUF3, and EUF6) was improvement agronomic by corresponding N accumulation.

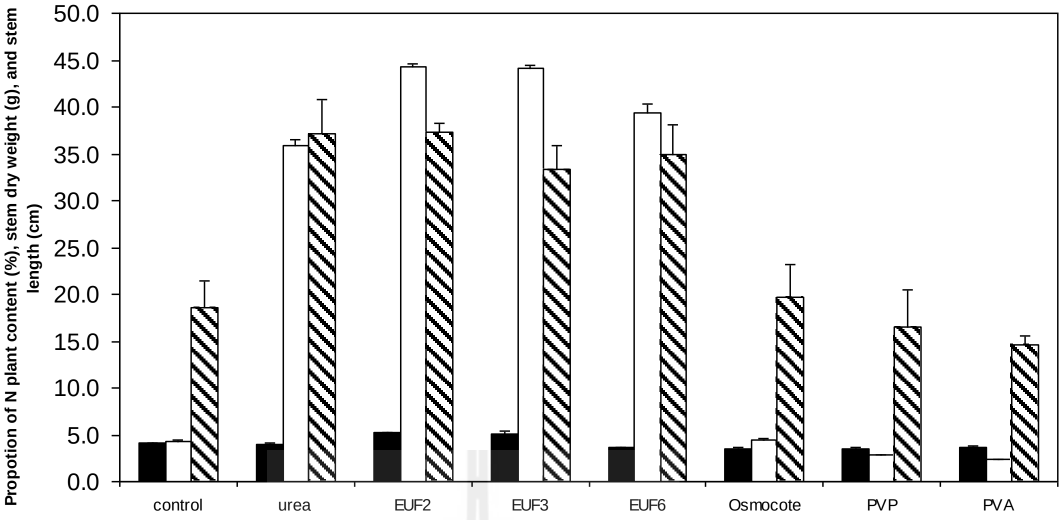

Fig. 23 Proportion of N plant content (%) (■), stem dry weight (g) (□) and stem length (cm) (▧) in kale plant which treated with un-coated and coated urea.

In the soil, urea is converted from carbamide nitrogen to ammonium ions (NH_4^+) by a series of enzyme reactions. Under normal soil conditions, NH_4^+ are absorbed by the soil become attached to the negatively charged soil particle. Nitrogen becomes available to plant, either in its ammonium form or as nitrate following microbial oxidation. In the experiment, a soil test was taken from each of 40 plots after kale plant culture had showed in Table 8. The data was showed a decreasing nutrient which compared with original soil. The levels of N started at 0.37 mg/kg and decreased between 0.20-0.33 mg/kg. The levels of % OM started at 7.4% and decreased between 4.03-6.56%. The levels of available P were started 29.6 mg/kg while the sowing showed between 11.46-28.12 mg/kg. The levels of available K were started 877.15 mg/kg while sowing showed between 715.41-818.69 mg/kg. Moisture content played an important role in determining soil resistance to penetration and as the soil moisture increased, the resistance decreased for this treatment. This decrease in soil resistance did not differ between treatments except EUF2.

Table 8 Chemical characteristics of the soil after kale plant cultivation.

Treatment	pH	EC (mS/cm)	moisture	% OM	N (mg/kg)	P (mg/kg)	K (mg/kg)
Control (N = 0)	7.78	0.33	27.1	4.03^{f}	0.20^{f}	11.46^{g}	818.69^{a}
Urea (N = 46)	7.87	0.31	22.2	5.83^{bc}	0.29^{bc}	28.12^{a}	715.41^{d}
EUF2 (N = 46)	7.84	0.33	10.4	6.56^{a}	0.33^{a}	22.55^{b}	733.73^{cd}
EUF3 (N = 46)	7.84	0.31	22.7	6.42^{ab}	0.32^{ab}	19.09^{de}	730.31^{cd}
EUF6 (N = 46)	7.82	0.33	32.3	6.38^{ab}	0.32^{ab}	14.09^{fg}	761.01^{bc}
Osmocote (N = 13)	7.85	0.33	27.8	4.31^{ef}	0.22^{ef}	20.12^{cd}	812.93^{a}
PVP (N = 12.6)	7.83	0.35	24.3	4.73^{de}	0.24^{de}	24.70^{b}	793.22^{b}
PVA (N = 0)	7.77	0.36	26.1	5.31^{cd}	0.27^{cd}	16.31^{ef}	769.54^{b}
%CV	-	-	-	5.38	5.38	6.67	1.89

Values followed by the same letter are not significantly different at $P \leq 0.05$ by DMRT

It was suggested that the high levels of percentage OM in this study showed in coated urea (EUF2, EUF3, and EUF6). The lower value of percentage OM showed in control, osmocote, PVP, and PVA. This may caused by undisturbed natural environments, the first is biological N fixation, the conversion of atmospheric N_2 to inorganic N by various soil microorganisms, some symbiotic with plants. The second is N mineralization, which is the conversion of organic N contained in soil organic matter into inorganic, plant-available N as it is decomposed by soil bacteria and fungi. Enzymatic processes are occurred during organic matter decomposition release ammonium into the soil solution.

The coated urea have reduced NH_3 volatilization and encouraged more efficiency utilization than un-coated urea. Because of high release N is effected on rapid urea hydrolysis which increased greater potential for NH_3 lost under alkaline soil condition (soil pH). In fact, when preferred N sources are available for plant, the utilization of the alternative N sources and most organic molecules is repressed. This mechanism is known as N regulation (Magasanik, 1993). Following the interaction of N mineralization and immobilization processes is closely tied to the carbon (C) cycle, because decomposing microorganisms derive their energy from carbon compounds they find in soil organic matter. Activity of soil microbes is mainly stimulated by NH_4^+. Immobilized nitrogen it is not immediately available for plant uptake, but need to be mineralized first. It is also one cause that organic matter was decreased due to decompose by microorganism.

The level of mineral N in soil before and after fertilizer application is index which determines lost of N from the level of N absorbed by plants. The content of N loss was ranged from 10.61-17.19 mg/kg (Fig. 24). This investigation showed that coated urea was lower N loss than un-coated urea (10.61 mg/kg and 17.19 mg/kg). N influenced on growth that marketable on weight of kale, which indicated the efficiency of fertilizer on product of plant. From this work would summarized the quality of coated urea was enhanced the growing of kale under greenhouse cultivation. It is obvious that in dry weight, length of stem, and leaf area index of kale, including physiological are well characteristics (Fig. 22). CRFs have to be considered in fertilization recommendations in order to minimize use of mineral fertilizers. Application of coated urea was improved effect on plant with the optimum N applied via CRFs was due mainly to their positive action on growth. Under the experiment, the calculation of the N budget inputs 30 kg N/rai for testing N loss found that urea coated with PVA and PVP showed lower N loss when compared with un-coated urea, thus resulting in this work.

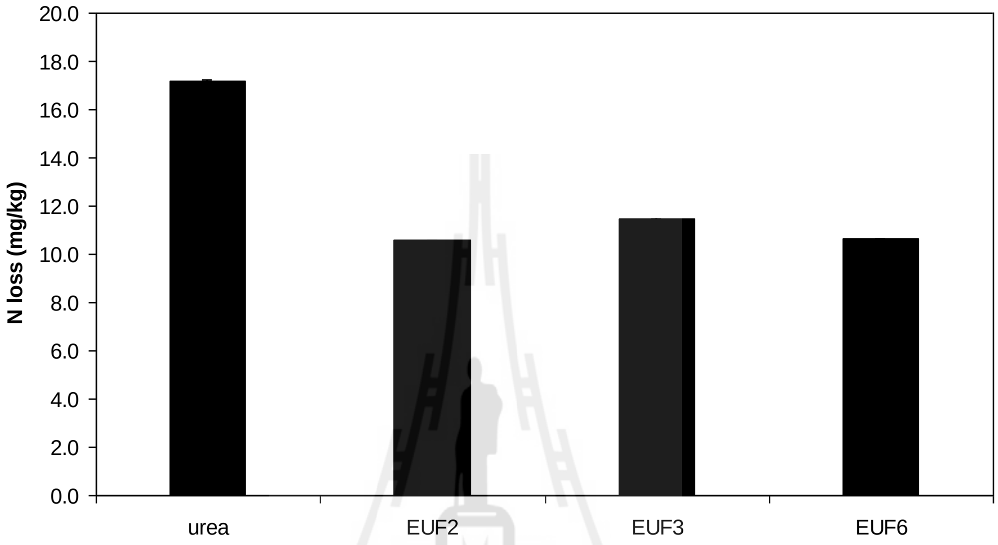

Fig. 24 N loss (mg/kg) in soil treatments of coated urea in various formula (EUF2, EUF3 and EUF6) and un-coated urea.

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CHAPTER IV

CONCLUSIONS

The optimal formula for biopolymer coating (PVA/PVP) by encapsulated urea fertilizer (EUF) was preliminary studied. The encapsulation is able to control the release rate of urea fertilizer by using Fick’s second law mention. The optimal formula of EUF was high controlled releasing rate which obtained at room temperature for PVA/PVP in a mass ratio of 1:0 (EUF2) and 1:0.25 (EUF3). The EUF is able to prolong time more than un-coated urea, it seemed in the n value is in the range of 0.98 and 0.69, respectively.

The structure of coated urea was depicted by using SEM and polarized microscope analysis. The morphology of coated urea showed various crystals shape which effected on strong surface and protected humidity than un-coated urea. Looking on granules, there are showed porous which can be absorbed water for releasing. Plant can be used immediately for growth. The functional groups of materials coating was observed from FT-IR spectrometer. The spectrum of the blend was similar to that of spectrum of urea. It must be pointed out that, the amount of materials coating (PVA/PVP) is markedly smaller than that pure solid urea.

Urea fertilizers between coated with biopolymer and un-coated were tested in greenhouse system to estimated plant growth. Chinese kale (*Brassica alboglabra* Bailey) was applied EUF2, EUF3, and EUF6 as a fertilizer to study the effect of EUF on plant growth. The parameter of plant growth included stem wet weight, root wet

weight, stem dry weight, root dry weight and element analysis (N) were investigated. Results showed that EUF2, EUF3, and EUF6 can be promoted plant growth better than un-coated urea significantly different ($P \leq 0.05$). A comparison of the level total nitrogen in kale showed that applied urea was lower but higher in kale applied EUF. Moreover, consider the best formula for controlled-release fertilizer was showed empirical parameter characterizing the release mechanism from Fick's second law and plant growth regulator was corresponded (EUF2 and EUF3).

BIOGRAPHY

The author's name Sirima Pinpeangchan. She was born on 21th December 1985 in Nakhonratchasima, Thailand. She studied in School of Crop Production Technology, Institute of Agricultural Technology, Suranaree University of Technology. She graduated the Bachelor's of Science in Crop Production Technology in 2008. After graduated, in 2009, she was Master's in School of Biotechnology at Suranaree University of Technology. She conducted the research in the topic of Controlled-release urea fertilizer by biopolymeric encapsulation. The result of this project has been presented as oral presentation at the Burapha University International Conference, July 9-12, 2012 Pattaya, Thailand. The results from some part of this study have been presented 1st International Colloquium, July 16-20, 2012, Suranaree University of Technology, Nakhonratchasima, Thailand. During master degree enrollment, she has been an assistant researcher of Associate Professor Dr. Chokchai Wanapu in School of Biotechnology.