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PREPARATION OF POLYGLYCEROL-BASED POLYURETHANE FOR SLOW-RELEASED FERTILIZER

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ปุ๋ยปลดปล่อยช้าเตรียมได้จากการเคลือบปุ๋ยด้วยพอลิยูริเทนที่ได้ปฏิกิริยาระหว่างเมทิลีนไดเฟนิล ไดไอโซไซยาเนต (MDI) และพอลิออล (polyol) พอลิออลที่สังเคราะห์ได้จากปฏิกิริยากลีเซอรอไลซิส ระหว่างกลีเซอรอลและน้ำมันสามชนิด คือ น้ำมันปาล์มอิพอกซิไดซ์ น้ำมันปาล์ม และน้ำมันละหุ่งจะถูก นำไปใช้เป็นสารตั้งต้นสำหรับการเตรียมเป็นพอลิยูรีเทนเพื่อชะลอการปลดปล่อยธาตุอาหาร เมื่อนำพอลิยูรี เทนทั้งสามชนิดไปเคลือบบนปุ๋ยยูเรียตั้งแต่ 1-5 ชั้น และศึกษาอัตราการปลดปล่อยยูเรีย โดยใช้เทคนิค ยูวี วิสิเบิล สเปกโตรโฟโตเมตรี พบว่าปุ๋ยที่ผ่านการเคลือบแล้ว สามารถลดอัตราการปลดปล่อยยูเรียได้ เมื่อ ความหนาของชั้นเคลือบมากขึ้นจะทำให้อัตราการปลดปล่อยลดลง เมื่อทำการเปลี่ยนแปลงสภาวะในการ ทดสอบปุ๋ยที่เคลือบได้ พบว่าเมื่อเพิ่มอุณหภูมิจะทำให้ปุ๋ยมีการปลดปล่อยยูเรียเพิ่มขึ้น ในสภาวะที่เป็น ด่างจะชะลอการปลดปล่อยยูเรียให้ช้าลง สำหรับปุ๋ยที่เคลือบด้วยพอลิยูรีเทน 1-3 ชั้น ยูเรียจะถูกปลดปล่อย หมดภายในเวลา 30 วันเช่นเดียวกัน ส่วนปุ๋ยที่เคลือบ 5 ชั้น จะมีอัตราการปลดปล่อยที่ลดลงจากเดิมและมี แนวโน้มการปลดปล่อยที่สม่ำเสมอมากขึ้น นอกจากนี้พบว่าภายใน 30 วัน ยูเรียที่มีการเคลือบด้วย 5 ชั้นของ พอลิยูรีเทนฐานพอลิออลน้ำมันปาล์มอิพอกซิไดซ์, ฐานพอลิออลน้ำมันปาล์ม, ฐานพอลิออลน้ำมันละหุ่ง ถูก ปลดปล่อยออกมาร้อยละ 85, 90 และ 94 ตามลำดับ

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WATSAMON SAETAE: PREPARATION OF POLYGLYCEROL-BASED POLYURETHANE   FOR   SLOW - RELEASED   FERTILIZER.   THESIS ADVISOR: ASSOC. PROF. SURACHAI PORNPAKAKUL, Ph.D., 86 pp.

Slow released fertilizer was prepared by coating a fertilizer with polyurethane (PU) from the reaction of methylene diphenyl diisocyanate (MDI) and polyol. The polyols synthesized by glycerolysis reaction of glycerol and epoxidized palm oil, palm oil, and castor oil were used as starting material for preparing polyurethane used for slow releasing of nutrient. The PU was coated on the urea fertilizer for 1-5 layer and the coated fertilizer was studied the releasing rate by UV-Visible spectrophotometry technique. It was found that the coated fertilizer exhibited the slow released properties. When thickness of the PU coating was increased, the releasing rate of urea decreased and increasing ambient temperature resulted in increasing of releasing rate. Furthermore, basic condition decreased releasing rate of urea. For 1-3 layer coated fertilizer, urea completely released within 30 days while the 5 layer coated fertilizer gave a slower and constant releasing rate. Furthermore, it was found that the urea of 5 layers coated with epoxidized palm oil polyol based, palm oil polyol based and castor oil based polyurethane was released within 30 days by 85, 90 and 94%, respectively.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Field of Study...Petrochemistry and Polymer Science...Student's Signature...... Watsamon Saetae

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

LIST OF ABBREVIATIONS

MDI	methylene diphenyl diisocyanate
PU	polyurethane
PG	polyglycerol
PGPU	polyglycerol PU
PGCF	polyglycerol PU coated fertilizer
EPPO	epoxidized palm oil polyol
EPPU	epoxidized palm oil PU
EPPUCF	epoxidized palm oil PU coated fertilizer
PPO	palm oil polyol
PPU	palm oil PU
PPUCF	palm oil PU coated fertilizer
CPO	castor oil polyol
CPU	castor oil PU
CPUCF	castor oil PU coated fertilizer
S.D.	the standard deviation
$^{\circ}$C	degree celsius
SEM	scanning electron microscope
nm	nanometer
min	minute
g	gram
FT-IR	fourier transform infrared spectroscopy
NMR	nuclear magnetic resonance spectroscopy
GPC	gel permeation chromatography
ASTM	American Standard Test Method
mL	milliliter
h	hour
cm	centimeter
cm^{-1}	wavenumber

CHAPTER I

INTRODUCTION

1.1 Introduction

Slow-release fertilizer is a modified fertilizer to help a gardener reducing a leaching of nutrient in water soluble fertilizer, lead to a fertilizer burn and environmental toxicities. A slow-release fertilizer composed of a semipermeable membrane (sulfur or polymer) and water-soluble fertilizers. For the coated slow-release fertilizer, main mechanism of nutrients release are diffusion of water passing through the membrane, causing an internal pressure to disrupt the membrane. Moreover releasing rate depends on soil (temperature, moisture, pH) and thickness of the coating.

Polyurethane (PU) is a type of polymer use in many industries; automobiles, packaging, implant surgery, and agriculture. Similar to other polymeric materials, in general PU relies on petroleum oil as the feedstock. Recently, because of the less predictable petroleum market, PU feedstocks were replaced by natural oil. They have not only a potential to substitute petroleum in some applications but also environmental friendly.

Since 10% of glycerol is produced from biodiesel production. The higher production of biodiesel will cause the growth of available glycerol stocks in the next few years. Glycerol has three hydroxy groups in molecule and can be reacted with isocyanate to form polyurethane. Conventional glycerol has too low molecular weight and hygroscopic to use for slow-released application, polymerization and substitution a portion of hydroxy groups with hydrophobic part are required. Polyglycerol was synthesized via based catalyzed polymerization at high temperature (>200°C) but by-product are also generated [1]

Thus glycerol, polyglycerol and a polyol with long chain alkyl groups were use as staring materials for polyurethane for coating

1.2 Objectives

1. To prepare slow-release fertilizer with polyglycerol-based polyurethane.

2. To study effect of pH, temperature, thickness, and types of polyol on releasing rate.

3. To prepare slow released fertilizer with appropriate releasing rate.

1.3 Scope

The stepwise investigation was carried out as follows.

1. Literature survey for related research work.

2. Preparation of slow-release fertilizers from urea fertilizers

3. Investigation of slow-release fertilizer morphology and thickness by Scanning Electron Microscope (SEM)

4. Optimization of a condition to coat a fertilizer

5. Characterization of a synthesized product.

   - ^{1}H NMR for following epoxidation and glycerolysis reaction

   - FT-IR for identifying a functional group of film

   - GPC for measuring molecular weight of polyglycerol.

6. Investigation of factors ex. temperature, pH, thickness, and types of polyol on releasing rate.

   - UV-Visible spectroscopy for determining urea content

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Fertilizers and nutrients [2]

There are 16 essential elements that plants require for their growth and development (see Table 2.1). Carbon, hydrogen, and oxygen are derived from the atmosphere and soil water. The remaining 13 essential elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, zinc, manganese, copper, boron, molybdenum, and chlorine) are supplied either from soil minerals and soil organic matter or by organic or inorganic fertilizers. Each type of plant is unique and has an optimum nutrient range as well as a minimum requirement level.

Table 2.1 Essential plant nutrients: their relative amounts in plants, functions and classification [2].

Name	Chemical symbol	Relative % in plant*	Function in plant
1° macronutrients			
Nitrogen	N	100	Proteins, amino acids
Phosphorus	P	6	Nucleic acids, ATP
Potassium	K	25	Catalyst, ion transport
2° macronutrients			
Calcium	Ca	12.5	Cell wall component
Magnesium	Mg	8	Part of chlorophyll
Sulfur	S	3	Amino acids
Micronutrients			
Iron	Fe	0.2	Chlorophyll synthesis
Copper	Cu	0.01	Component of enzymes
Manganese	Mn	0.1	Activates enzymes
Zinc	Zn	0.03	Activates enzymes
Boron	B	0.2	Cell wall component
Molybdenum	Mo	0.0001	Involved in N fixation
Chlorine	Cl	0.3	Photosynthesis reactions

*Relative amounts of mineral elements compared to nitrogen in dry shoot tissue. May vary depending on plant species.

Below this minimum level, plants start to show nutrient deficiency symptoms (see Table 2.2). Excessive nutrient uptake can cause poor growth because of toxicity.

Table 2.2 Generalized symptoms of plant nutrient deficiency or excess [2]

Plant Nutrient	Type	Visual symptoms
Nitrogen	Deficiency	Light green to yellow appearance of leaves, especially older leaves; stunted growth; poor fruit development.
	Excess	Dark green foliage which may be susceptible to lodging, drought, disease and insect invasion. Fruit and seed crops may fail to yield.
Phosphorus	Deficiency	Leaves may develop purple coloration; stunted plant growth and delay in plant development.
	Excess	Excess phosphorus may cause micronutrient deficiencies, especially iron or zinc.
Potassium	Deficiency	Older leaves turn yellow initially around margins and die; irregular fruit development.
	Excess	Excess potassium may cause deficiencies in magnesium and possibly calcium.
Calcium	Deficiency	Reduced growth or death of growing tips; blossom-end rot of tomato; poor fruit development and appearance.
	Excess	Excess calcium may cause deficiency in either magnesium or potassium
Magnesium	Deficiency	Initial yellowing of older leaves between leaf veins spreading to younger leaves; poor fruit development and production.
	Excess	High concentration tolerated in plant; however, imbalance with calcium and potassium may reduce growth.
Sulfur	Deficiency	Initial yellowing of young leaves spreading to whole plant; similar symptoms to nitrogen deficiency but occurs on new growth.
	Excess	Excess of sulfur may cause premature dropping of leaves.
Iron	Deficiency	Initial distinct yellow or white areas between veins of young leaves leading to spots of dead leaf tissue.
	Excess	Possible bronzing of leaves with tiny brown spots.
Manganese	Deficiency	Interveinal yellowing or mottling of young leaves.
	Excess	Older leaves have brown spots surrounded by a chlorotic circle or zone.
Zinc	Deficiency	Interveinal yellowing on young leaves; reduced leaf size.
	Excess	Excess zinc may cause iron deficiency in some plants.
Boron	Deficiency	Death of growing points and deformation of leaves with areas of discoloration.
	Excess	Leaf tips become yellow followed by necrosis. Leaves get a scorched appearance and later fall off.

2.2 Nitrogen Fertilizer [3]

The three primary soluble N sources are ammonium sulfate, ammonium nitrate, and urea.

Ammonium Sulfate is a white crystalline material containing 20-21% N and 24% S. If produced in the pure crystalline form it is rice-like in appearance, but the pure form is seldom marketed. The marketed product may be grayish in color due to carbon contamination during manufacture.

Ammonium Nitrate is generally in prilled form containing 33-34% N. It is highly soluble and is also in solution form. Prilled ammonium nitrate may be bright white in color, indicating that the prill has been coated with magnesium chloride, or beige in color, indicating that the product has been coated with a mixture of clays.

Urea is a white crystalline solid, generally marketed in prill form, containing 45-46% N. It has good physical properties and is not as hygroscopic as ammonium nitrate.

(a)   (b)   (c)

Figure 2.1 Three types of nitrogen source; (a) ammonium sulfate, (b) ammonium nitrate, (c) urea.

Nitrogen in the soil is lost by three process, (1) denitrification, (2) leaching, and (3) surface volatilization [4].

1. Denitrification

This process occurs when O_2 levels are low, bacteria and microorganisms in the soils convert the oxygen from the nitrate to nitrogen gas (N_2) or nitrous oxide (N_2O) and volatilize from the soil.

2. Surface volatilization

This process occurs when urea forms of nitrogen are broken to form ammonia gases. The rate of volatilization depends on moisture , temperature and surface pH of the soil. In the moist soil surface, the water evaporates into the air. Ammonia released from the urea is picked up in the water vapor and lost. On dry soil surfaces, less urea-N is lost. Temperatures greater than $50^{\circ}F$ (10° Celsius) and pH greater than 6.5 significantly increase the rate of urea conversion to ammonia gases. Applying urea-type fertilizers when weather is cooler slows down nitrogen loss.

3. Leaching

All water-soluble nitrogen species are moved with the water when soils have more water content than they can hold. In the case of ammonium forms of nitrogen, which have a positive charge and are held by the negative sites on the clay in the soil, it leaches very little. In contrast, nitrate have a negative charge.

2.3 Slow-release fertilizers and their development [3]

Slow-release fertilizer in which a physical barrier is used to reduce their dissolution rate are commonly prepared by encapsulation (coating or matrix formation) of water soluble granular plant nutrients with low permeability hydrophobic membranes [5]. This fertilizer is an alternative for uniform supply of nutrients to plants, and minimizing potential leaching which lead to a fertilizer burn and environmental toxicities.

They also have an advantage of reducing labor cost during farm application. Several groups of slow-release fertilizer are classified based on the process by which the nutrients are released.

- **Ureaformaldehyde reaction products**, the oldest controlled-release nitrogen technologies, had been first produced in 1936 and commercialized in 1955. The mechanism of N release from UF is involve dissolution and microbial decomposition.

Figure 2.2   Ureaformaldehyde reaction products; Nitroform.

- **Isobutylidene diurea (IBDU)** obtained from the reaction of urea with isobutyraldehyde forms a single oligomer. The compound will be hydrolyzed to urea and isobutyraldehyde. The hydrolysis rate depends on acidity and high temperature.

Figure 2.3   Isobutylidene diurea (IBDU).

- **Sulfur-coated fertilizers (SCF)** was developed in the 1960s and 1970s. The mechanism of N release from SCF is by water penetration through micropores or imperfections in the coating.

Figure 2.4   Sulfur coated urea.

- **Polymer-coated fertilizers** is the most advanced slow-release technology. Most of polymer-coated fertilizer release by diffusion through a semipermeable membrane, the releasing rate can be varied by compositions and thickness of the coating. Polymer coatings can be classified as thermoset or thermoplastic resins. Because of the high costs of process on polymer-coated products, their uses have been limited to high-value applications.

(a)   (b)

Figure 2.5   Polymer coated fertilizers; (a) Thermoplastic resin coated urea; Meister product, (b) Polyurethane coated urea; Polyon.

2.4 Model of releasing [6]

2.4.1 Solution/diffusion through continuous plasticized polymer phase

The polymer and other additives are dispersed homogeneously in continuous phase. The polymer film has molecular sized openings between the cross-linked polymer chains. The openings must be wetted for nutrients to diffuse
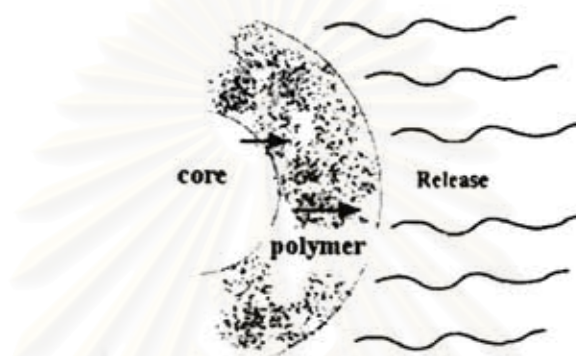
Figure 2.6   Solution/diffusion through continuous plasticized polymer phase.

2.4.2 Solution/diffusion through plasticizer channels

When the solubility of the nutrients in the plasticizer is higher than that in water, it is possible that the nutrients would be preferentially transported through such plasticizer channels.
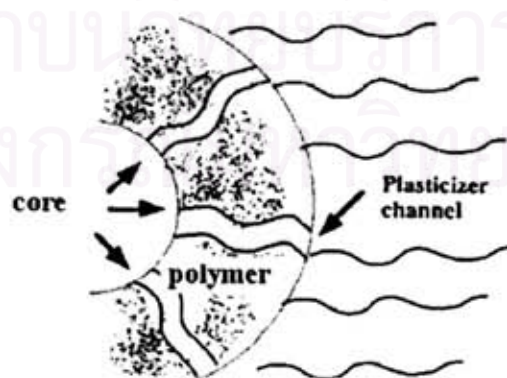
Figure 2.7   Solution/diffusion through plasticizer channels.

2.4.3 Diffusion through aqueous pores

This model described a non-homogeneous and discontinuous coating but punctuated with pores. These pores filled with solution when the dosage form comes in contact with an aqueous medium, and thereby facilitate the diffusion of the nutrients. The transport mechanism in these pores can range from pure molecular diffusion to convection, depending on the pore size.
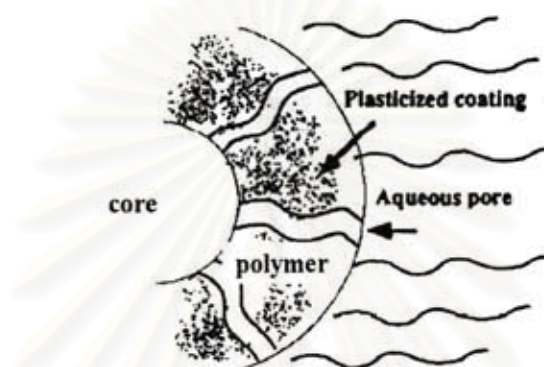
Figure 2.8 Diffusion through aqueous pores.

2.4.4 Osmotically driven release

The osmotically driven release is a well known model for porous membranes. When the sufficient osmotic pressure is generated by the core material, the water molecule penetrated to high osmotic pressure location and dissolved nutrients out.
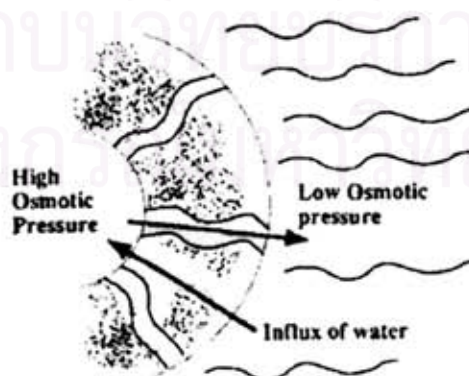
Figure 2.9 Osmotically driven release.

2.5 Nutrient releasing mechanism

When applied the fertilizer in a soil, the releasing of nutrients are occurred with a combination of mechanism outside those of the coating materials.

Microbial action

Microorganisms in soil and/or environment act to breakdown the fertilizer elements into more basic compounds. The activity levels of micro-organisms depends on a soil temperature. Cold temperatures affect less activity and less breakdown, while warmer temperatures increase activity and breakdown.

Osmosis

Nutrients will move from a place of higher concentration to that of lower concentration. For example, the higher concentrations of nitrogen in the fertilizer granule will slowly migrate to the soil where is a less nutrient-rich.

Hydrolysis

Hydrolysis is an interaction of water with the fertilizer or coatings will break down the compounds and release the nutrients into the soil. The hydrolyzed rate of fertilizer or coatings is depends on a types of functional groups, materials, moisture and temperature.

Physical Breakdown

The fertilizer handle can make a cracking and breaking on fertilizer due to nutrient released with rapid or inappropriate rate.

2.6 Polyurethane [7]

Polyurethane (PU) is a well-known class of polymers, which have a urethane linkage as a characteristic unit. By proper selection of reactants result PU in various characters, for example, a rigid crystalline plastic, flexible elastomer, or foam.
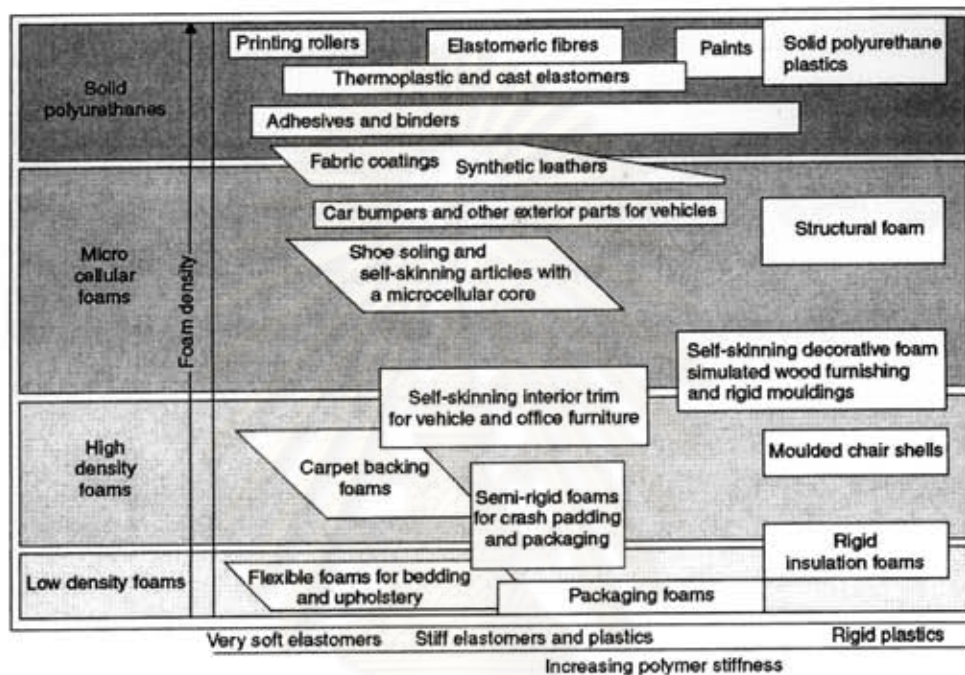
Figure 2.10   Various applications of polyurethane.

One valuable and important use of polyurethanes is in the manufacture of coatings. Polyurethane coatings can be devided to the five general types by the American Society for Testing Materials (ASTM).

Type I is cured prepolymer by reacting it with a hydrogen donor, for example, moisture, polyhydroxy compound or amine to give the final polymer product.

Type II is a moisture curable urethane prepolymer.

Type III is known as a blocked urethane and is extensively used in coatings which are baked after application.

Type IV is a two-package urethane, one of which contains the NCO prepolymer, the other of which contains a highly reactive diamine and other components to promote flow, bubble release.

Type V is a two-package formulation consist of the NCO prepolymer and the second component is a polyol.

2.7 Diisocyanates and its chemistry [8, 9]

In commercial, isocyanates are prepared by phosgenation of primary amines. toluene diisocyanates (TDI), diphenylmethane diisocyanates (MDI), naphthylene diisocyanates (NDI) and hexamethylene diisocyanates (HDI) are the most widely used isocyanates in polyurethane synthesis. The aromatic-ring containing isocyanates are more reactive than aliphatic ones.
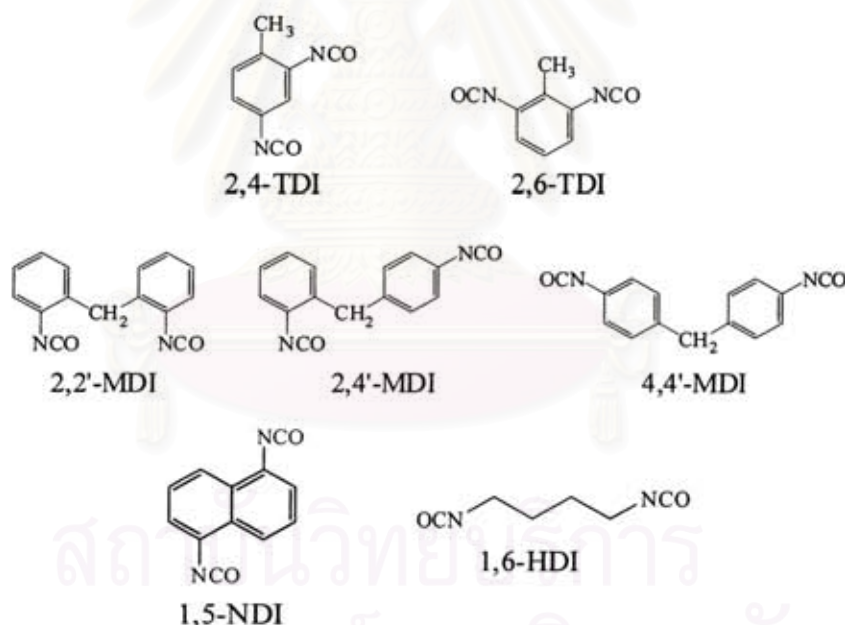
Figure 2.11 Some types of diisocyanates.

Diisocyanates consist of two isocyanates group (-N=C=O) is a highly unsaturated and reactive group, containing two cumulative double bonds. It can react with both electron donor and electron acceptor functional groups. Isocyanates can react for three types of reactions; e.g. primary, secondary reactions and polymerization.

2.7.1 Primary reactions

Primary reactions are faster and occur at relatively lower temperatures compared to the secondary reactions. The various primary reactions of isocyanates are described as follow.

- Reaction of isocyanate with hydroxyl group is the exothermic reaction, which produce urethane linkage. The isocyanate reacts readily with primary hydroxyl groups than secondary ones.

$$R-NCO + R'-OH \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-OR'$$
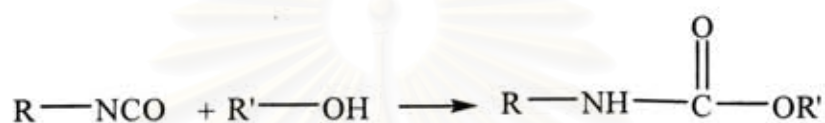
- Reaction of isocyanate with amine groups at 0-25°C to form substituted urea. Primary amine groups have higher reactivity with isocyanates than secondary ones.

$$R-NCO + R'-NH_2 \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-R' + CO_2$$
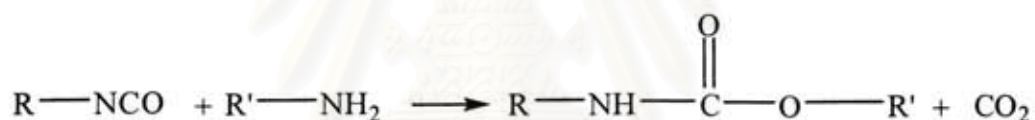
- Reaction of isocyanate with carboxylic acid leads to the formation of amide linkage, which is similar to urethane linkage. This reaction produces carbon dioxide gas.

$$R-NCO + R'-COOH \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-O-R' + CO_2$$
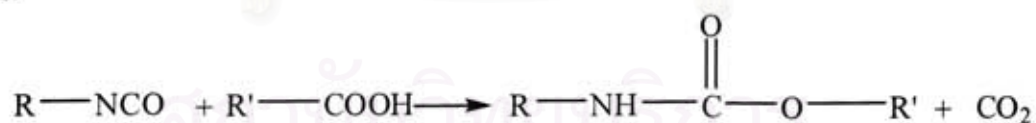
- Reaction of isocyanate with water produces amines and carbon dioxide gas. The carbon dioxide gas causes foaming which is undesirable in coating or non-foam applications.

$$R-NCO + H_2O \longrightarrow R-NH-\overset{\overset{\textstyle O}{\|}}{C}-OH \longrightarrow R-NH_2 + CO_2$$
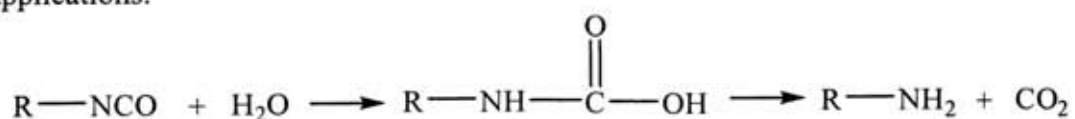
2.7.2 Secondary reactions

Isocyanate reacts with the secondary amine group of urethanes, ureas, and amide forming allophanates, substituted biurets, and acyl ureas respectively The secondary reactions leads to cross-linking and the resulting polyurethane becomes insoluble and infusible.
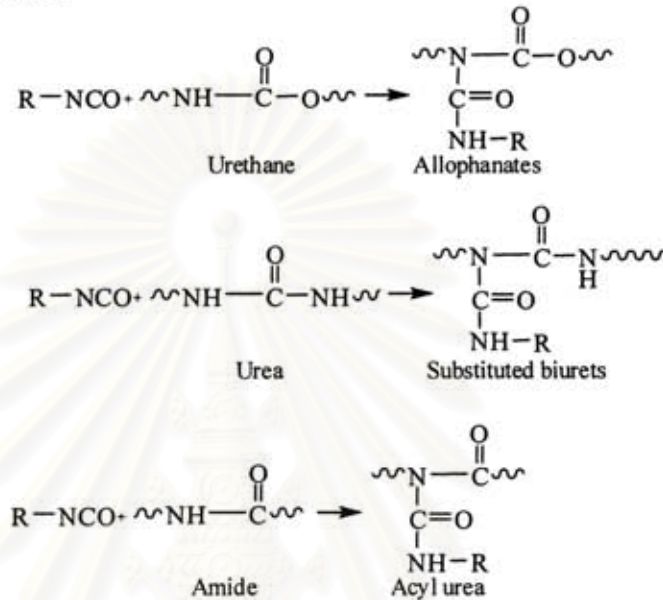
2.7.3 Polymerization

Polymerization also occured, which may be termed self addition. Examples of this reaction are dimerization to uretidione and trimerization to give isocyanurates (Figure 2.12).
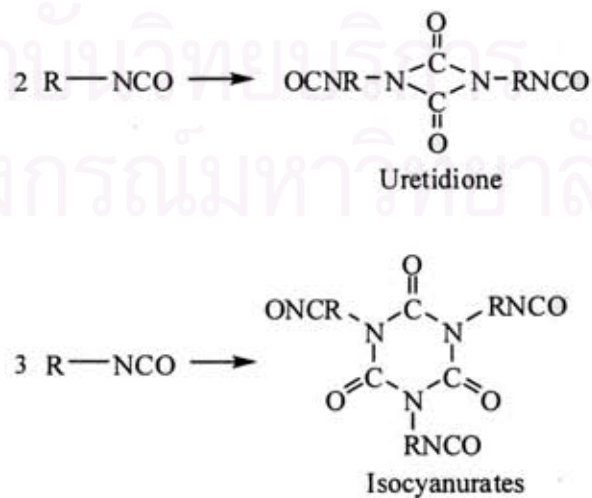
Figure 2.12 Dimerization and trimerization of isocyanates.

2.8 Castor oil [10]

Castor oil is obtained from extracting the seed of a plant called *Ricinus communis* of the family Eurphorbiacae (see Figure 2.13). Castor oil is a viscous, pale yellow and non-volatile oil. On the average, they contain about 46–55% oil by weight. Castor seeds are poisonous to humans and animals because they contain ricin, ricinine and certain allergens that are toxic. The chemistry of castor oil involve on a fatty acid called ricinoleic acid and the three types of functionality in the molecule; (1) the carboxyl group providing a wide range of etherification; (2) the unsaturation which can be hydrogenated or epoxidized and (3) the hydroxyl group which can be acetylated, alkoxylated, or dehydration to increase the unsaturation of the compound. The ricinoleic acid comprises over 80% of all fatty acid in the oil (Table 2.3). The presence of hydroxyl groups and double bonds make the oil suitable for many chemical reactions and modifications (Table 2.4).

2.9 Palm oil [7, 11]

Palm oil obtains from the fruit and kernels (seeds) of the *Arecaceae Elaeis* oil palm (see Figure 2.14). It contains a high amount of beta-carotene. Palm oil is one of the few vegetable oils relatively high in saturated fats and thus semi-solid at room temperature. The oil is widely used as cooking oil, and a component of many foods. For non-food application, it is also an important component of many personal care products and a feedstock for biodiesel. Palm oil composes of oleic and palmitic acid as a major composition (Table 2.3).

Figure 2.13   Castor seeds.
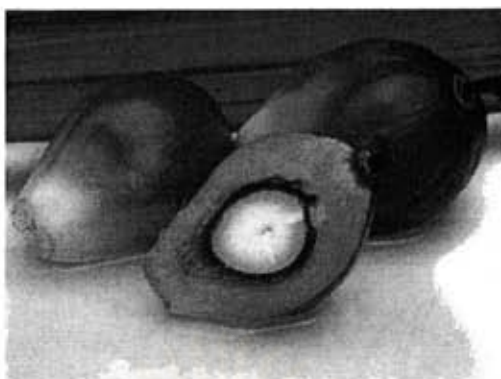
Figure 2.14 Palm seeds.

Table 2.3 Fatty acid composition of oils [11]

Fatty acid	Formula	Castor oil (%)	Palm oil (%)
Palmitic acid	$C_{16}H_{32}O_2$	1.5	39.0
Stearic acid	$C_{18}H_{36}O_2$	0.5	5.0
Oleic acid	$C_{18}H_{34}O_2$	5.0	45.0
Linoleic acid	$C_{18}H_{32}O_2$	4.0	9.0
Linolenic acid	$C_{18}H_{30}O_2$	0.5	-
Ricinoleic acid	$C_{18}H_{33}O_3$	87.5	-
Licanic acid	$C_{18}H_{28}O_3$	-	-
Other		-	2.0

2.10 Epoxidized palm oil [12]

Epoxidized palm oil can be produced by reacting palm oil with peracids. The use of epoxidized oils lies in the versatility of epoxide rings. They are easily converted to other useful functional groups. Epoxidized palm oil can be converted to various polyols by reacting them with short chain polyhydric alcohols in the presence of catalysts. Polyols when reacted with isocyanates produce polyurethane foams.

Table 2.4 The functional group in oil and its chemical reactions [10]

	Reaction	Reactants	Type of Products
Ester	Hydrolysis	Acid, enzyme	Fatty acids, glycerol
	Esterification	Monohydric alcohols	Esters
Linkage	Alcoholysis	Glycerol, glycols polydydric alcohol	Mono- and diglycerides, monoglycols, etc.
	Amidation	Alkyl amines	Amine salts, amides
	Halogenation	$SOCl_2$	Fatty acid halogens
Double	Epoxidation	Peracid	Epoxidized oils
Bond	Sulfonation	H_2SO_4	Sulfonated Oils
	Dehydration, Hydrolysis, distillation	Catalyst (plus heat)	Dehydrated castor oil, Octadecadienoic acid
Hydroxyl	Pyrolysis	High heat	Undecylenic acid, heptaldehyde
	Halogenation	PCl_5, $POCl_3$	Halogenated castor oils
	Alkoxylation	Ethylene and/or propylene oxide	Alkoxylated castor oils
Group	Esterification	Acetic-, maleic-, phthalic anhydrides	Alkyl and alkylaryl esters, phosphate esters
	Sulfation	H_2SO_4	Sulfated oil
	Urethane reactions	Isocyanates	Urethane polymers

2.11 Organotin catalyst

Organotin compounds or stannous have one or more C-Sn covalent bonds. The organotin compounds can be classified based on the number of tin with hydrocarbon substituents. These are denominated as mono-, di-, tri-, and tetraorganotin compounds with the general structure:

$$R_nSn\,X_{4-n}$$
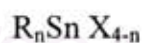
where   R   = an alkyl or aryl group

              Sn = the central tin atom in the oxidation state +4

              X   = a singly charged anion or an anionic organic group

Tetraorganotins are very stable molecules with low toxicity and low biological activity. Triorganotins are very toxic. Depending on the organic groups, they can be powerful bactericides and fungicides. Diorganotins have no antifungal activity, low

toxicity, and low antibacterial activity. Monoorganotins have no biocidal activity and their toxicity to mammals is very low.
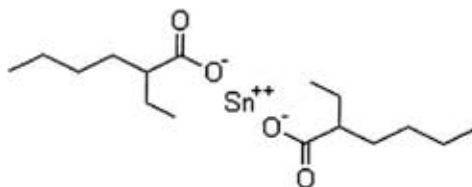
Figure 2.15   The structure of stannous octoate.

Stannous octoate, a type of an organotin compounds, which is a widespread catalyst for making polyurethane. Stannous octoate was prepared by the following reactions [12].

$$2NaOH \;+\; 2C_7H_{15}COOH \;\longrightarrow\; 2NaO_2CC_7H_{15} \;+\; 2H_2O$$

$$2NaO_2CC_7H_{15} \;+\; SnCl_2 \;\longrightarrow\; Sn(O_2CC_7H_{15})_2 \;+\; 2NaCl$$
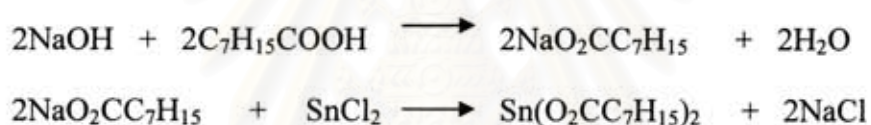
2.12 Ehrlich's reaction [14]

The reaction between *p*-Dimethylaminobenzaldehyde (*p*-DMAB) and urea in the presence of acid give a light yellow complex called lemon kelly.
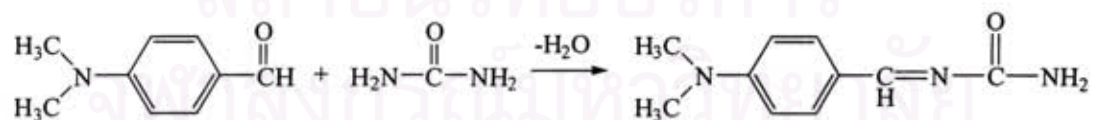
Scheme 2.1   The Ehrlich's reaction.

2.13 Literature reviews

In 2000, Al-Zahrani prepared controlled release fertilizer by using paraffin and polyethylene waxes. Dissolution of urea of two types coating was tested. It was found that the coated fertilizer with polyethylene wax gave longer release time than that with the paraffin wax [15].

In 2001, Prashantha and coworkers synthesized an interpenetrating polymer networks (IPNs) of glycerol modified castor oil polyurethane (GC-PU) and poly[2-hydroxyethylmethacrylate] (PHEMA) using benzoyl peroxide as initiator and N,N-methylenebis acrylamide as crosslinker. The percent weight loss of IPNs were determined in H_2SO_4, CH_3COOH, HCl, HNO_3, NaCl and NaOH. The results indicated that all the IPNs show excellent acid and alkali resistance as compared to unmodified castor oil polyurethane/PHEMA IPNs [16].

In 2002, Ge and coworkers prepared biodegradable polyurethane foams (PUFs) as coating materials for the controlled release of fertilizer. PUFs were prepared from diisocyanates, polyester, Acacia mearnsi bark, and corn starch. The ammonium sulfate fertilizer was used to evaluate the effects of the preparation on the release ratio. The release ratio of ammonium sulfate decreased with an increasing amount of biomass in PUFs and increasing sizes of sample particles. The remaining fertilizer in the polyurethane seemed to be released completely because the PUFs were degradable, to some extent, by soil microorganism [17].

In 2002, Tomaszewska prepared polysulfone coated NPK granular fertilizer. It was found that the release rate of nutrients from coated granules decreases with the decrease of the coating porosity. In addition, the coating led to improvement of handing properties and the crushing strength of all coated fertilizers was an average of 40% higher than that of uncoated NPK fertilizer [18].

In 2003, Jarosiewicz prepared a NPK6-20-30 fertilizer coated with polysulfone (PSF), polyacrylonitrile (PAN), and cellulose acetate (CA). The release rate of NPK in the core of the coated fertilizer was studied. In the case of PAN

coating with 60.45% porosity, prepared from a 16% polymer solution, 100% of NH_4^+ and P_2O_5 was completely released after 4 h and 99.7% of K^+ after 5 h, whereas in the case of coating with 48.8% porosity, 31.8% of NH_4^+, 16.7% of P_2O_5, and 11.6% of K^+ was released after 5 h. It was found that the release of potassium through the PSF and PAN coatings was the slowest. The same trend was observed for the release of nitrogen through CA coatings [19].

In 2005, Guo and coworkers prepared a slow-release membrane-encapsulated urea fertilizer composed of cross-linked starch (the first layer) and a copolymer of acrylic acid and acrylamide (the second layer) to obtain superabsorbent and moisture preservation. The slow-release behavior and water holding capacity of the membrane are investigated. The elemental analysis showed that more than 90% of N released from uncoated urea fertilizer. On the other hand, coated urea fertilizer had only 10% of N released. The water-holding experiment showed the largest water-holding ratio of the soil mixed with membrane was 12.45% higher than that without it [20].

In 2006, Jose and coworkers studied the biodegradation of a polyurethane foam derived from castor oil using cultivation of microorganisms derived from biological grease-degrading agents; Fungi *Aspergillus sp* and Bacteria *Chryseobacterium meningosepticum*. The biodegradation was analyzed by scanning electron microscopy (SEM), thermogravimetry (TG) and Fourier-transform infrared spectroscopy with accessory for attenuated total reflectance (FTIR-ATR). The result showed in TG curve indicated that the composition process occurred in three steps, the first step (100-300 °C) is the loss of volatile compounds, such as the additives of polyurethane; the second step (300-400 °C) is the decomposition of polyurethane by the rupture of the urethane links and the third step (400-500 °C) is related to the rupture of the ester links. In this third step of degradation corresponded to the ester links that disappeared after attacked by microorganisms. The degradation of ester links was proved by the decreasing of intensity of infrared spectrum band at 1042 cm⁻¹. The results from SEM showed the rougher surface of attacked polyurethane than the original [21].

In 2007, Chen and coworkers prepared a slow-release membrane-encapsulated urea fertilizer with starch-g-PLLA by solution-casting. The release behavior of urea encapsulated in the films was studied. It was found that the introduction of hydrophobic PLLA reduced the swellability of starch matrix and decreased the release rate of urea, the urea release rate could be controlled from several hours to 1 day by adjusting the graft efficiency. From scanning electron microscopy (SEM) revealed that the urea encapsulated within the starch matrix was uniformly dispersed. The urea encapsulated in the modified starch film released through a diffusion mechanism [14].

In 2007, Kaushik and coworkers studied the kinetics of the uncatalyzed reaction of diphenyl methane diisocyanates (MDI) and castor oil (CO) trimethylol propane (TMP) polyol, with xylene as solvent at different temperatures, solvent concentration and NCO=OH ratios were investigated. The polyol was synthesized with equivalent ratio of 1:3 via transesterification mechanism. Polyol was then characterized using FTIR spectroscopy and liquid chromatography mass spectroscopy (LCMS). All the reactions obeyed second order kinetics [22].

In 2008, Wu and coworkers prepared a new type of chitosan-coated NPK fertilizer with controlled-release, water-retention and biodegradability. The coated fertilizer composed of three layers; NPK fertilizer granular, chitosan, poly(acrylic acid-co-acrylamide) (P(AA-co-AM)) superabsorbent polymer. The results from atomic absorption spectrophotometer showed that the nutrients released did not exceed 75% within 30 days [23].

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Urea fertilizer 46-0-0	: Rojpanakitt Co., Ltd.
2. Methylene diphenyl diisocyanate (MDI)	: Mitsui
3. Stannous octoate	: Aldrich
4. 99.5% Glycerol	: Carlo
5. Commercial castor oil	: Vittayasom Co., Ltd.
6. Commercial palm oil	: Lamsoon Co., Ltd.
7. Calcium oxide	: May & Baker
8. *p*-Dimethylaminobenzaldehyde (*p*-DMAB)	: May & Baker
9. Hydrochloric acid	: Merck
10. Ethanol	: Merck
11. Sulfuric acid	: Merck
12. Glacial acetic acid	: Merck
13. Hydrogen peroxide	: Merck

3.2 Equipments

3.2.1 Stereo Microscope

The stereo microscope SZH-10 model Olympus, Tokyo Japan, provided a three-dimensional visualization, was used to study an overall appearance of PU film.
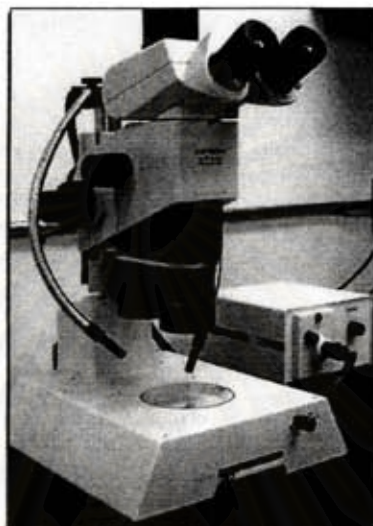
Figure 3.1   Stereo microscope.

3.2.2 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) model JSM-5410-LV, JEOL, Tokyo Japan, was used to measure the thickness of coatings and observe the morphology of surfaces.

3.2.3 UV-Spectrophotometer

The UV absorbance was read at $\lambda = 440$ nm [14] on Microtiter plate reader, model Sunrise, Tecan Austria for determining the contents of released urea.

3.2.4 Fourier transform Infrared Spectrometer (FT-IR)

The FT-IR spectra were recorded on a Perkin Elmer, Nicolet Impact 410 Fourier Transform Infrared Spectrophotometer. Solid samples were formally examined by incorporating the sample with potassium bromide (KBr) to form a pellet. Liquid sample was cast on the KBr disk.

3.2.5 Pan Coater

A drug coating equipment, provided by Faculty of Pharmaceutical, Chulalongkorn University, could be adapted to lab-scale fertilizer coating. The pan coater combined with a rotatable pan for mixing and adjustable blower for drying.

Figure 3.2   Pan coater.

3.2.6 Gel Permeation Chromatography (GPC)

The molecular weight and molecular weight distributions of polyglycerol were determined by gel permeation chromatography (GPC) using HPLC grade THF as eluent, Water E600 column connected to the refractive index detector. The flow rate was 1 mL/min. Narrow PS standards were used for the calibration curve.

3.2.7 Nuclear Magnetic Resonance Spectroscopy

The ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian, model Mercury+400 nuclear magnetic resonance spectrometer operating at 400 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent signal as a reference.

3.2.8 Rotary Vacuum Evaporator

A Buchi Rotavapor model R-200 use for the efficient and gentle removal of solvents. The solvents dispersed in the reaction mixture was heated, condensed and evaporated under reduced pressure.

3.2.9 Water bath

A Memmert water bath model WB 22 was used for controlling the temperature

3.3 Experiments

Four types of polyol including polyglycerol, epoxidized palm oil polyol, palm oil polyol and castor oil polyol were prepared before reacting with MDI to form PU. Polyglycerol was synthesized by based catalyzed polymerization. The three types oil were reacted with glycerol in the presence of CaO as a catalyst. Palm oil was prior epoxidized by peracetic acid obtaining epoxidized palm oil.
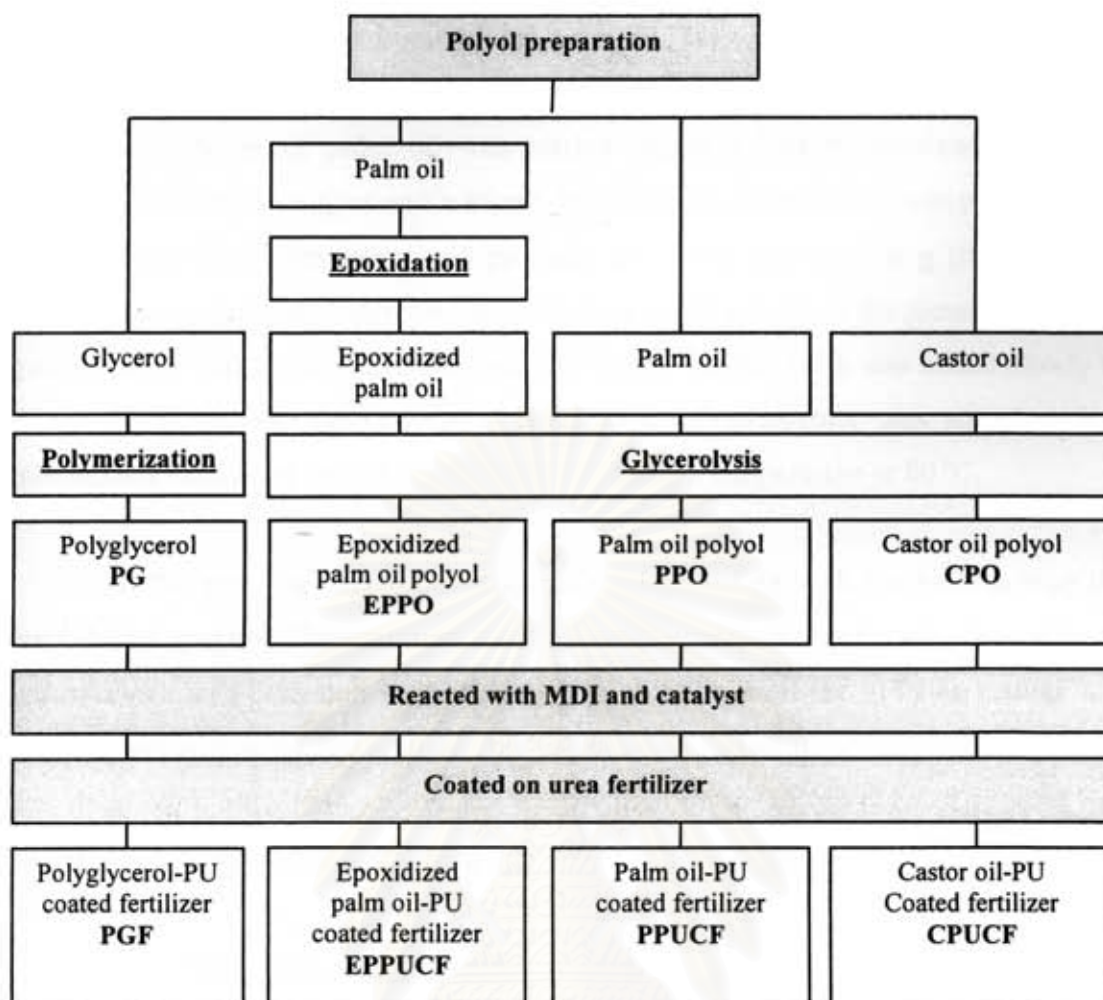
Figure 3.3   The experimental procedures.

3.3.1 Synthesis of polyglycerol

99.5 % of glycerol was refluxed with dried NaOH powder in 1:1 mol equivalent. The reaction mixture was heated by mechanical stirrer to the reaction temperatures 240 $^{\circ}$C for 6 hr. At the end, the mixture was neutralized with sulfuric acid, and then centrifuged to separate a precipitate. The mixture was heated to 100-120 $^{\circ}$C for reduction of a viscosity and the hot mixture was dried over anhydrous sodium sulfate. The molecular weight of the product was determined by GPC.

3.3.2 Preparation of epoxidized palm oil [24]

Epoxidation of palm oil was carried out in a 250-mL two-necked round-bottom flask with a stopper and a stirrer. Palm oil (65 g, 0.08 mol) was placed in the round-bottom flask. Peracetic acid prepared in situ by reacting 16 g (0.27 mol) of 99.5% glacial acetic acid with 66.1 g (0.68 mol) of 35% H_2O_2 in the presence of small quantities (0.1 mL) of concentrated sulphuric acid for about 3 h was added slowly to the palm oil in the round-bottom flask. The reaction mixture was stirred with a mechanical stirrer and heated to maintain the reaction temperature at 80 °C.

At the end, the mixture was quenched by cooling with ice bath to stop the epoxidation reaction. The mixture was separated by separation funnel. The oil layer was washed with saturated sodium carbonate solution until the pH was neutral, and then washed with saturated sodium chloride solution and distilled water. The oil phase was dried over anhydrous sodium sulfate and then filtered. This purified product was further reacted with glycerol to form a polyol in the next steps.

3.3.3 Preparation of polyol by glycerolysis [16]
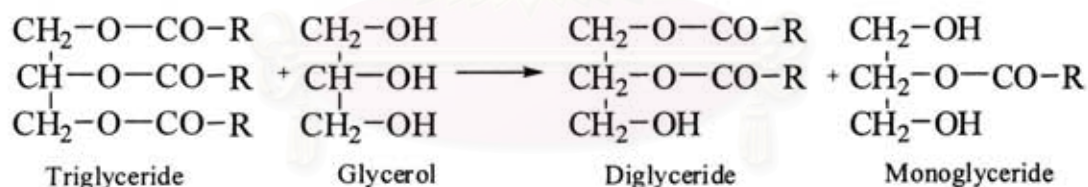
Scheme 3.1   The glycerolysis reaction

The polyol was synthesized in a 250-mL two-necked round-bottom flask equipped with a reflux condenser, a stirrer and a thermometer. 62.25 g of oil, 6.91 g of glycerol and 0.6 g of CaO catalyst were added into the flask. The reaction mixture was heated to 240°C for 3 hours. Every 1 hour, the reaction mixture was followed by ^{1}HNMR. The product was allowed to cool to room temperature. Its chemical structure was analyzed using FTIR spectrophotometer.

3.3.4 Film coating

To give a good appearance of film for coating , the ratio of polyol, MDI and a catalytic amount of stannous octoate were determined by casting polyurethane on a glass slide and cured at 80°C.

3.3.5 Preparation of slow released urea fertilizer

A urea fertilizer granule was heated at 100°C to remove moisture. A 1:1 mixture of MDI and polyol (or polyglycerol) were slowly added on the urea fertilizer while continuous rotation for 3 minute in the coating pan, then added catalyst, and blow with an air to prevent sticky fertilizers before curing in an oven at 80°C for 15 minutes. Further coatings were repeated following the same methodology by using materials as in Table 3.1. The releasing rate of each types of coated fertilizer was determined.
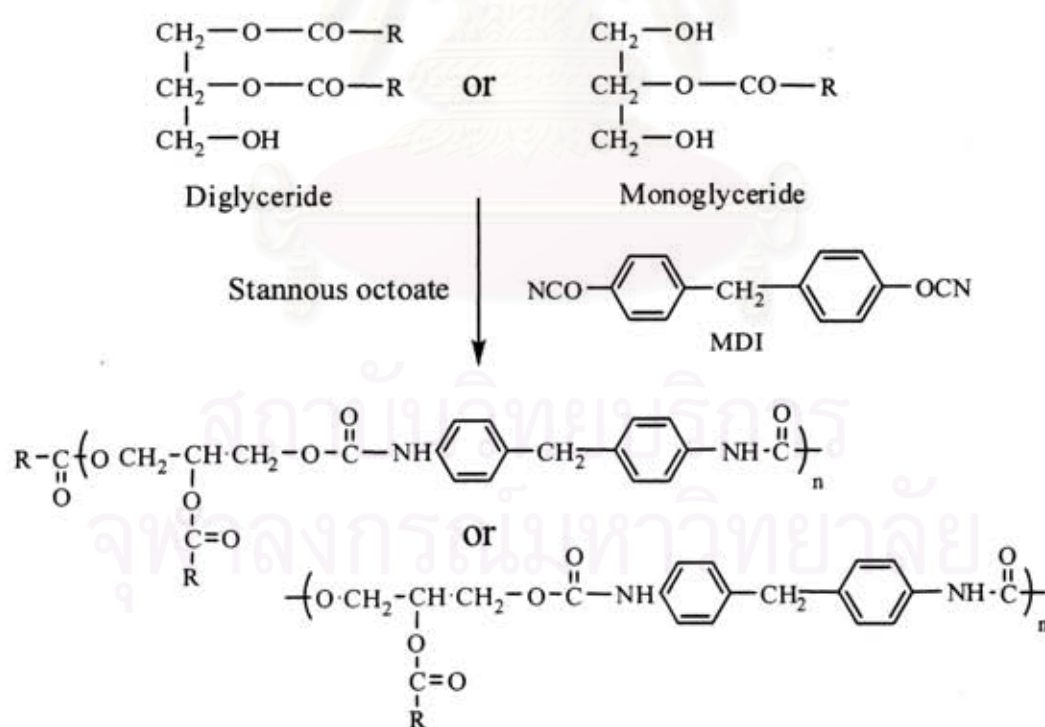
Scheme 3.2 The polyurethane formation

Table. 3.1 The condition for coating

	Weight of fertilizer (g)		MDI (g)	Polyol (g)	Catalyst (g)
1st coating	400	(uncoated fertilizer)	10.00	10.00	0.10
2nd coating	320	(1 layer coated fertilizer)	8.00	8.00	0.08
3rd coating	240	(2 layers coated fertilizer)	6.00	6.00	0.06
4th coating	160	(3 layers coated fertilizer)	4.00	4.00	0.04
5th coating	80	(4 layers coated fertilizer)	2.00	2.00	0.02

3.3.6 Released experiments

3.3.6.1 The method for determination of urea content [14]

The urea releasing from coated fertilizers was determined by using colorimetric method following to analytical protocol described by Potts [25]. *p*-Dimethylaminobenzaldehyde (*p*-DMAB) reacts rapidly with many primary amines. According to Ehrlich reaction, *p*-dimethylamino benzaldehyde could react with urea to give lemon Kelly color which absorbs visible light at 440 nm.

3.3.6.2 Calibration curve [27]

The standard urea solutions were prepared by dissolving 1.00 g urea in 1000 mL distilled water. Then, pipetted 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 mL of standard urea solution into 25 mL volumetric flasks and diluted to volume with DI water. Before determining the urea released content, the absorbance of standard urea solution was determine and calibration curve was plotted.

3.3.6.3 Reagent

8.00 g of *p*-Dimethylaminobenzaldehyde (*p*-DMAB) was dissolved in 95 % ethyl alcohol (500 mL) and then concentrated HCl (50 mL) was added into the mixture while shaking thoroughly. *p*-DMAB solution was stable for 1 month.

3.3.6.4 Sample preparation

Approximately 0.4 g of coated fertilizer were placed in 100 mL. of deionized water maintained at room temperature. When reached the settle time, fertilizer was filtered from the urea solution. Urea content of the urea solution was determined by using UV-Vis spectroscopy. A nearly thickness of each coated fertilizer was performed to study the effect of pH, temperature.

3.3.6.5 Determination of urea concentration

The sample solution was mixed with DMAB solution in ratio 1:1 by volume. The mixture was allowed to react at room temperature for 10 minutes. Then the mixture was transferred into a 96-well microtiter plate and the absorbance of urea-DMAB complex was measured at 440 nm [14] and using a 1:1 mixture of water and DMAB solution as blank (100 % transmittance). The measuring of absorbance for each sample was duplicated.

3.3.7 Determination of %coating [28]

Coated urea fertilizer (10 g) was ground with mortar and pestle and added into 250 mL deionized water. After 15 minute, the solution was filtered and the insoluble solid was washed with deionized water to ensure that no urea remained and dried in the oven at 100°C for 4 hours or until its weight become constant.

3.3.8 The Scanning electron microscopy (SEM) analysis

The samples were dried under vacuum for 24 h then sputtered with gold before analyzed.

3.3.8.1 The surface morphology observation

The coated fertilizer were soaked in deionized water until the urea fertilizer completely dissolved. The remaining solid was filtered, washed, and dried in an oven at 100°C before sputtered with gold.

3.3.8.2 The average thickness of coatings

The coated fertilizer was cross sectioned to obtain equal two pieces before sputtered with gold. On SEM micrograph, at least three different locations were measured. The thickness of each sample was averaged and calculated the standard deviation (S.D.).

CHAPTER IV

RESULTS AND DISCUSSIONS

In this research, PU coated fertilizer was prepared by coating with polyurethane from the reaction of MDI with four types of glycerol based polyol. The effect of pH and temperature on PF was studied in the term of releasing rate. Various characterized techniques were used to study including Fourier Transform Infrared spectroscopy (FT-IR), UV-Vis spectroscopy, Scanning Electron Microscope, and NMR spectroscopy.

4.1 Preparation of polyglycerol

Polyglycerol was prepared by based catalyzed polymerization. After neutralization with sulfuric acid, the obtained product was a clear viscous liquid.
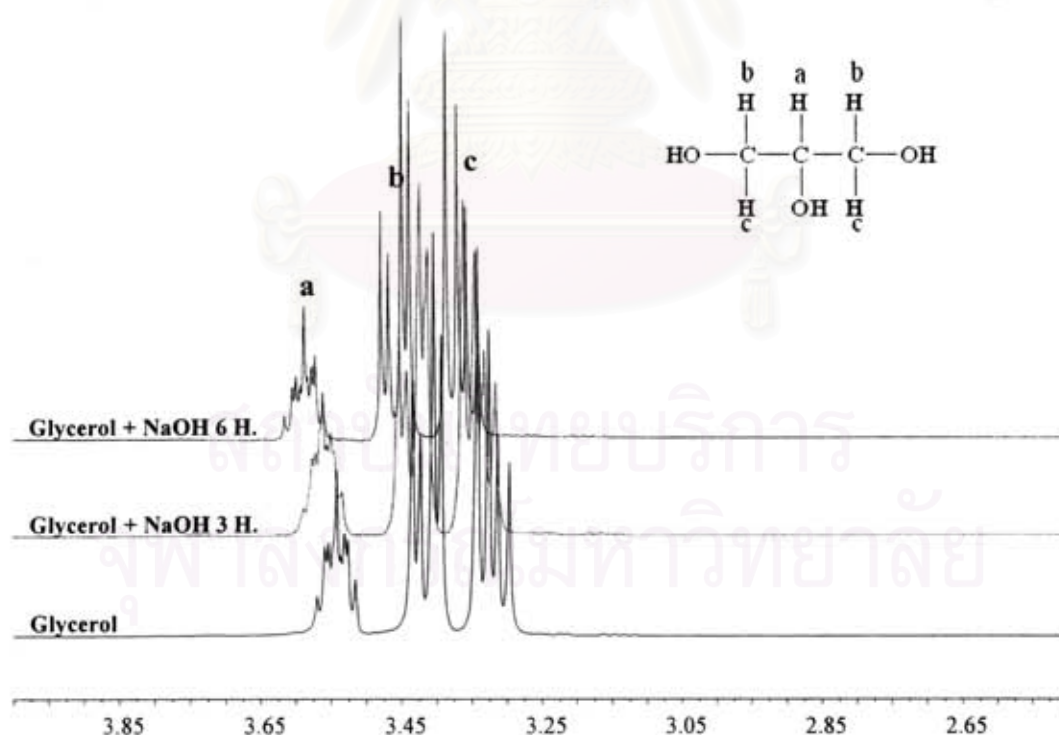

Figure 4.1 ^{1}H NMR spectra of glycerol and synthesized glycerol (in D_2O).

The ^{1}H NMR spectra revealed a little change in chemical shift. Chemical shift of Ha of glycerol at 3.54 was shifted to 3.56 and 3.59 ppm for synthesized glycerol at reaction time 3 h and 6 h respectively. However, the only result from NMR could not clearly describes the differences of starting materials and the products because the splitting pattern of two synthesized glycerol was still similar as before.
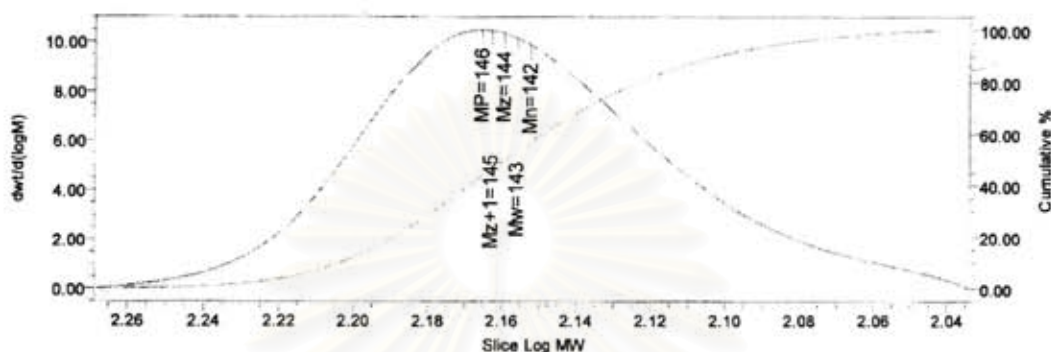
Figure 4.2 GPC chromatogram of the synthesized glycerol.

According to a GPC chromatogram showed in Figure 4.2, the molecular weight of the synthesized glycerol was 143 g/mol which was increased from that of the starting glycerol (94 g/mol). Because the low molecular weight obtained from the synthesized glycerol, it was assumed that the reaction occurred with the synthesized glycerol was further formed only an oligomers. In addition, the molecular weight calculated from GPC (Figure 4.3) show a little different value from the accurate molecular weight of glycerol (92.1 g/mol).

Figure 4.3 GPC chromatogram of the glycerol.

4.2 Preparation of epoxidized palm oil

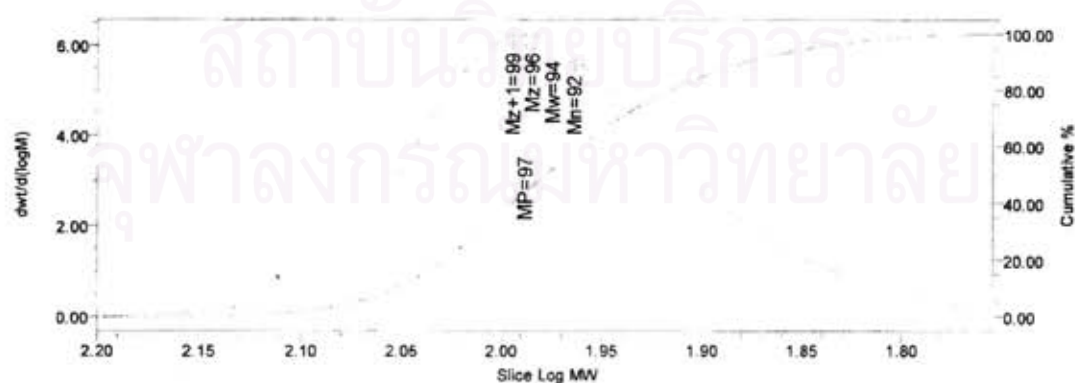Palm oil was epoxidized by peracetic acid, obtaining from the mixture of glacial acetic acid, hydrogen peroxide and catalytic amount of sulfuric acid. Palm oil had about 45% double bond-containing fatty acid called oleic acid. The epoxidation occurred at double bond site resulting an epoxide. The spectrum in Figure 4.4 showed the decreasing in intensity at 5.3 ppm ($\underline{H}C=C\underline{H}$), the absence of signal at chemical shift 2.0 ppm and the unchanged chemical shift at 4.1-4.3 ppm (triglyceride) after reacted with peracetic acid. It was confirmed that the epoxidation occurred and selectively reacted at double bond site. The percentage of epoxidation was 82.
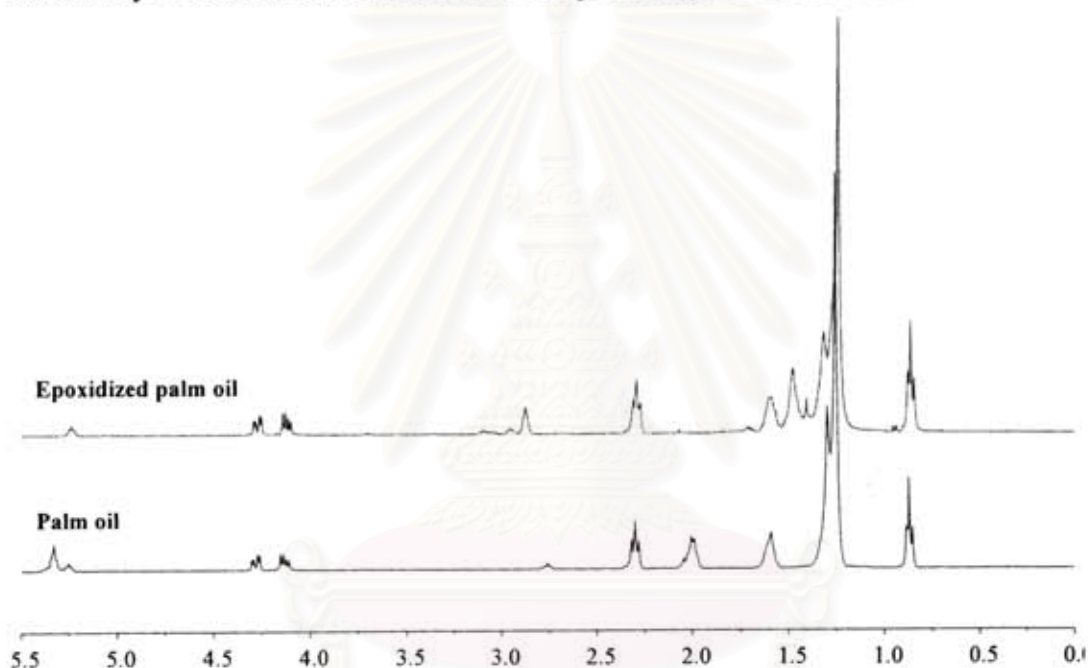
Figure 4.4 ^{1}H NMR spectra of palm oil and epoxidized palm oil (in CDCl$_3$).

4.3 Preparation of polyol via glycerolysis

4.3.1 Epoxidized palm oil polyol (EPPO) and epoxidized palm oil polyurethane (EPPU)

^{1}H NMR spectrum of epoxidized palm oil polyol (Figure 4.4) showed the decreasing in multiplet signal of triglyceride protons at chemical shift 4.1-4.3 ppm. The presence of broad multiplet signal of mono and diglyceride were observed at the

same chemical shift as in epoxidized palm oil and the absence of chemical shift at 2.6-
3.2 indicated that all of the epoxide rings were opened.
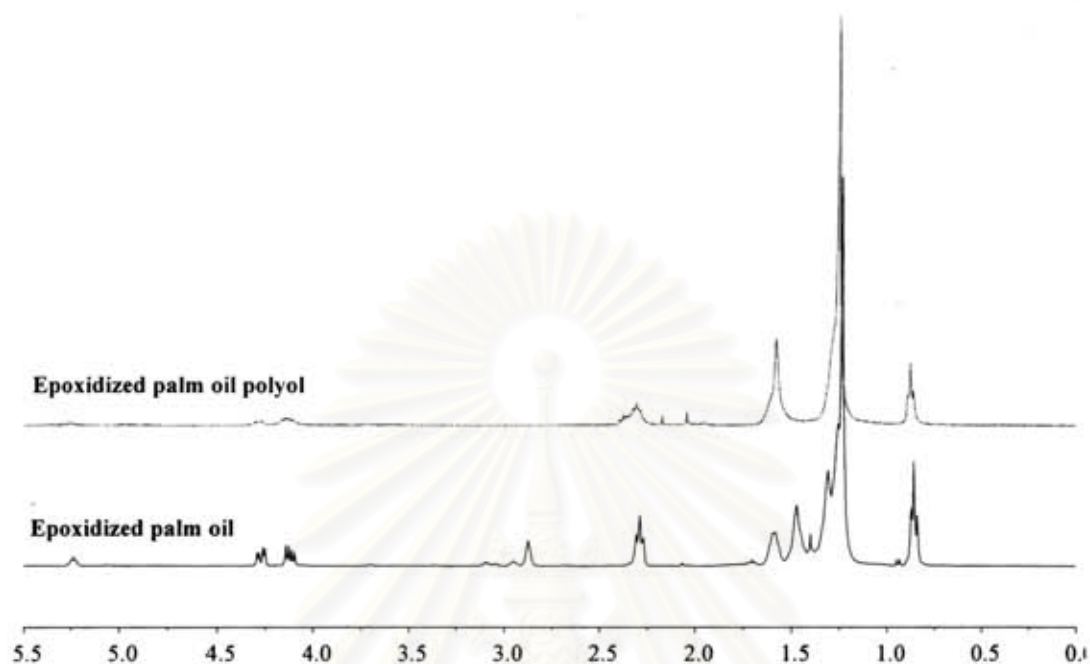
Figure 4.5 ^{1}H NMR spectra of epoxidized palm oil and epoxidized palm oil polyol (in
CDCl$_3$).

IR spectrum of epoxidized palm oil polyol (EPPO) in Figure 4.6 exhibit the
broad absorption peak of O-H stretching vibration at 3414 cm^{-1} , C-H stretching
vibration at 2923, 2851 cm^{-1} , C=O stretching vibration at 1740 cm^{-1}. In EPPU
spectrum, the vibration of N-H in EPPU overlapped that of O-H causing the sharp
absorption peak nearly at 3400 cm^{-1}. Moreover, the vibration of NCO groups in
unreacted MDI was showed at 2276 cm^{-1}.
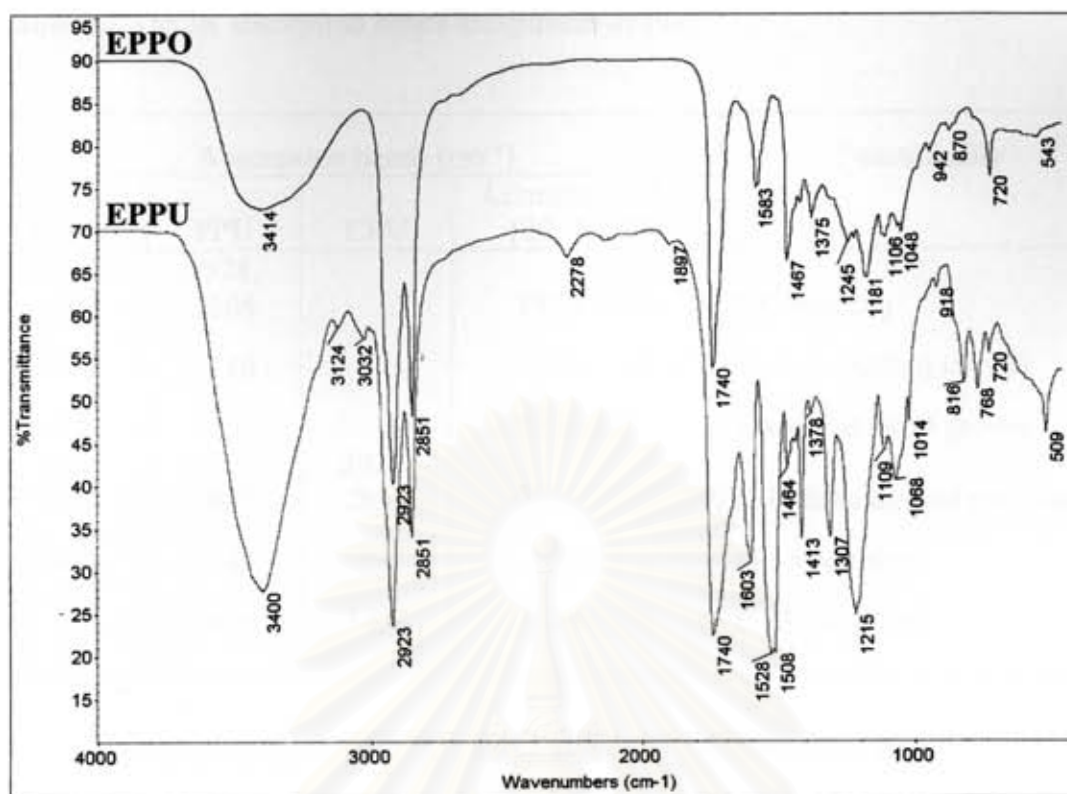
Figure 4.6 IR spectra of EPPO and EPPU

Table 4.1 The IR absorption bands assignment of polyol.

Absorpsion bands (cm⁻¹)				Functionality
EPPO	PPO	CPO	Literature value [29, 30, 31]	
1181	1170	1177	1160	C-O-C functions of the ester group
1740	1743	1740	1735-1750	C=O stretching of ester
2923, 2851	2923, 2848	2926, 2855	2850-2930	C-H stretching of paraffin
	3005	3005	3020-3080	C-H stretching of olefin
3414	3465	3400	3300-3600	O-H stretching

Table 4.2 The IR absorption bands assignment of PU.

Absorpsion bands (cm^{-1})				Functionality
EPPU	PPU	CPU	Literature value [29, 30, 31]	
1528, 1508	1528, 1508		1500-1560	NH bending
1740	1740		1735-1750	C=O stretching in ester
2278			2270-2273	unreacted NCO groups
2923, 2851	2923, 2855	2926, 2855	2850-2930	C-H stretching of paraffin
3400	3345	3345	3385	NH stretching
	3455	3438	3300-3600	O-H stretching

4.3.2 Palm oil polyol (PPO) and palm oil polyurethane (PPU)

Figure 4.7 showed the ^{1}H NMR spectra of palm oil polyol. In glycerolysis reaction, glycerol reacted with triglyceride in palm oil resulting a mixture of mono and diglyceride which broaden the multiplet signal at chemical shift 4.1-4.3 ppm. In comparison with palm oil spectrum, the unchanged signal of olefinic protons at chemical shift 5.3 ppm revealed that the glycerolysis favored reacted with the ester.
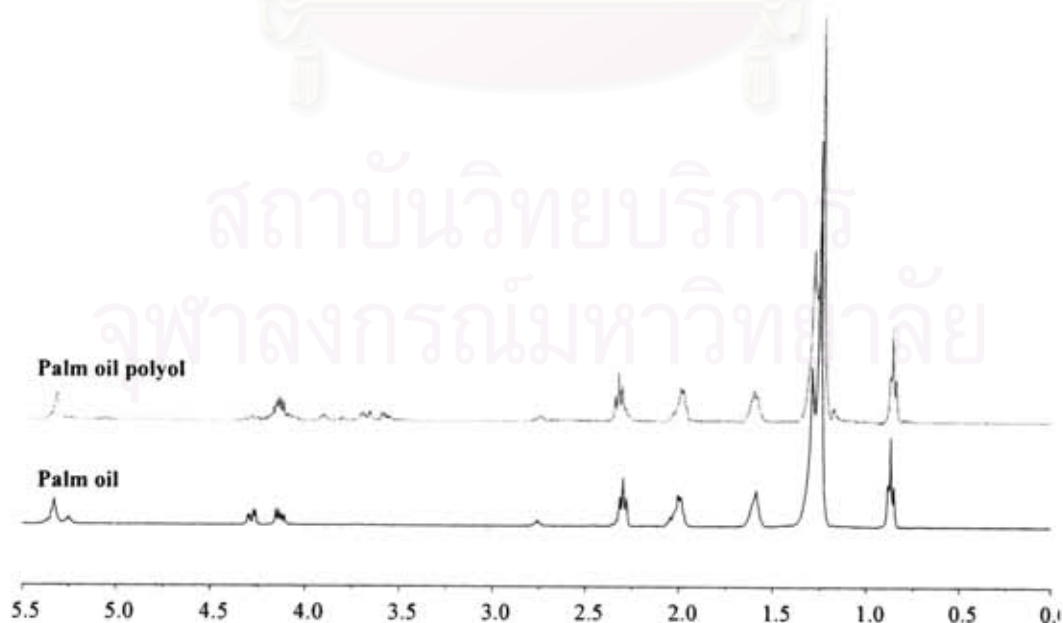
Figure 4.7 ^{1}H NMR spectra of palm oil and palm oil polyol (in CDCl$_3$).

IR spectrum of PPO in Figure 4.8 showed the broad absorption peak of O-H stretching vibration at 3465 cm^{-1}, C-H stretching vibration at 2923, 2848 cm^{-1}, C-H stretching vibration of olefin (in unsaturated fatty acid of palm oil) at 3005 cm^{-1}, C=O stretching vibration at 1743 cm^{-1}. In PPU spectrum, the vibration of N-H and O-H was splited into two peaks. The absence of the vibration of NCO groups indicated that MDI was completely reacted
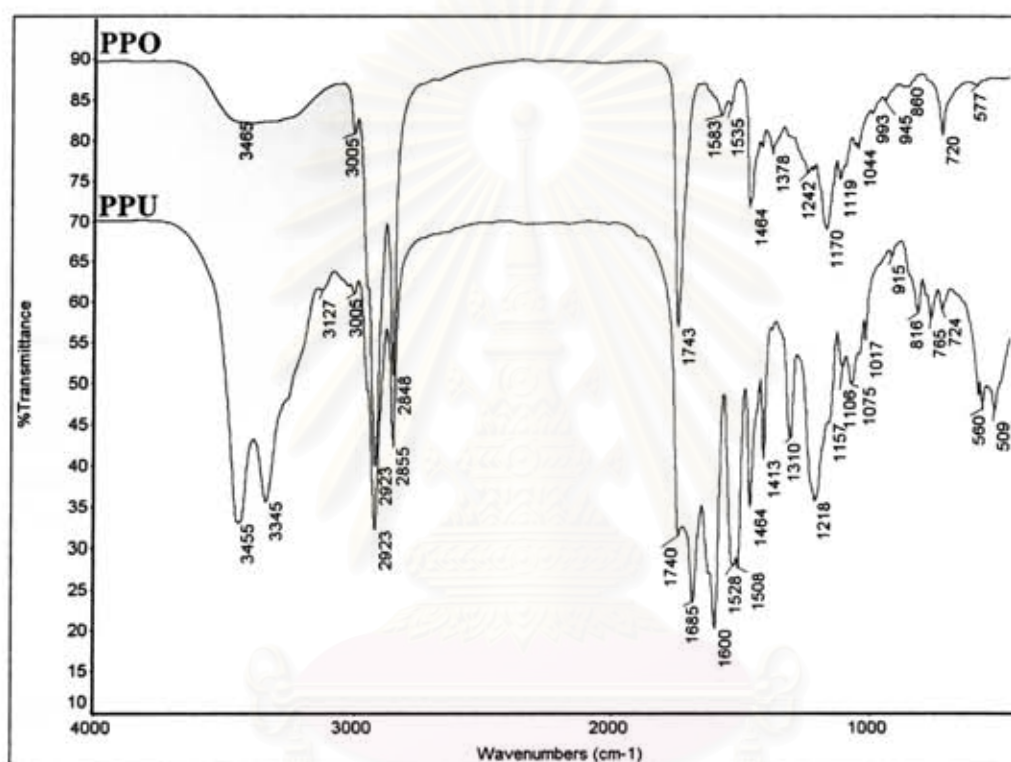

Figure 4.8   IR spectra of PPO and PPU.

4.3.3 Castor oil polyol (CPO) and castor oil polyurethane (CPU)

However, castor oil contained both OH groups and double bond in the molecule, but the signal of double bond at 5.3 ppm and 2.0 ppm was still unchanged. Only the signals at 4.1-4.3 ppm, which represented triglyceride of castor oil polyol, showed the similar changes as in palm oil polyol (Figure 4.9).
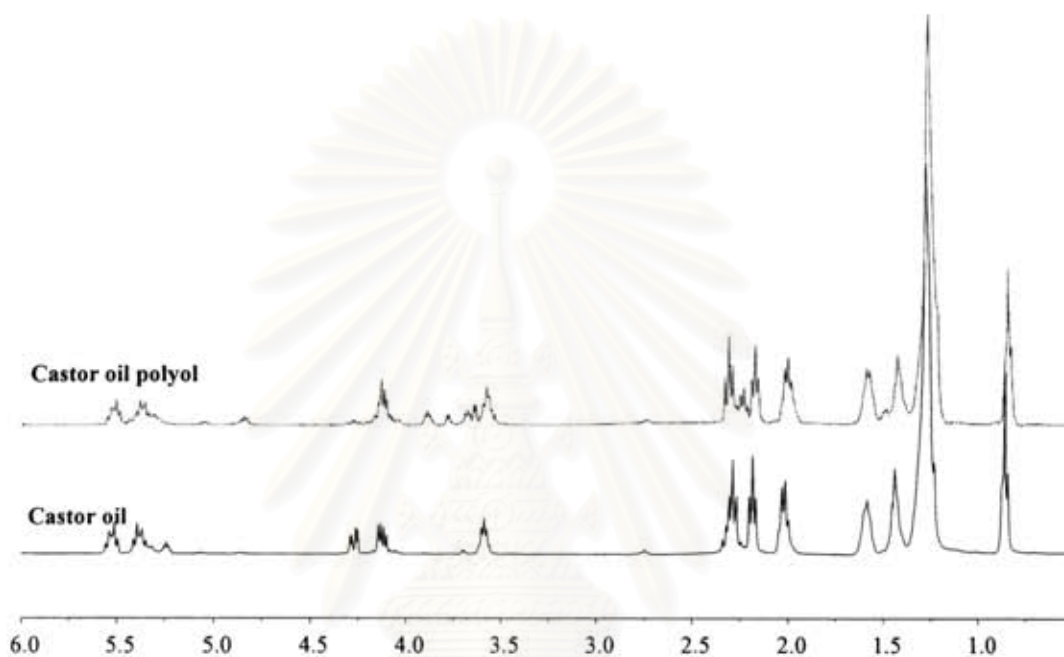
Figure 4.9 ^{1}H NMR spectra of castor oil and castor oil polyol (in CDCl$_3$).

IR spectrum of CPO in Figure 4.10 showed the broad absorption peak of O-H stretching vibration at 3400 cm^{-1}, C-H stretching vibration at 2926, 2855 cm^{-1}, C-H stretching vibration of olefin (in unsaturated fatty acid of castor oil) at 3005 cm^{-1}, C=O stretching vibration at 1740 cm^{-1}. In CPU spectrum, the vibration of N-H and O-H was splited to three peaks. The possibility for these vibration ranges were OH stretching in free glycerol, in ricinoleic acid of castor oil and NH stretching.
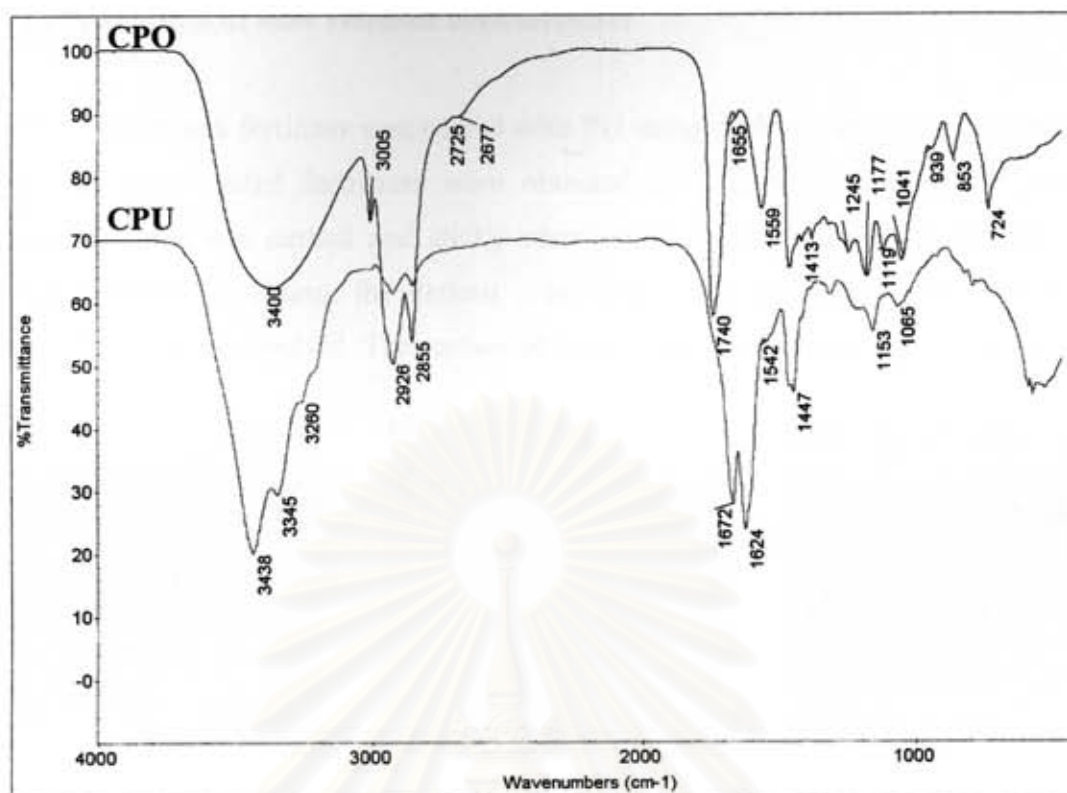
Figure 4.10 IR spectra of CPO and CPU

4.4 Film coating

The smooth surface film was observed on CPU and PPU. EPPU had a wavy surface because of its high viscosity while polymerized. Light color is an advantage for coating in order to add a pigment for classifying types of fertilizer.

(a)   (b)   (c)
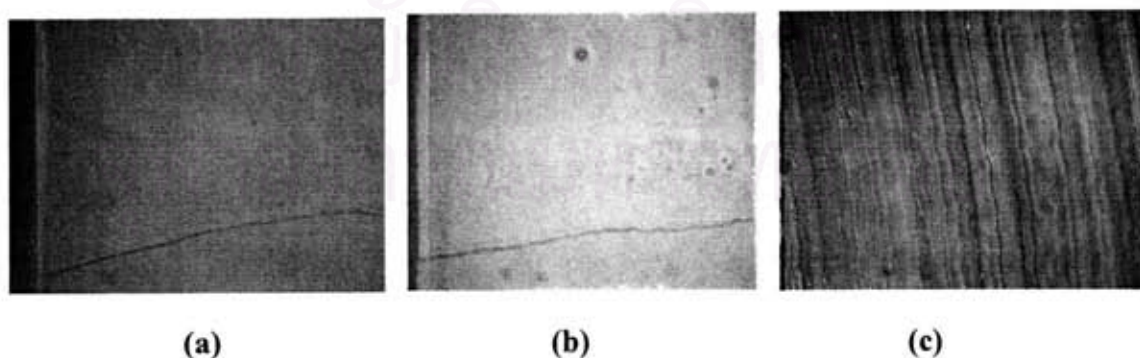
Figure 4.11 Characteristic of PU film using three types of polyol at 80°C for 15 minute; (a) CPU, (b) PPU, (c) EPPU

4.5 Preparation of slow released urea fertilizer

After urea fertilizer was coated with PU using different three types of polyol, the one layer coated fertilizers were obtained as light yellow solid. The coated fertilizer color was darken and sticky when increasing the number of coating. For equal number of coating, the darkest color was observed on the coatings with an epoxidized palm oil polyol. The surface of the coating was smooth and a little glossy.
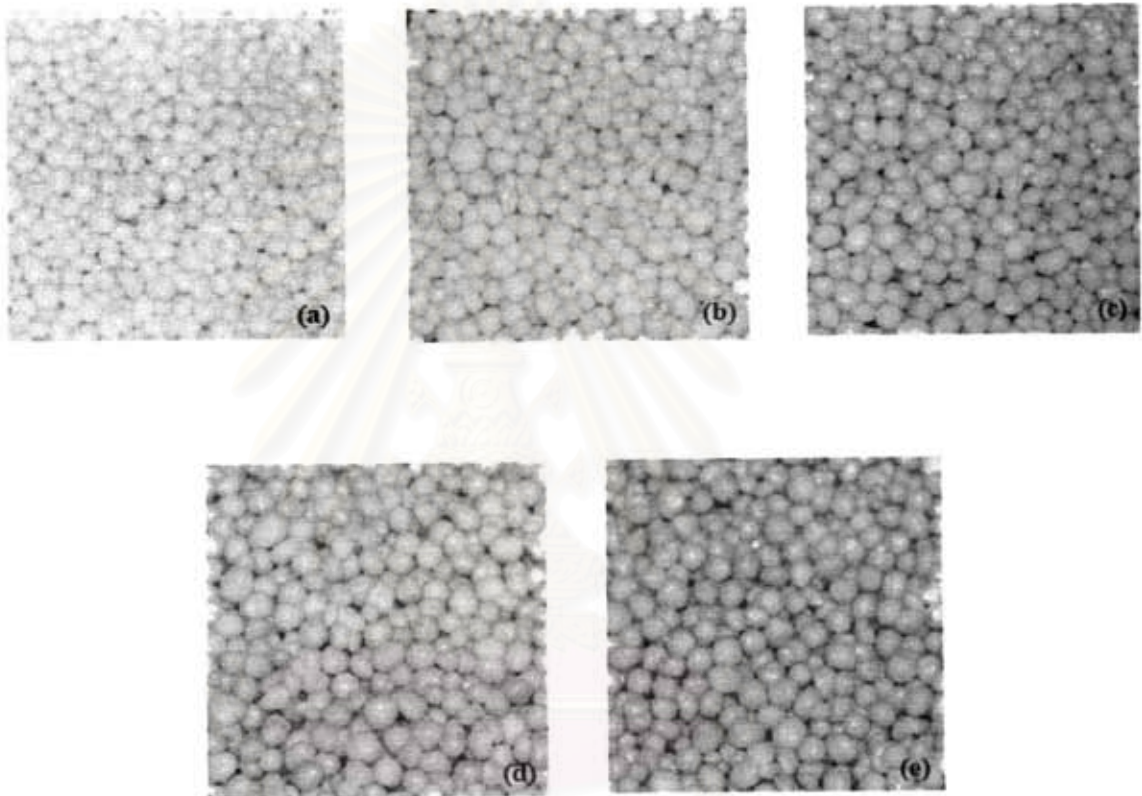
Figure 4.12 Epoxidized palm oil PU coated fertilizer (EPPUCF).

(a) One layer

(b) Two layers

(c) Three layers

(d) Four layers
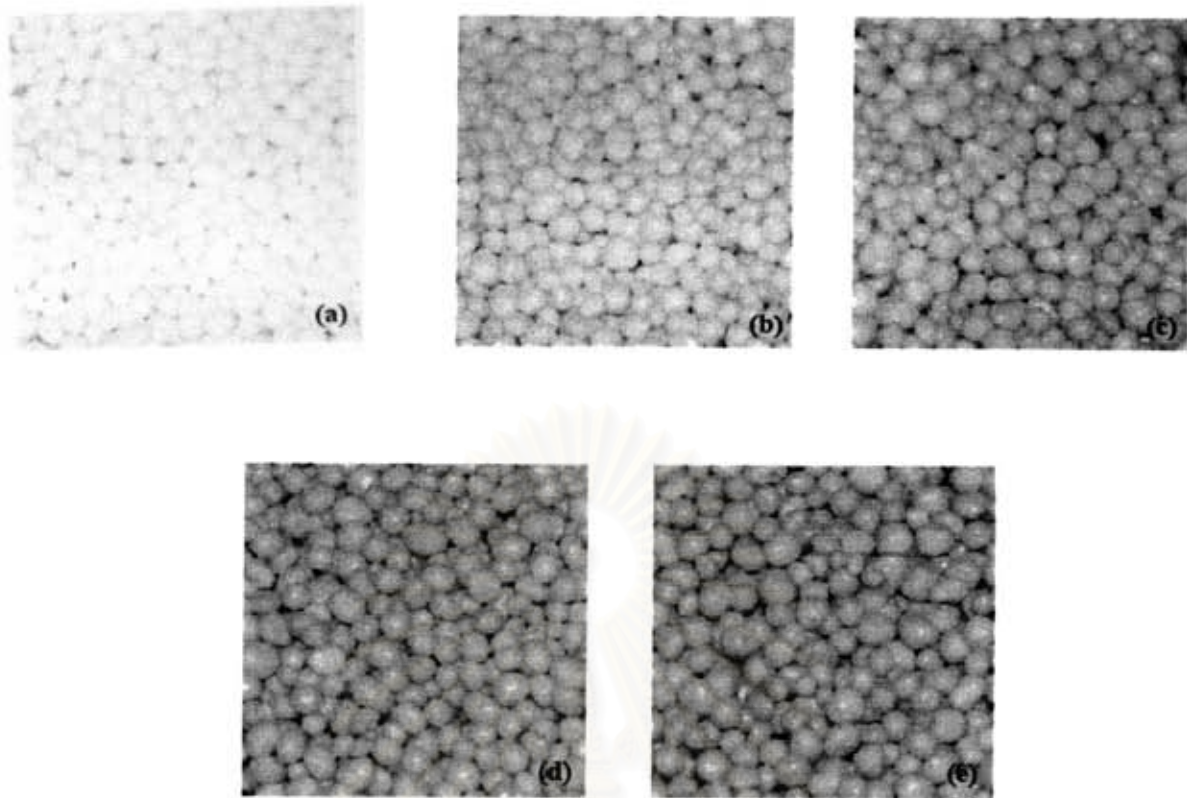
(e) Five layers

Figure 4.13 Palm oil PU coated fertilizer; PPUCF.

(a) One layer

(b) Two layers

(c) Three layers

(d) Four layers
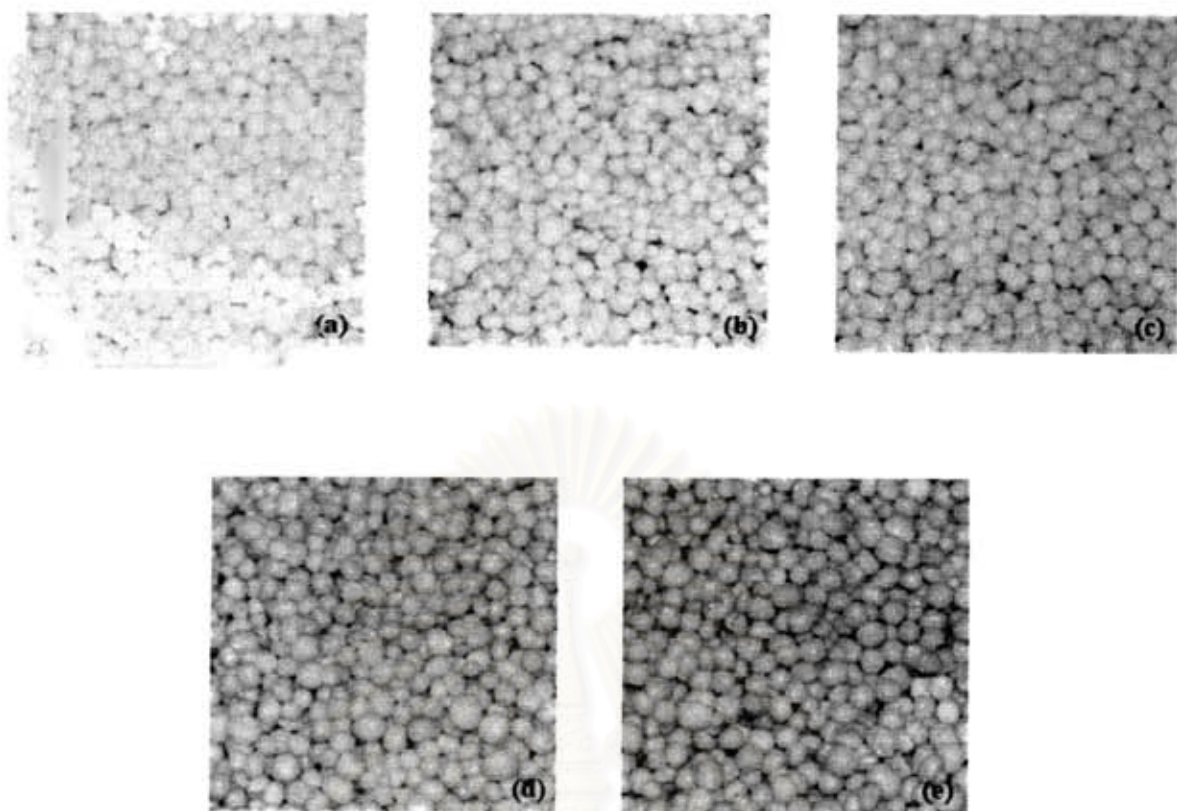
(e) Five layers

Figure 4.14 Castor oil PU coated fertilizer; CPUCF.

(a) One layer

(b) Two layers

(c) Three layers

(d) Four layers

(e) Five layers

4.6 The solubility of uncoated urea fertilizer

An appearance of commercial urea fertilizer is white solid (Figure 4.15). Its granule contains 46% of nitrogen. About only 23% of urea in uncoated fertilizer (Figure 4.16) could be detected from UV-Vis spectroscopy which correspond to the fertilizer formula 46-0-0. The uncoated urea fertilizer (0.4 g) completely dissolved in 100 ml deionized water within 5 minutes (Figure 4.17).

Figure 4.15 The uncoated urea fertilizer
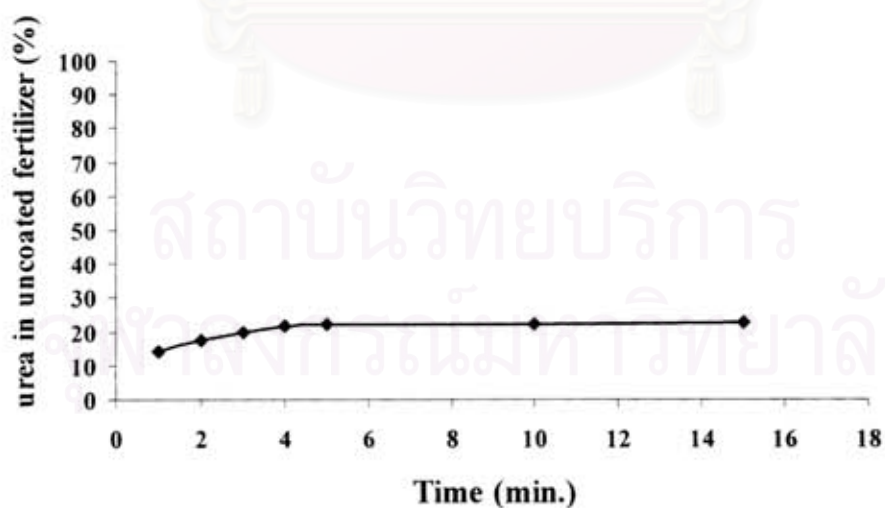
Figure 4.16 The urea content in the uncoated fertilizer.
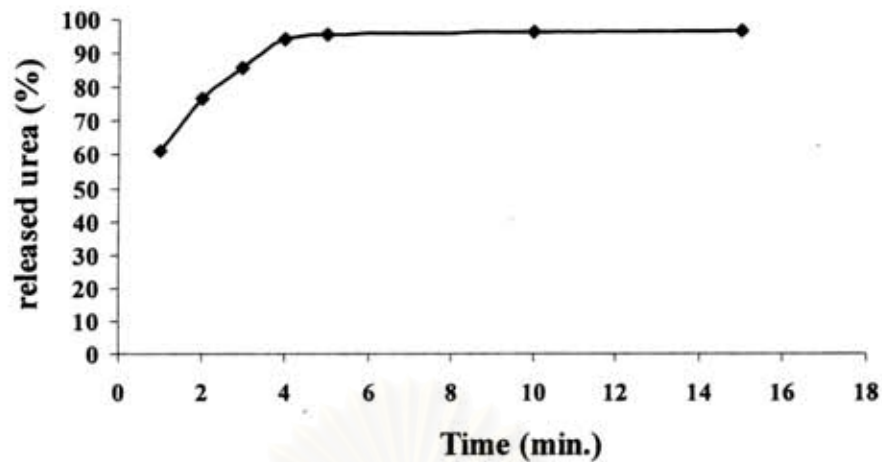
Figure 4.17 The solubility of uncoated urea fertilizer.

4.7 Effect of pH on releasing rate of coated urea fertilizer

For three types of coated urea fertilizer, the lower releasing rate obtained from the condition with pH 9 because pH greater than 6.5 significantly increased the rate of urea conversion to ammonia gases [4]. EPPUCF exhibited the good slow released properties with the consistent rate. In Figure 4.18, pH did not affect to the releasing rate of EPPUCF significantly. EPPU consists of 2 types of OH groups. There were OH groups from glycerolysis and ring opening of epoxides. The presence of high OH groups gave more active site to react with MDI leading to a high degree of crosslink. Water was difficult to penetrate through the coating to dissolve out the urea.
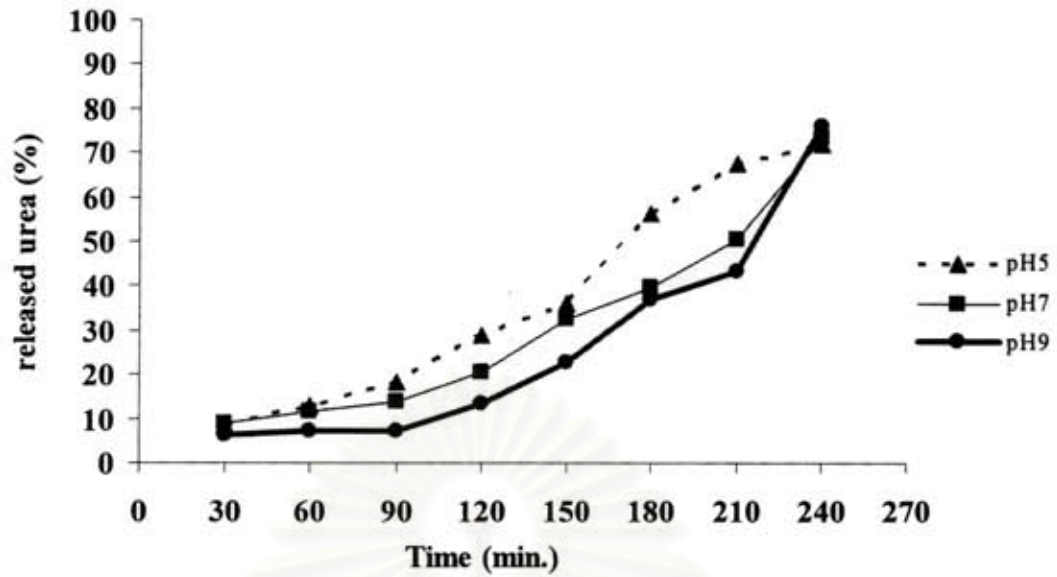
Figure 4.18 Effect of pH on releasing rate on EPPUCF.

In Figure 4.19, pH affected to the releasing rate of PPUCF obviously. The PPU coating consisted of PPO which had only one type of OH groups obtained from glycerolysis. Because the lower amount of OH groups reacted with MDI, it probably that the unreacted mono, diglyceride from PPO were hydrolyzed than that from EPPO.
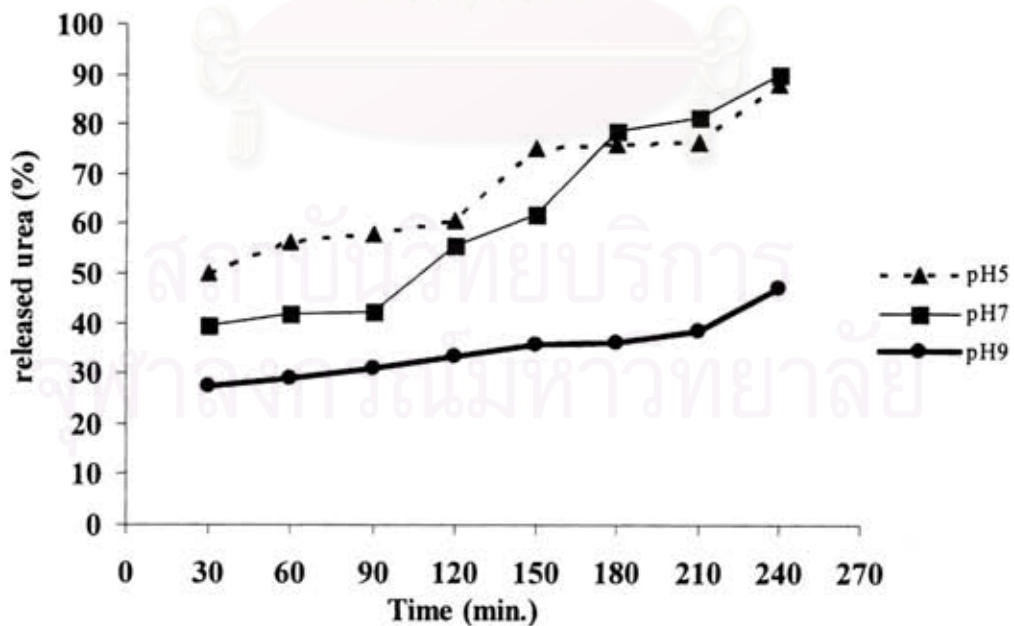
Figure 4.19 Effect of pH on releasing rate on PPUCF.

In Figure 4.20 showed the trends of releasing rate of CPUCF was similar to that of EPPUCF but the initial releasing rate of CPUCF was higher than that of EPPUCF at every pH. The OH groups contained in CPO were from glycerolysis and the OH-containing fatty acid in the castor oil. Although the high amount of OH containing in the CPO, the higher releasing rate of CPUCF was obtained because the high viscosity of castor oil is a problem in uniform coating.
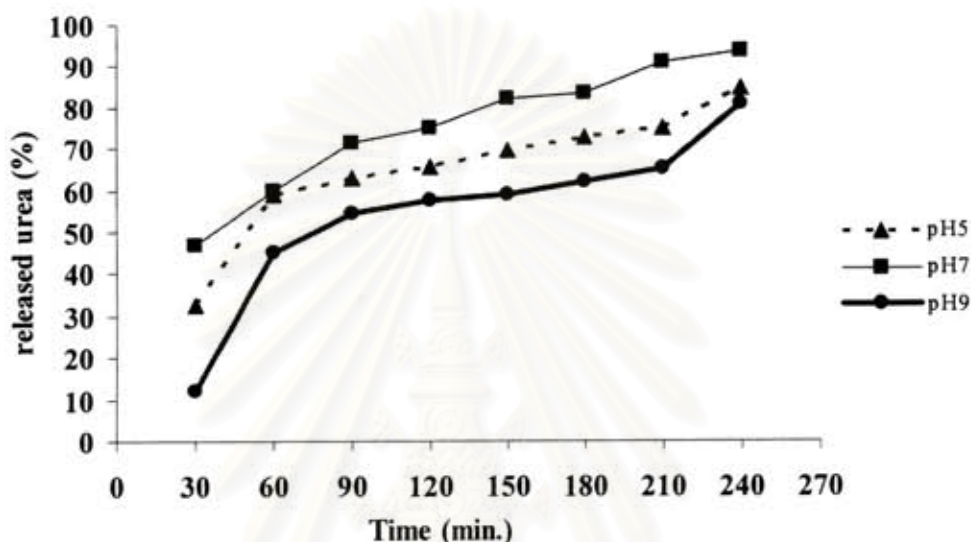
Figure 4.20 Effect of pH on releasing rate on CPUCF

4.8 Effect of temperature on releasing rate of coated urea fertilizer.

The temperature affected the releasing rate of all three types coated fertilizer (EPPUCF, PPUCF, CPUCF) in the similar trend. The higher releasing rate was observed at high temperature. Because of no bubbles or pore in the coating surface, the probable released mechanism was diffusion which rate of diffusion was controlled by the temperature. If the temperature was raised, water molecule more penetrated to the coating to dissolve out the urea.
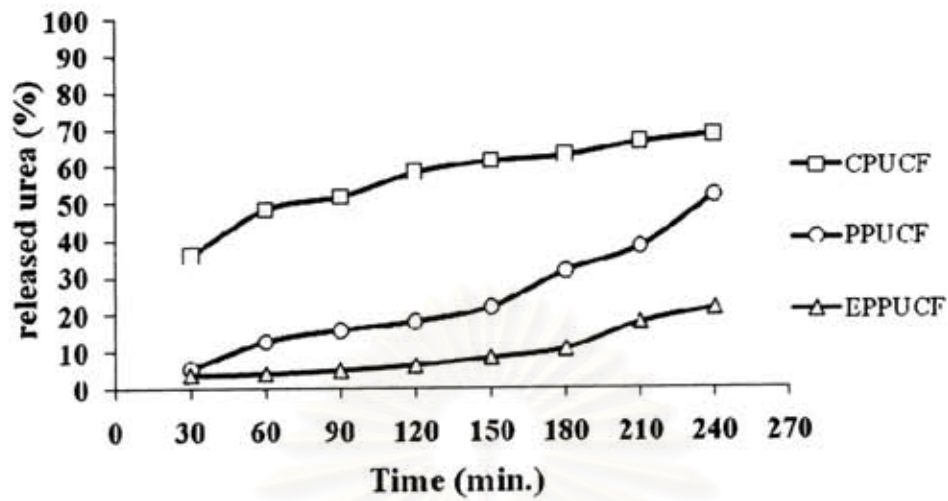
Figure 4.21 Comparison of the releasing rate of PU coated fertilizer using three types of polyols at 20 °C.
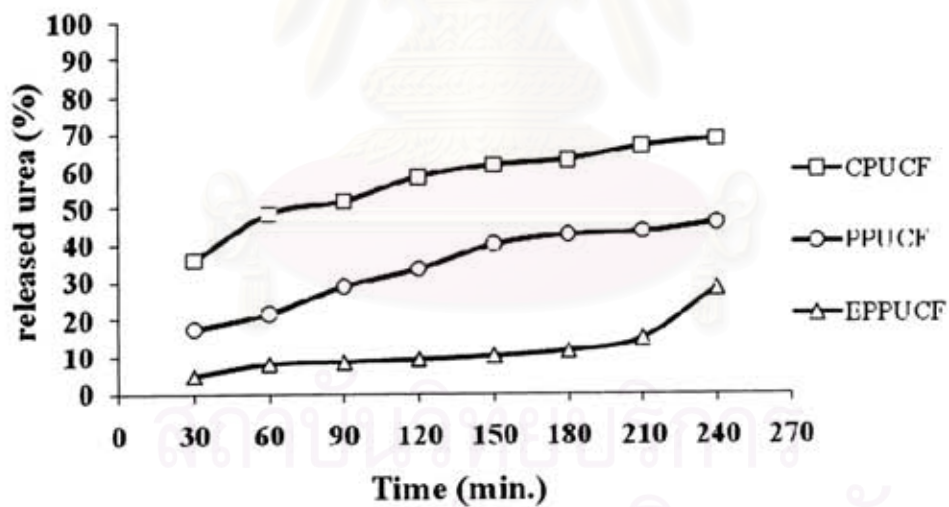
Figure 4.22 Comparison of the releasing rate of PU coated fertilizer using three types of polyols at 30 °C.
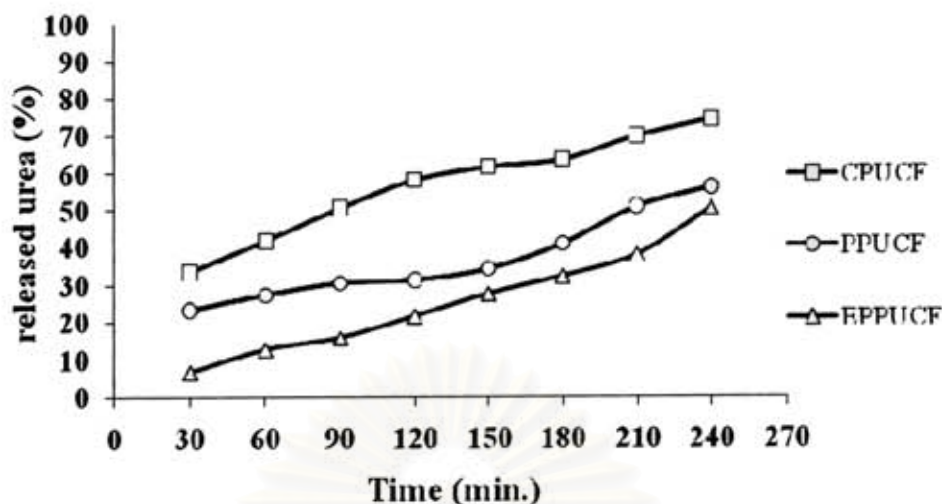
Figure 4.23 Comparison of the releasing rate of PU coated fertilizer using three types of polyols at 40 °C.

4.9 Effect of polyol on releasing rate of coated urea fertilizer

The releasing rate of all coated fertilizer decreased when increased the number of coating and urea completely released within 2 days for 1 layer coated fertilizer. At the equal number of coating, EPPUCF gave the slowest releasing rate (Figure 4.24) because the presence of high OH groups which obtained from the ring opening of epoxide and from glycerolysis. The lower amount of OH in PPU which had only OH group from the glycerolysis reaction led to a higher releasing rate of PPUCF (Figure 4.25). The highest releasing rate of CPUCF was observed (Figure 4.26) because the high viscosity of CPU led to the ununiform coating.

In Figure 4.24, the slowest releasing rate of EPPUCF obtained from the 5 layer and the approximate urea released at 30 days were 99%, 98%,and 85% for 1, 3, 5 layers coating respectively.
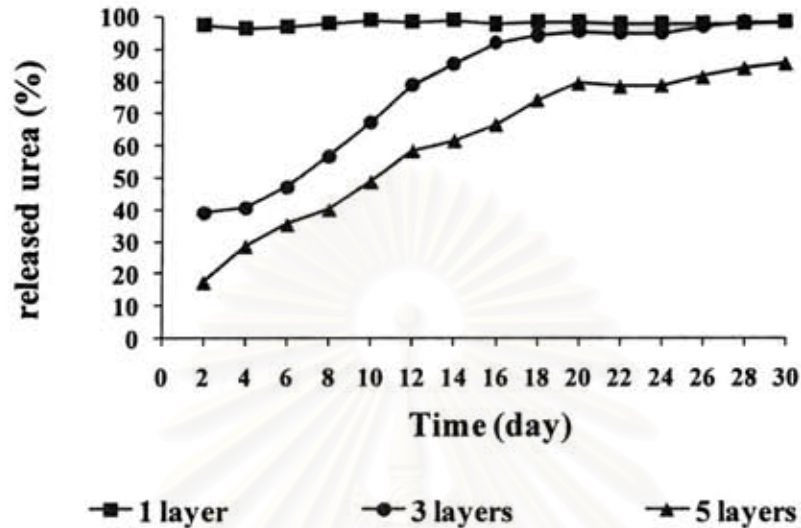
Figure 4.24 The releasing rate of 1, 3, 5 layers coating of EPPUCF.

In the case of 1 and 3 layer, the approximate urea released of PPUCF were equal to that of EPPUCF while the releasing rate of 5 layer PPUCF was 5% higher than that of EPPUCF (Figure 4.24, 4.25).
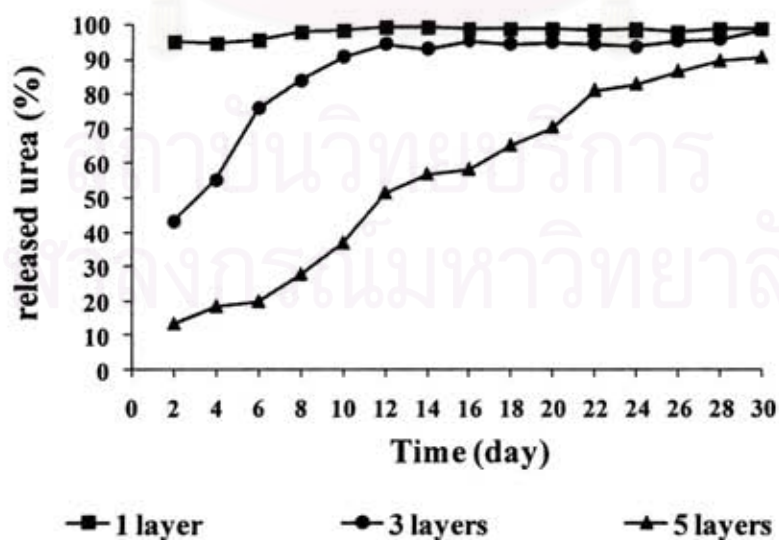
Figure 4.25 The releasing rate of 1, 3, 5 layers coating of PPUCF.

In Figure 4.26 indicated that the urea completely released from 1 and 3 layer CPUCF within 22 days. The slowest releasing rate obtained from the 5 layer of CPUCF and the approximate urea released was 94%.
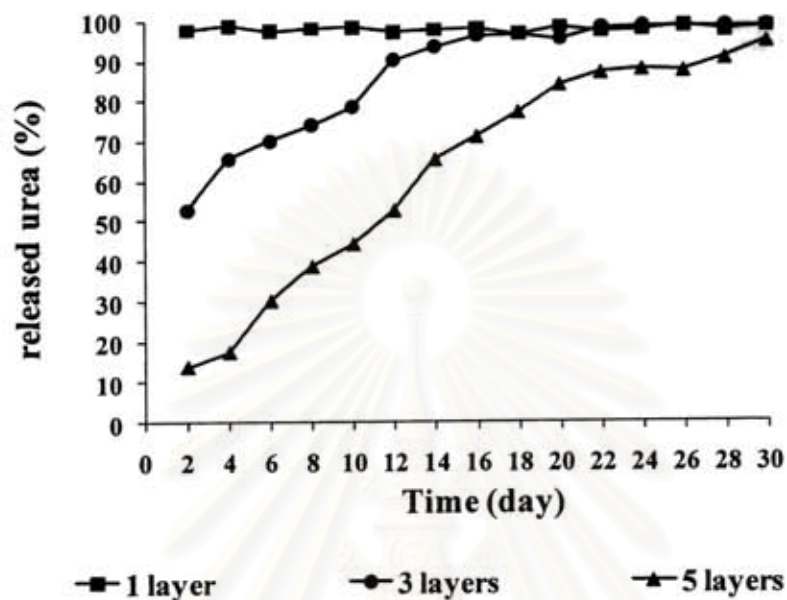
Figure 4.26 The releasing rate of 1, 3, 5 layers coating of CPUCF.

4.10 Percentage of coating

In Figure 4.27, the percentage coating of EPPU was approximate to that of PPU and CPU. The average percentage of three types PU coating were 4.14, 7.82, 10.97, 14.11, 16.03 for one, two, three, four, and five layers coating respectively. EPPU coating gave the highest percentage of coating because the high viscosity of CPO led to high amount coating when reacted with isocyanate and applied on the fertilizer.
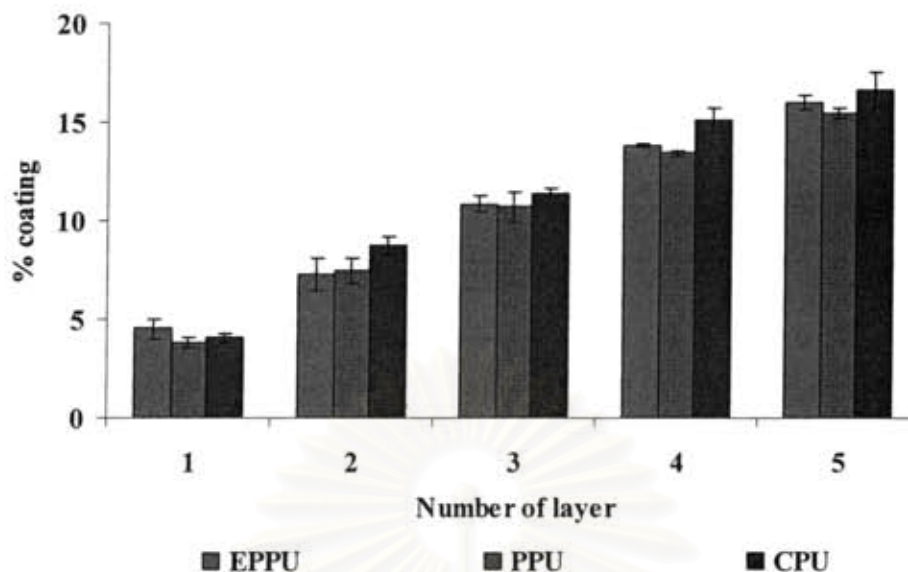
Figure 4.27 The percentage of coating.

4.11 The scanning electron microscopy (SEM) analysis

The thickness of coating was determined from SEM micrographs. From Figure 4.28 showed the average thickness of EPPU, PPU, and CPU coating that corresponded to the percent coating (Figure 4.27). The higher thickness was observed from CPU coating. In addition, the thickness of CPU coating differed from that EPPU and PPU coating when increased the number of coating. In the case of CPU, a higher thickness was observed because the free hydroxyl group from the fatty acid in unreacted castor oil was more rapidly reacted with an isocyanate forming a viscous mixture while a fertilizer was coated.
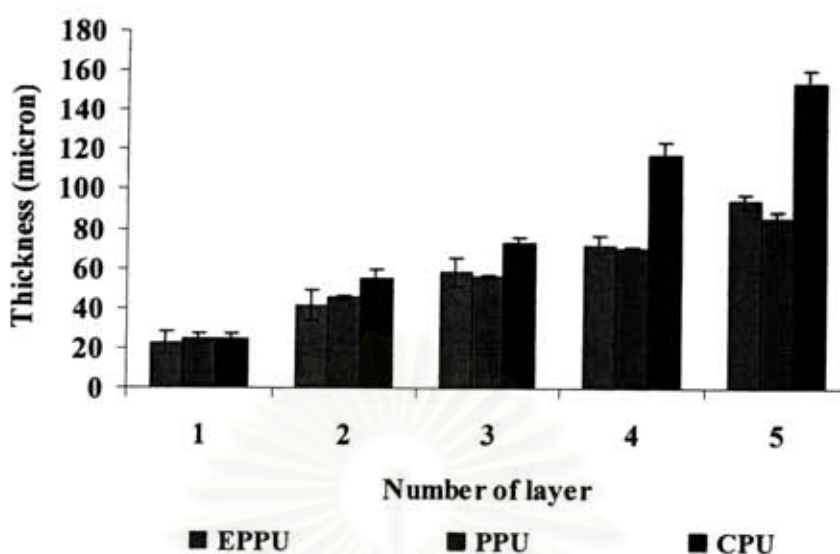
Figure 4.28 The average thickness of coatings.

4.12 The surface morphology observation.

The microscopic structure of coated fertilizer was investigated by using scanning electron microscope (SEM). SEM micrographs in Figures 4.29, 4.30 and 4.31 showed the increasing thickness when increased the number of coating. The coating layer was completely separated from the urea core. The surface morphology of PPUCF was smoother than those of EPPUCF and CPUCF.

Figure 4.29 SEM micrographs of EPPUCF.
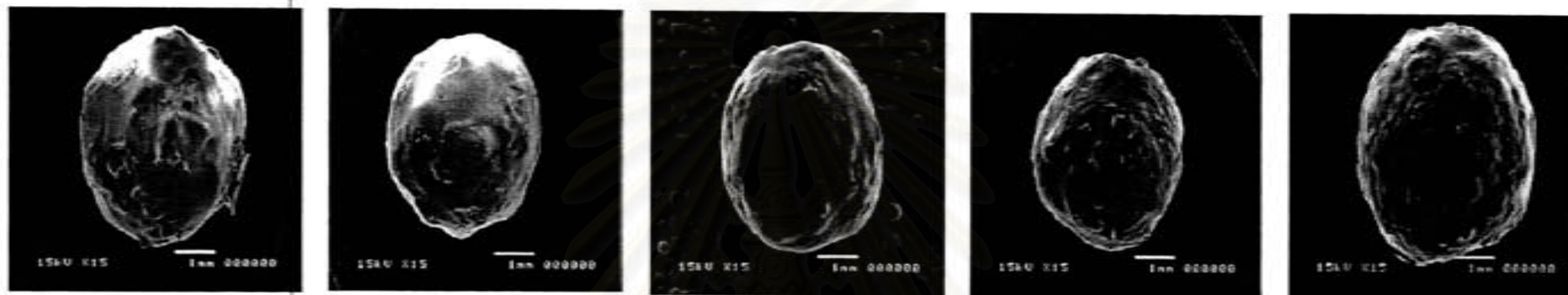
(a) 1 layer coated fertilizer (b) 2 layers coated fertilizer (c) 3 layers coated fertilizer (d) 4 layers coated fertilizer (e) 5 layers coated fertilizer
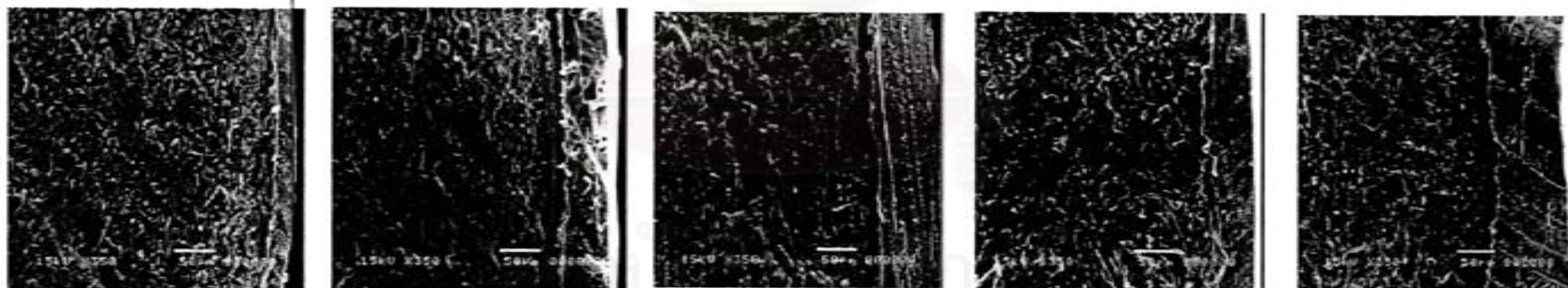
(f) 1 layer cross section (g) 2 layers cross section (h) 3 layers cross section (i) 4 layers cross section (j) 5 layers cross section

Figure 4.30 SEM micrographs of PPUCF.

(a) 1 layer coated fertilizer **(b)** 2 layers coated fertilizer **(c)** 3 layers coated fertilizer **(d)** 4 layers coated fertilizer **(e)** 5 layers coated fertilizer

(f) 1 layer cross section **(g)** 2 layers cross section **(h)** 3 layers cross section **(i)** 4 layers cross section **(j)** 5 layers cross section

Figure 4.31   SEM micrographs of CPUCF.
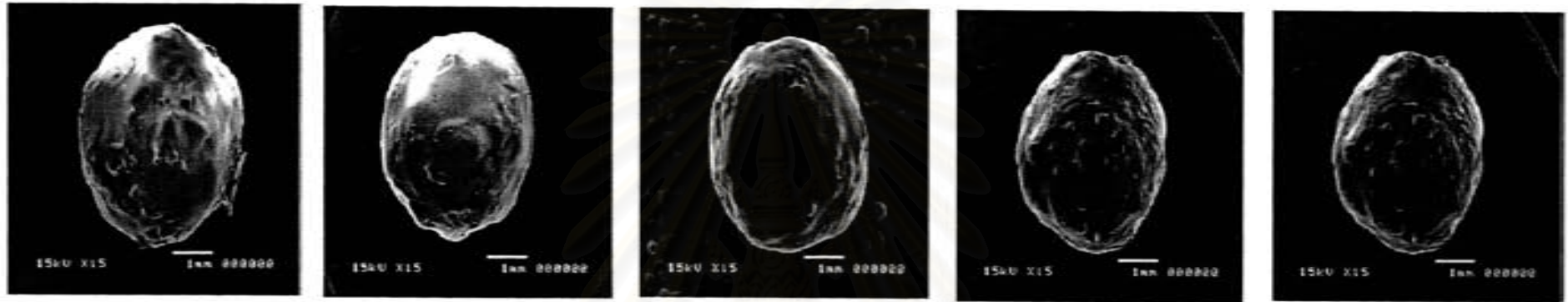
(a) 1 layer coated fertilizer (b) 2 layers coated fertilizer (c) 3 layers coated fertilizer (d) 4 layers coated fertilizer (e) 5 layers coated fertilizer
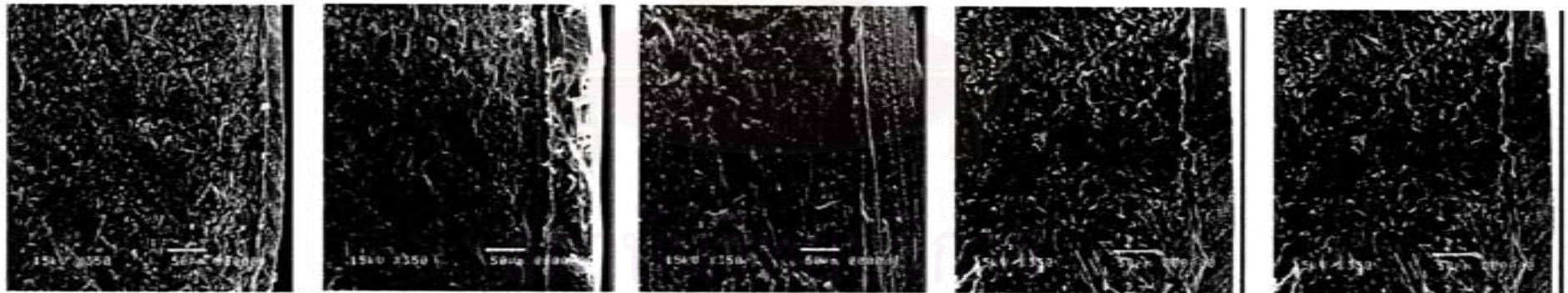
(f) 1 layer cross section   (g) 2 layers cross section   (h) 3 layers cross section   (i) 4 layers cross section   (j) 5 layers cross section

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The slow released fertilizer was prepared by coating polyurethane (PU) obtained from the epoxidized palm oil polyol, palm oil polyol, and castor oil polyol. The polyol was synthesized by glycerolysis for reduction of hydroscopic property of conventional glycerol which was a problem for coating applications because it led to foam forming. The PU coated fertilizer showed the slow released property. When thickness of the PU coating was increased, the releasing rate of urea decreased and increasing temperature resulted in increasing of releasing rate. Furthermore, high pH was found to decrease releasing rate of urea.

For 1-3 layer of all PU coated fertilizer, urea completely released within 30 days while the 5 layer coated fertilizer gives a slower and constant releasing rate. Furthermore, it was found that the urea of 5 layers coated with epoxidized palm oil polyol based, palm oil polyol based and castor oil based polyurethane was released within 30 days by 85, 90 and 94%, respectively. The PU coating fertilizer in the experiment had a high releasing rate but gave a similar released behavior compared with the commercial slow released fertilizer. Although it was too high cost for applying as the rice fertilizer (19.63 Baht/kg), it had a potential to develop to lower cost slow released.

5.2 Suggestions

The efficiency of slow released fertilizer depended on many factors. The coating equipments and appropriate polyol yielded a good slow released property, uniform coating and reduction of number of coating. The further study was improving the property of coating by varying the ratio of glycerolysis reactant resulting a polyol, reducing an amount of diisocyanate in the coating and using other low cost catalyst and natural oil based polyol.

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APPENDICES

APPENDIX A
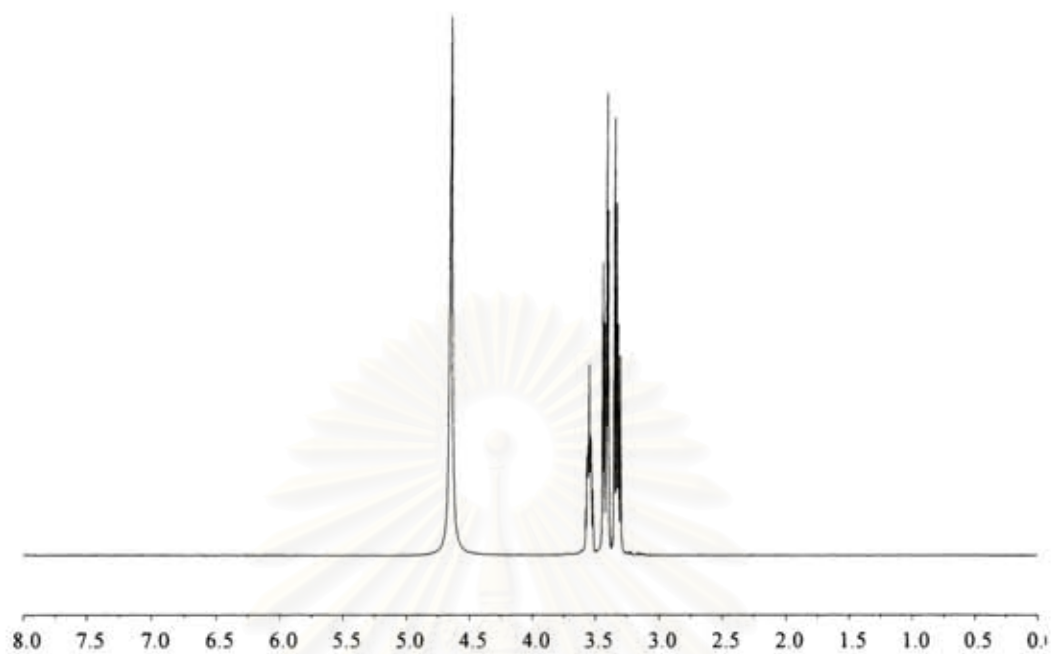
Figure A1 The ^{1}H-NMR (400 MHz, D$_2$O) of glycerol.
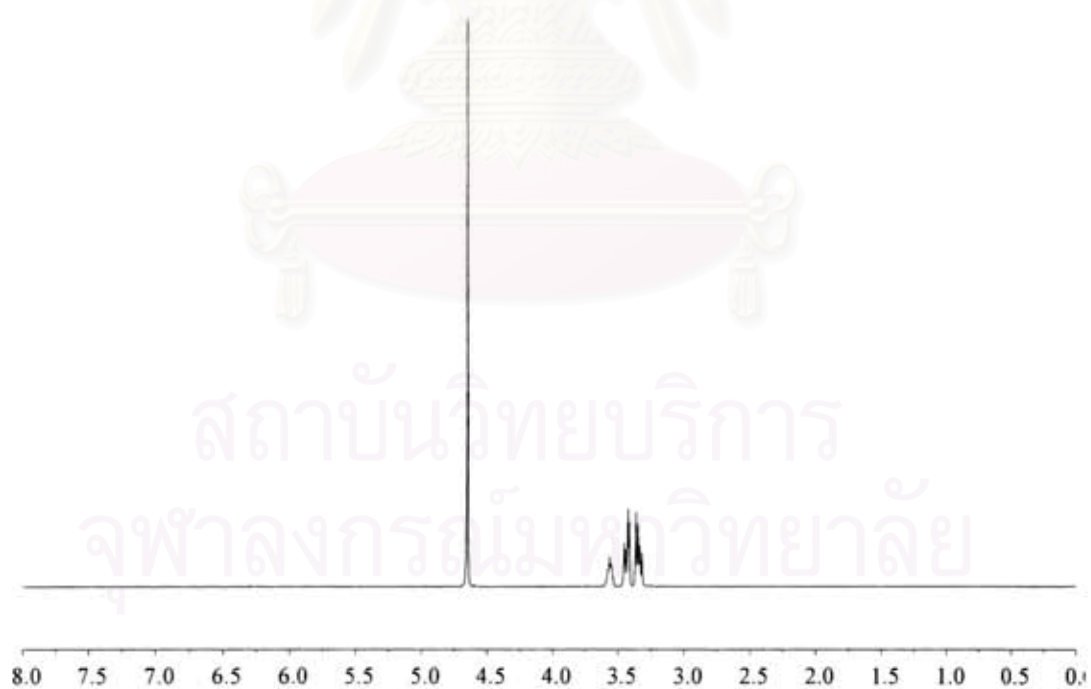
Figure A2 The ^{1}H-NMR (400 MHz, D$_2$O) spectrum of glycerol reacted with NaOH at 240°C for 3h.
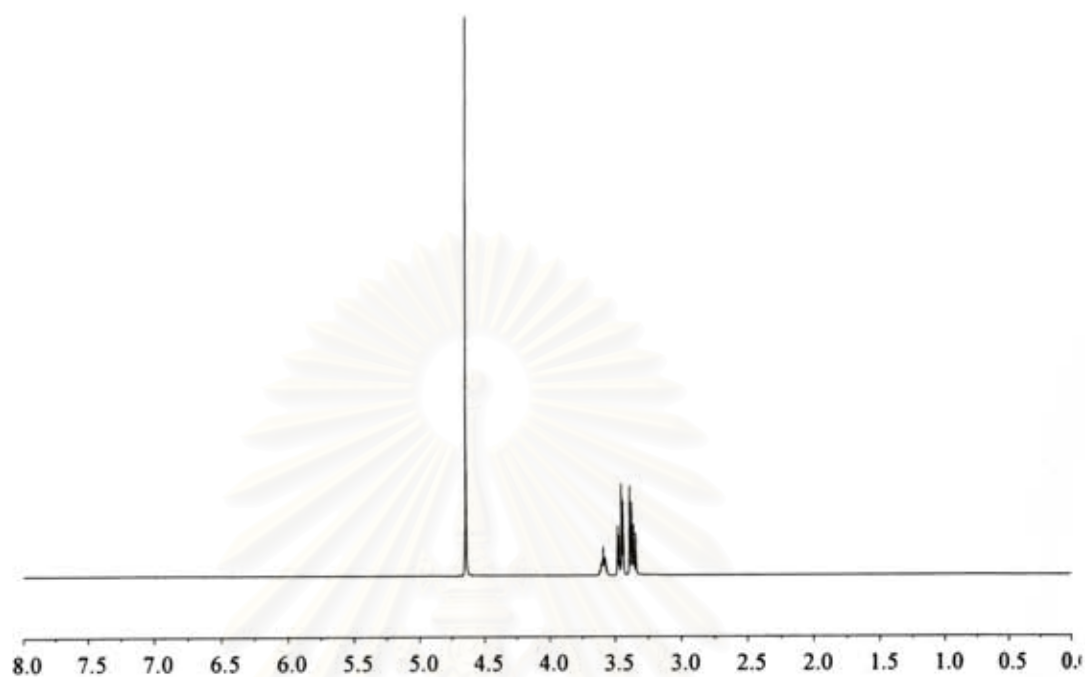
Figure A3 The ^{1}H-NMR (400 MHz, D$_2$O) spectrum of glycerol react with NaOH at 240°C for 6h.
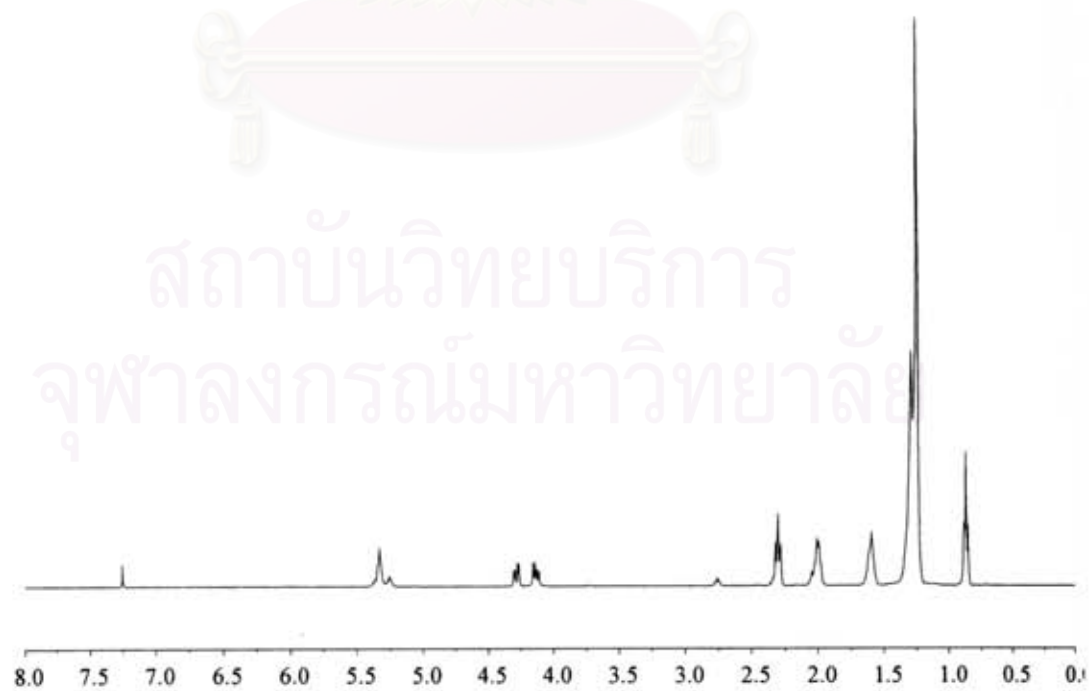
Figure A4 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of palm oil.
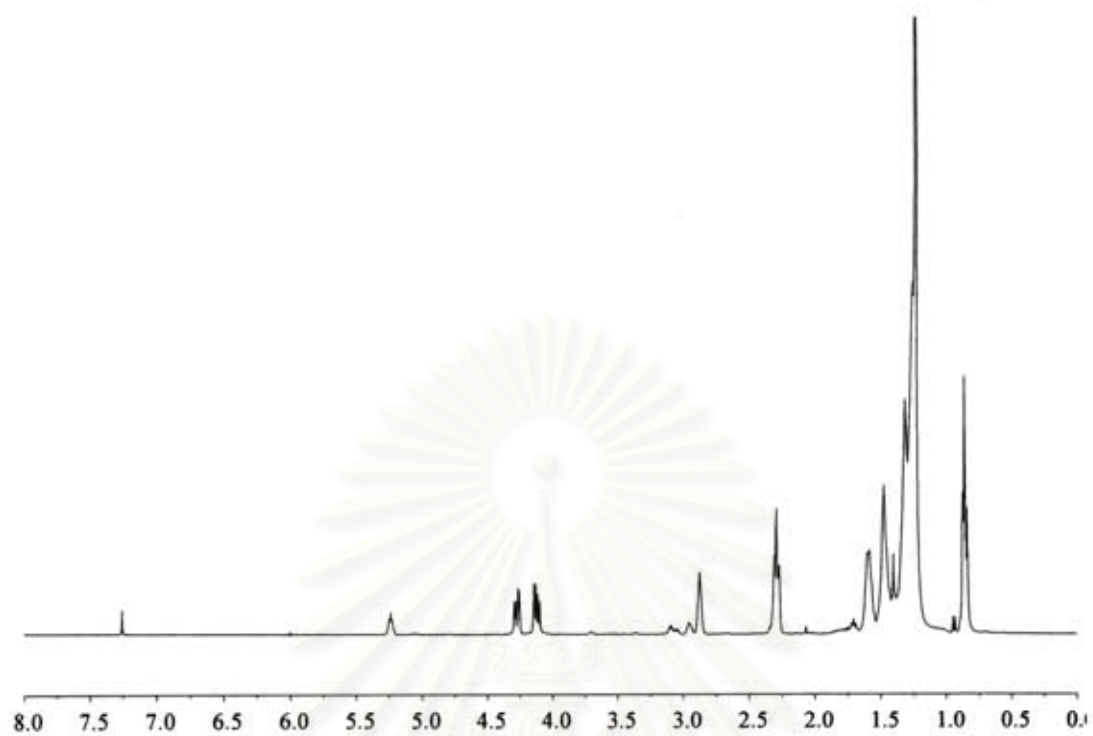
Figure A5 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of epoxidized palm oil.
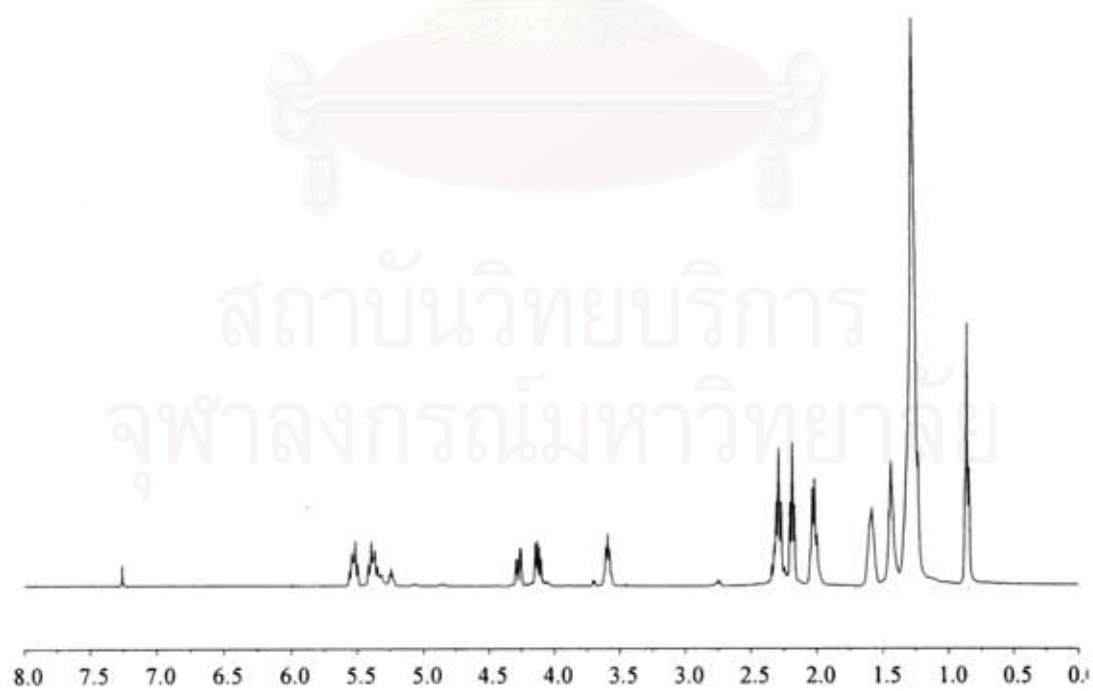
Figure A6 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of castor oil.
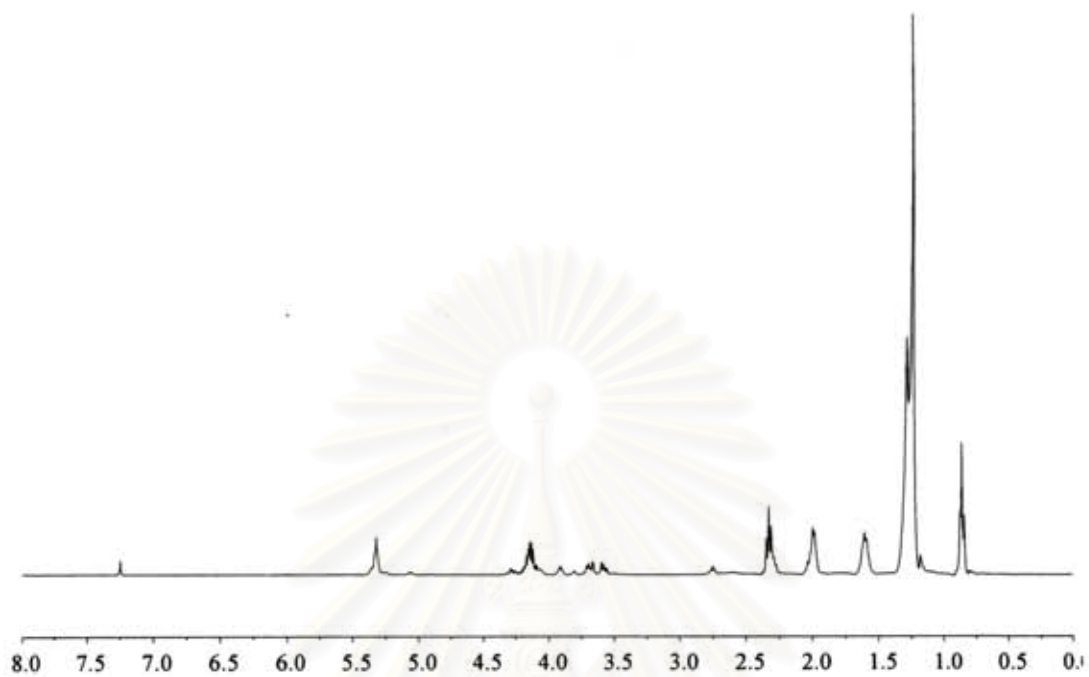
Figure A7 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of palm oil polyol (PPO).
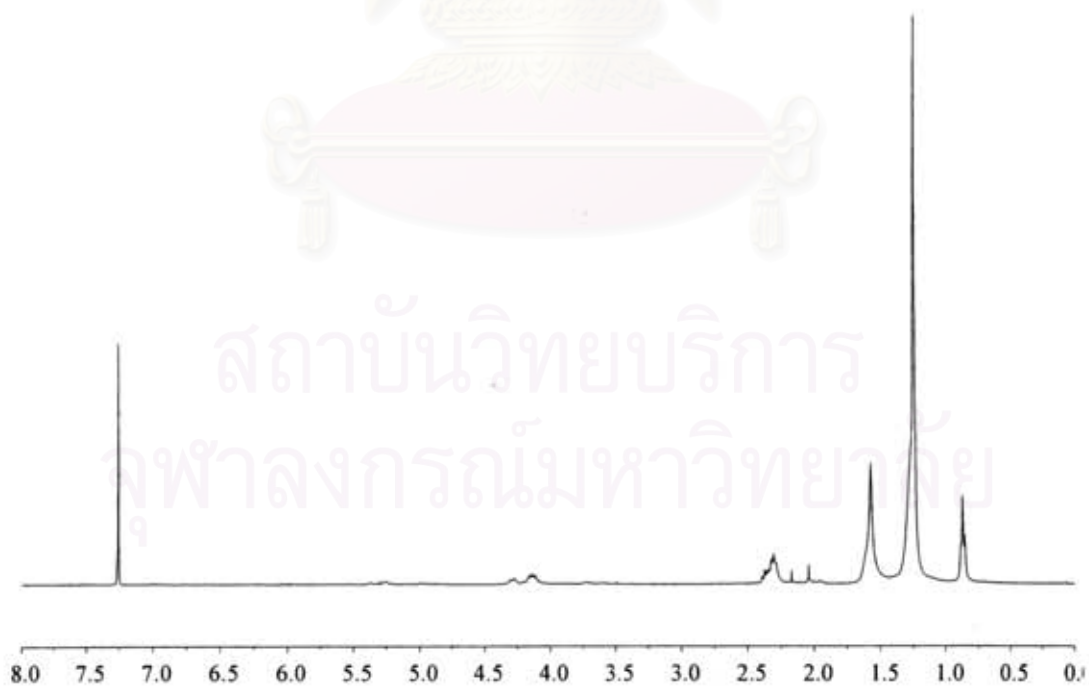
Figure A8 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of epoxidized palm oil polyol (EPO).
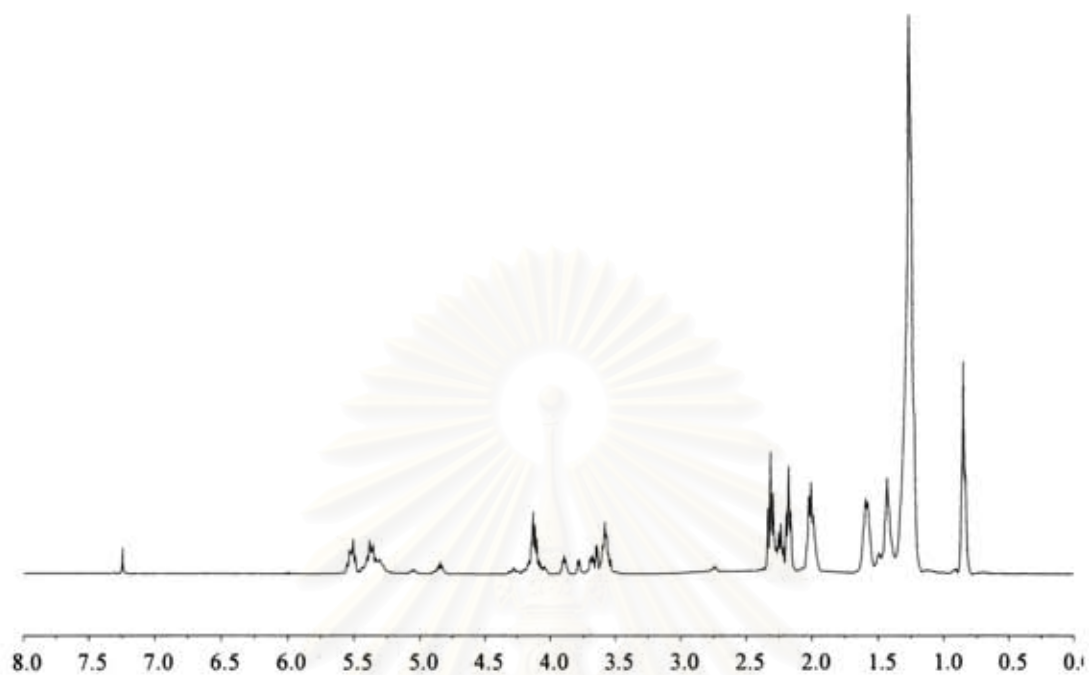
Figure A9 The ^{1}H-NMR (400 MHz, CDCl$_3$) spectrum of castor oil polyol (CPO).
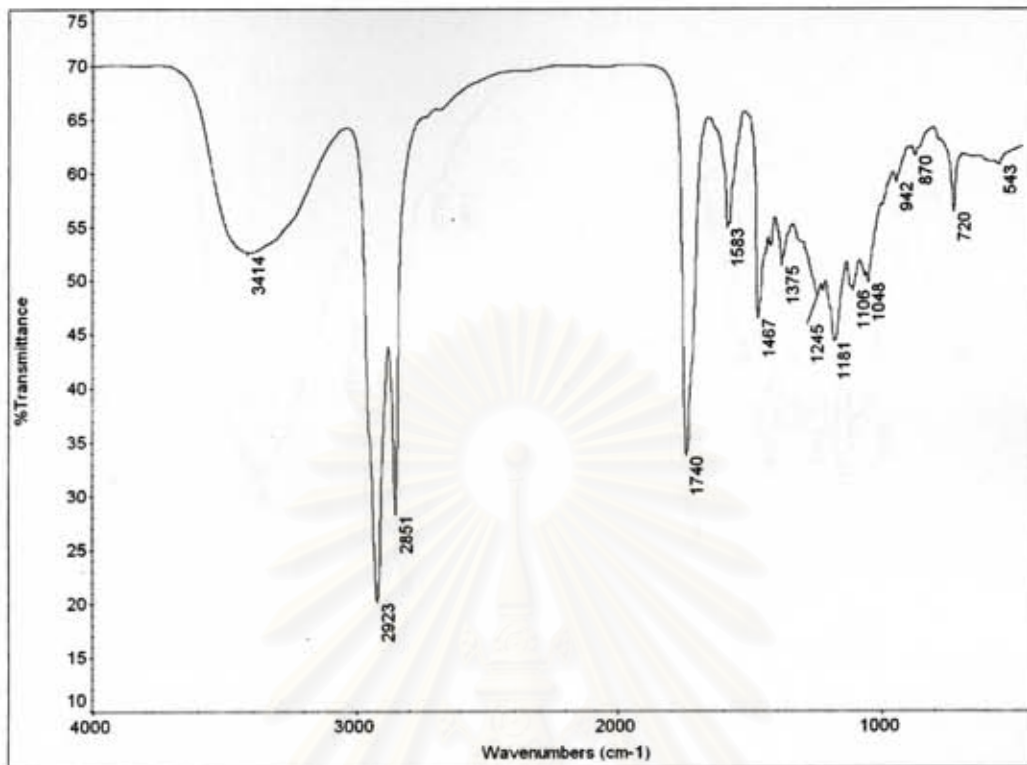
Figure A10 FT-IR spectrum of epoxidized palm oil polyol (EPO).
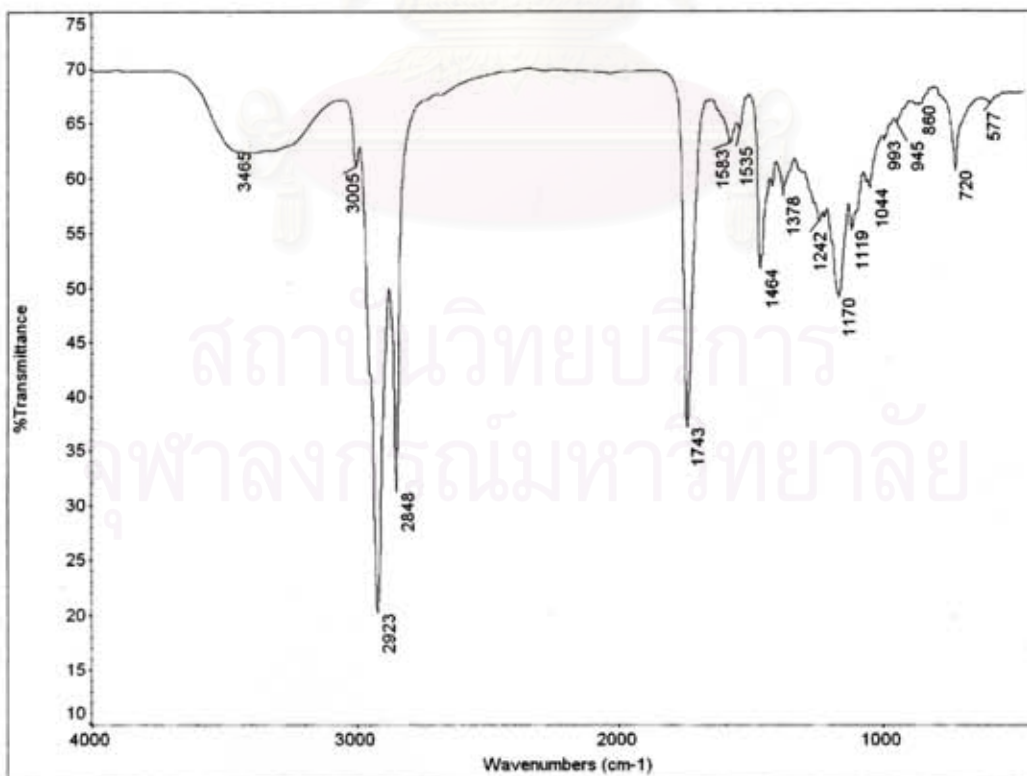
Figure A11 FT-IR spectrum of palm oil polyol (PPO).
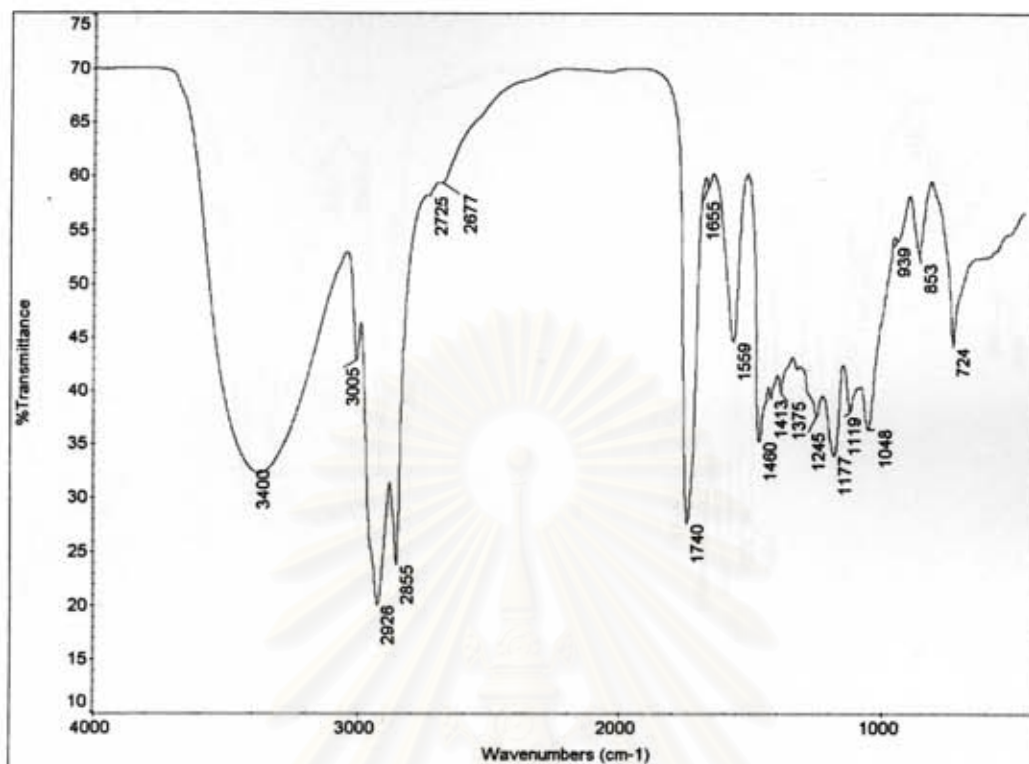
Figure A12 FT-IR spectrum of castor oil polyol (CPO).
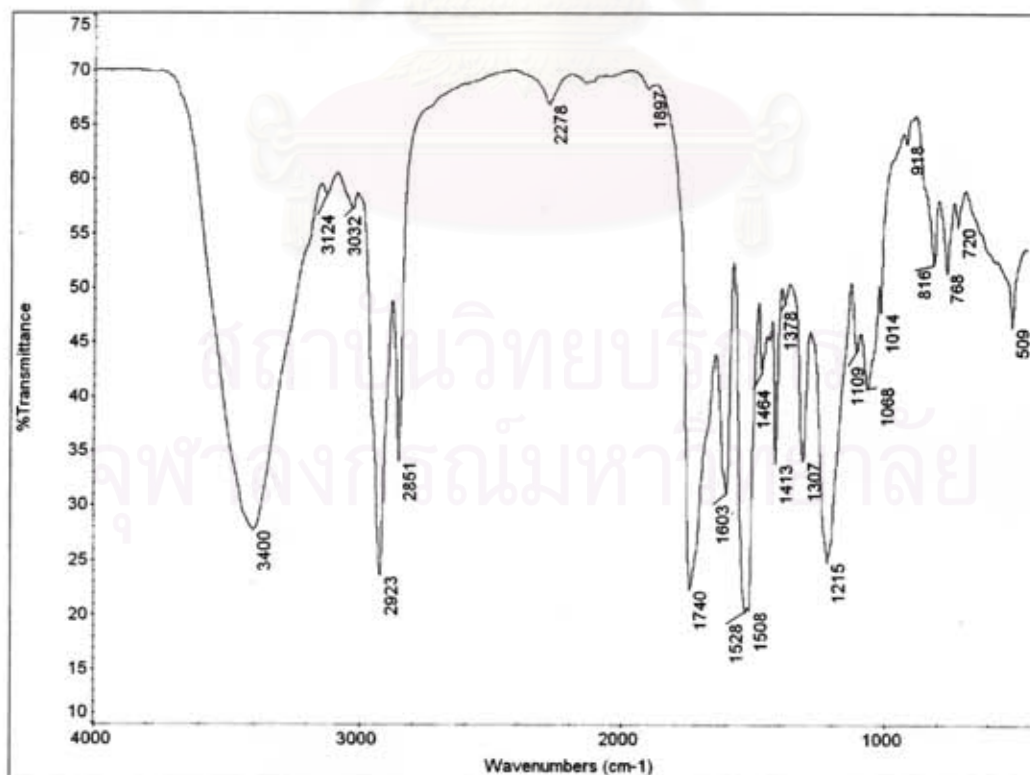
Figure A13 FT-IR spectrum of epoxidized palm oil polyurethane (EPU).
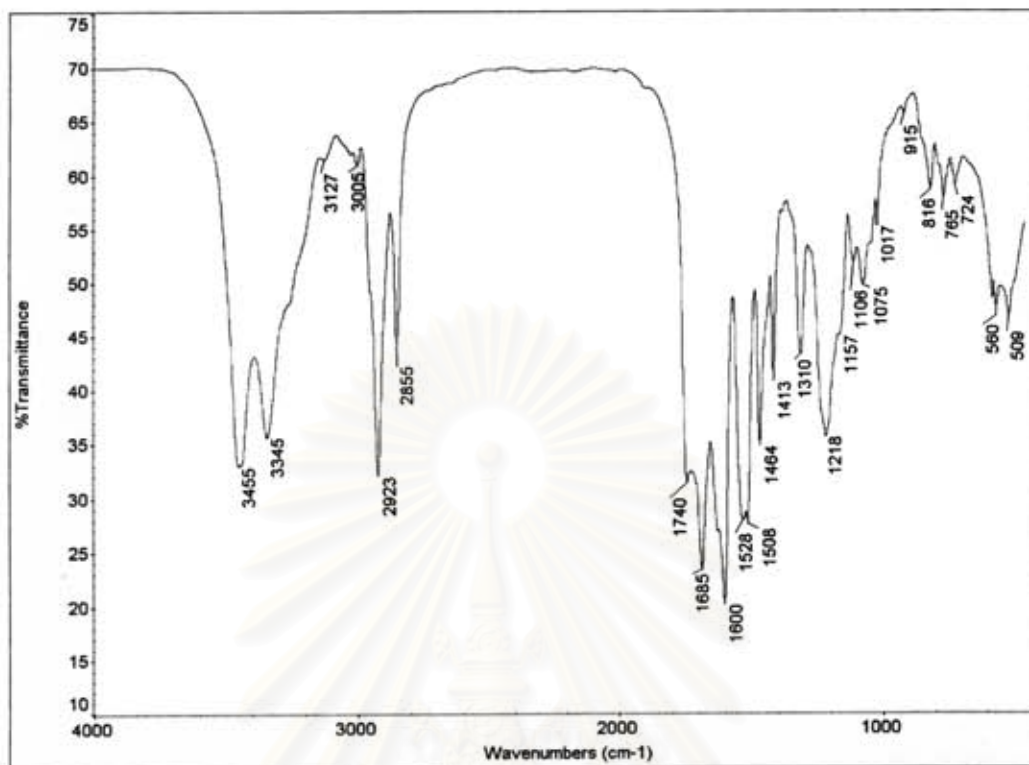
Figure A14 FT-IR spectrum of palm oil polyurethane (PPU).
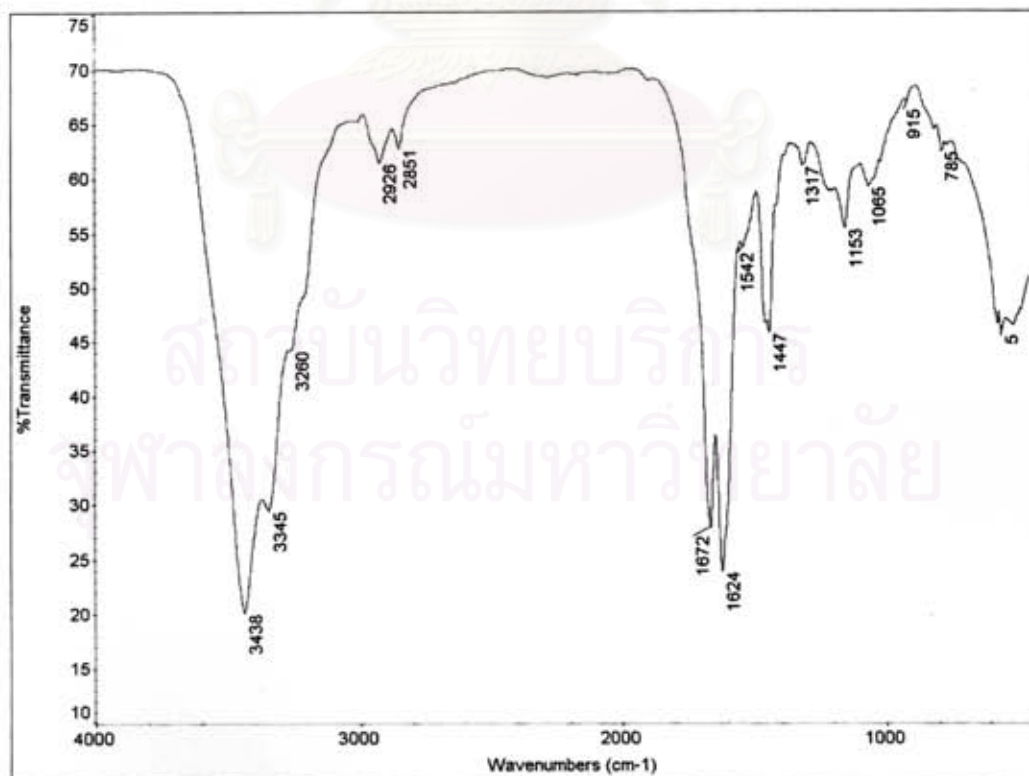
Figure A15 FT-IR spectrum of castor oil polyurethane (CPU).

APPENDIX B

Table B1 The solubility of uncoated urea fertilizer

Time (min)	Absorbance	Concentration (g/L)	Urea in fertilizer (%)	Released urea (%)
1*	0.222	0.57	14.05	61.08
2*	0.266	0.72	17.65	76.75
3*	0.291	0.80	19.78	85.99
4*	0.317	0.88	21.65	94.15
5*	0.322	0.90	22.04	95.82
10*	0.322	0.90	22.25	96.72
15*	0.325	0.91	22.55	98.03

Table B2 The average thickness of EPPU coatings

Number of layer	Thickness of coatings (micron)			Average (micron)	S.D.
	1	2	3		
1	15.9	24.7	27.1	22.6	5.9
2	49.2	42.1	33.9	41.7	7.7
3	66.7	54.9	53.3	58.3	7.3
4	68.6	76.6	71.6	72.3	4.0
5	94.4	90.7	97.7	94.3	3.5

Table B3 The average thickness of PPU coatings

Number of layer	Thickness of coatings (micron)			Average (micron)	S.D.
	1	2	3		
1	24.3	22.4	27.5	24.7	2.6
2	44.3	45.4	46.9	45.5	1.3
3	56.0	54.9	56.3	55.7	0.7
4	71.4	69.8	68.3	69.8	1.6
5	85.3	89.1	80.9	85.1	4.1

Table B4 The average thickness of CPU coatings

Number of layer	Thickness of coatings (micron)			Average (micron)	S.D.
	1	2	3		
1	24.8	27.4	22.7	25.0	2.4
2	56.6	58.7	49.0	54.8	5.1
3	69.5	76.0	72.4	72.6	3.3
4	111.0	119.0	123.0	117.7	6.1
5	147.0	161.0	156.0	154.7	7.1

Table B5 Coating percentage of EPPUCF

Number of layer	% Coating		Average (%)	S.D.
	1	2		
1	4.19	4.89	4.54	0.50
2	7.85	6.69	7.27	0.82
3	11.13	10.54	10.83	0.42
4	13.78	13.89	13.84	0.08
5	16.22	15.72	15.97	0.35

Table B6 Coating percentage of PPUCF

Number of layer	% Coating		Average	S.D.
	1	2	(%)	
1	3.64	3.99	3.82	0.25
2	6.97	7.89	7.43	0.65
3	10.15	11.23	10.69	0.76
4	13.32	13.51	13.42	0.13
5	15.68	15.24	15.46	0.31

Table B7 Coating percentage of CPUCF

Number of layer	% Coating		Average	S.D.
	1	2	(%)	
1	4.23	3.91	4.07	0.23
2	8.41	9.08	8.74	0.47
3	11.56	11.23	11.40	0.23
4	14.65	15.51	15.08	0.61
5	17.30	16.00	16.65	0.91

Table B8 Calibration curve of standard urea solution for urea content determination (UV-Vis Spectrophotometry)

Amount of 0.4 g/L urea stock solution (ml)	Concentration (g/L)	Absorbance
0	0.00	0.000
1	0.04	0.075
2	0.08	0.107
3	0.12	0.128
4	0.16	0.150
5	0.20	0.176
6	0.24	0.196
7	0.28	0.226
8	0.32	0.249
9	0.36	0.269
10	0.40	0.299
11	0.44	0.315
12	0.48	0.335
13	0.52	0.357
14	0.56	0.385
15	0.60	0.411
16	0.64	0.440
17	0.68	0.465
18	0.72	0.485
19	0.76	0.518
20	0.80	0.551

Table B9 Effect of temperature on releasing rate of EPPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
20°C				
30	0.064	0.0325	0.4202	3.77
60	0.065	0.0349	0.4147	4.10
90	0.070	0.0429	0.4188	5.00
120	0.077	0.0534	0.4155	6.26
150	0.088	0.0710	0.4143	8.36
180	0.101	0.0919	0.4197	10.68
210	0.136	0.1482	0.4069	17.76
240	0.155	0.1787	0.4045	21.54
30°C				
30	0.068	0.0402	0.4054	4.84
60	0.086	0.0678	0.4153	7.96
90	0.089	0.0734	0.4214	8.50
120	0.093	0.0791	0.4186	9.21
150	0.096	0.0847	0.4087	10.11
180	0.103	0.0959	0.4080	11.47
210	0.121	0.1249	0.4130	14.74
240	0.196	0.2446	0.4213	28.31
40°C				
30	0.079	0.0574	0.4193	6.67
60	0.111	0.1080	0.4134	12.74
90	0.128	0.1353	0.4156	15.88
120	0.157	0.1827	0.4135	21.55
150	0.192	0.2382	0.4212	27.57

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
180	0.213	0.2727	0.4127	32.22
210	0.248	0.3282	0.4220	37.92
240	0.315	0.4367	0.4215	50.52

Table B10 Effect of temperature on releasing rate of PPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
__40°C__				
30	0.163	0.1916	0.4040	23.09
60	0.188	0.2318	0.4153	27.17
90	0.202	0.2551	0.4095	30.32
120	0.212	0.2703	0.4228	31.13
150	0.225	0.2920	0.4172	34.08
180	0.256	0.3419	0.4079	40.80
210	0.308	0.4246	0.4068	50.82
240	0.346	0.4865	0.4229	56.00

Table B11 Effect of temperature on releasing rate of CPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
20°C				
30	0.236	0.3097	0.4108	35.92
60	0.312	0.4311	0.4244	48.39
90	0.324	0.4511	0.4150	51.79
120	0.355	0.5010	0.4092	58.33
150	0.384	0.5476	0.4247	61.43
180	0.384	0.5476	0.4153	62.82
210	0.393	0.5620	0.4034	66.38
240	0.411	0.5910	0.4116	68.41
30°C				
30	0.241	0.3169	0.4043	37.35
60	0.312	0.4311	0.4135	49.67
90	0.342	0.4801	0.4183	54.68
120	0.393	0.5620	0.4200	63.76
150	0.431	0.6231	0.4084	72.69
180	0.464	0.6753	0.4158	77.38
210	0.459	0.6681	0.4108	77.49
240	0.513	0.7549	0.4198	85.67
40°C				
30	0.219	0.2816	0.4031	33.28
60	0.266	0.3571	0.4090	41.60
90	0.311	0.4294	0.4054	50.47
120	0.357	0.5042	0.4142	57.99
150	0.383	0.5452	0.4221	61.53
180	0.380	0.5411	0.4066	63.41
210	0.427	0.6159	0.4209	69.71
240	0.447	0.6488	0.4167	74.18

Table B12 Effect of pH on releasing rate of EPPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
pH 5				
30	0.089	0.0726	0.4264	8.31
60	0.112	0.1104	0.4229	12.73
90	0.142	0.1586	0.4264	18.14
120	0.202	0.2543	0.4245	29.21
150	0.234	0.3065	0.4146	36.05
180	0.342	0.4801	0.4166	56.19
210	0.402	0.5757	0.4159	67.50
240	0.427	0.6167	0.4172	72.08
pH 7				
30	0.091	0.0759	0.4083	9.06
60	0.103	0.0951	0.4067	11.41
90	0.115	0.1144	0.4080	13.68
120	0.154	0.1779	0.4252	20.40
150	0.216	0.2768	0.4163	32.42
180	0.255	0.3394	0.4169	39.70
210	0.306	0.4222	0.4068	50.61
240	0.435	0.6295	0.4185	73.35
pH 9				
30	0.076	0.0526	0.4020	6.37
60	0.080	0.0590	0.4037	7.12
90	0.082	0.0622	0.4188	7.24
120	0.113	0.1120	0.4132	13.22
150	0.162	0.1908	0.4118	22.59

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
180	0.238	0.3121	0.4091	37.20
210	0.275	0.3724	0.4213	43.10
240	0.452	0.6561	0.4223	75.75

Table B13 Effect of pH on releasing rate of PPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
pH 5				
30*	0.176	0.4249	0.4136	50.02
60*	0.194	0.4828	0.4180	56.23
90*	0.217	0.5583	0.4714	57.66
120*	0.200	0.5037	0.4037	60.74
150*	0.245	0.6483	0.4217	74.85
180*	0.241	0.6339	0.4081	75.62
210*	0.245	0.6483	0.4139	76.26
240*	0.280	0.7592	0.4201	87.98
pH 7				
30*	0.145	0.3253	0.4005	39.54
60*	0.157	0.3639	0.4226	41.92
90*	0.155	0.3574	0.4112	42.32
120*	0.188	0.4635	0.4078	55.33
150*	0.207	0.5246	0.4128	61.87
180*	0.247	0.6532	0.4053	78.46
210*	0.255	0.6789	0.4066	81.28
240*	0.278	0.7528	0.4076	89.91

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
pH 9				
30*	0.228	0.5937	0.4044	27.45
60*	0.243	0.6403	0.4076	28.96
90*	0.263	0.7062	0.4125	31.04
120*	0.285	0.7753	0.4168	33.23
150*	0.306	0.8428	0.4169	35.67
180*	0.296	0.8123	0.4007	35.96
210*	0.318	0.8830	0.4052	38.21
240*	0.396	1.1321	0.4092	47.05

Table B14 Effect of pH on releasing rate of CPUCF

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
pH 5				
30*	0.130	0.2774	0.4075	32.43
60*	0.205	0.5202	0.4204	58.95
90*	0.212	0.5431	0.4101	63.09
120*	0.223	0.5776	0.4185	65.75
150*	0.229	0.5962	0.4081	69.61
180*	0.236	0.6198	0.4057	72.79
210*	0.248	0.6575	0.4171	75.10
240*	0.275	0.7462	0.4194	84.77
pH 7				
30*	0.166	0.3931	0.4002	46.79
60*	0.205	0.5191	0.4128	59.91
90*	0.239	0.6297	0.4187	71.65

Time (min.)	Absorbance	Concentration (g/L)	$W_{fertilizer}$ (g)	released urea (%)
120*	0.246	0.6507	0.4145	74.79
150*	0.264	0.7103	0.4126	82.01
180*	0.267	0.7205	0.4117	83.38
210*	0.290	0.7926	0.4148	91.04
240*	0.289	0.7890	0.4010	93.75
pH 9				
30*	0.076	0.1061	0.4190	12.06
60*	0.167	0.3983	0.4200	45.18
90*	0.191	0.4752	0.4164	54.37
120*	0.195	0.4889	0.4042	57.63
150*	0.202	0.5095	0.4116	58.98
180*	0.215	0.5531	0.4234	62.23
210*	0.220	0.5673	0.4138	65.31
240*	0.265	0.7114	0.4188	80.93

* 2 times dilution

Calculation of released urea
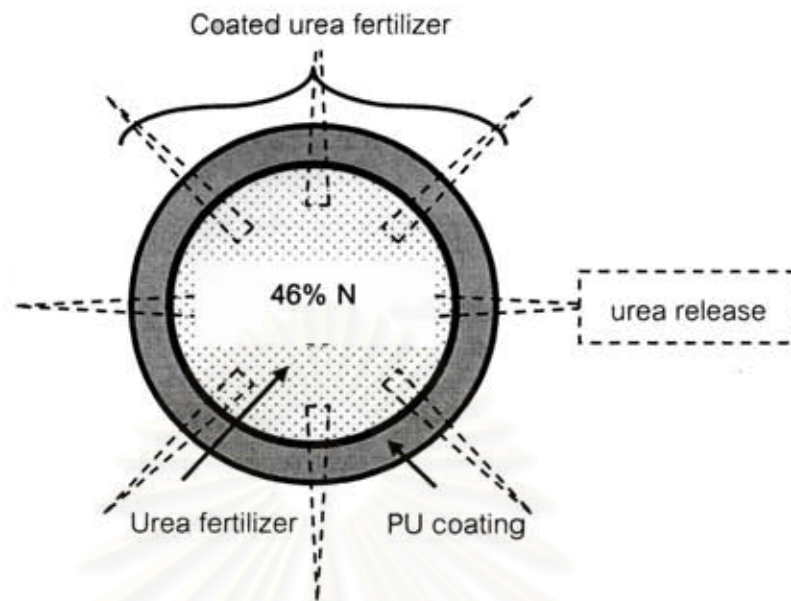
$$\text{released urea (\%)} \quad = \quad \frac{C/10 \times 100}{X_O} \qquad (1)$$

C; urea content (g/L) calculated from calibration curve

Because urea fertilizer contained 46% of N, the value of U should be nearly 23%. The actually amount of urea in uncoated fertilizer can be calculated from the following equation.

$$X_O; \text{ urea in uncoated fertilizer (g)} \quad = \quad \frac{W_F \times U}{100} \qquad (2)$$

U; % urea in uncoated fertilizer (Figure 4.16)

$$W_F; \text{ weight of uncoated fertilizer} \quad = \quad \frac{W_C \,(100 - \%\text{coating})}{100} \qquad (3)$$

W_C; weight of coated fertilizer

Determination of coating percentage [28]

10 g. of coated urea fertilizer was crushed and blended with deionized water to accelerate the dissolution and separate urea from the coating. The solution was filtered and washed with deionized water to ensure that no urea remained. The insoluble solid was dried in the oven at 100°C for 4 hours or until its weight become constant. The coating percentage was calculated by equation 4.

$$\% \text{ coating} = \frac{\text{weight of solid (g.)} \times 100}{10} \quad (4)$$

VITA

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Conference

19-21 November 2008   "Glycerol based polyurethane"

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