CHAPTER 1: INTRODUCTION

1.1 Background of study

In the past decade urea has surpassed and nearly replaced ammonium nitrate as a fertilizer. This has brought about new questions on urea and its use. Urea, white crystalline solid containing 46% nitrogen, is widely used in the agricultural industry as an animal feed additive and fertilizer. Here we discuss it only as a nitrogen fertilizer.

Commercially, fertilizer urea can be purchased as prills or as a granulated material. In the past, it was usually produced by dropping liquid urea from a "prilling tower" while drying the product. The prills formed a smaller and softer substance than other materials commonly used in fertilizer blends. Today, though, considerable urea is manufactured as granules. Granules are larger, harder, and more resistant to moisture. As a result, granulated urea has become a more suitable material for fertilizer blends.

Starch is a natural polymer which possesses many unique properties and some shortcoming simultaneously. Some synthetic polymers are biodegradable and can be tailor-made easily. Therefore, by combining the individual advantages of starch and synthetic polymers, starch-based completely biodegradable polymers (SCBP) are potential for applications in biomedical and environmental fields (Lu et al, 2009). Therefore it received great attention and was extensively investigated through this project.

Cellulose is the substance that makes up most of a plant's cell walls. Since it is made by all plants, it is probably the most abundant organic compound on Earth. Aside from being the primary building material for plants, cellulose has many others uses. According to how it is treated, cellulose can be used to make paper, film, explosives, and plastics, in addition to having many other industrial uses.

The project is focusing on developing the tapioca starch-cellulose blend, hence cross linked with sodium borate to come out with controlled-released urea fertilizer encapsulation mechanism.

1.2 Problem statement

Fertilizers are one of the most important products of the agrochemicals industry. They are added to the soil to release nutrients necessary for plant growth. Urea fertilizer used in agriculture is very soluble in water and easily decompose to release ammonia and carbon dioxide which lead to a serious loss. When it rains, about half of the applied fertilizers, depending on the methods and soil condition, are lost to the environment (O.A.Salman et al., 1989).

In most cases, the fertilizers containing nutrients essential for plant growth tend to easily soluble in rain water hence brought together with the flow of rain water away from the target area. This will lead to a major waste since the farmers have to apply the fertilizer in high scale or concentration for effective action. When this happens, another problem will be caused. With the application of high concentration of the fertilizers which are mostly made of non-biodegradable chemicals, it will be very harmful to the streams or rivers nearby. The fertilizers flow within the rain water will end up in these places, causing the water to be contaminated and endanger the aquatic lives.

Moreover, in sunny day, there will be also a problem with the conventional fertilizers. For example, urea fertilizers will be decomposing in the open air to release ammonia and carbon dioxide. Urea breakdown begins as soon as it is applied to the soil. If the soil is totally dry, no reaction happens. But with the enzyme urease, plus any small amount of soil moisture, urea normally hydrolyzes and converts to ammonium and carbon dioxide. This can occur in 2 to 4 days and happens quicker on high pH soils. Unless it rains, urea must be incorporated during this time to avoid ammonia loss. Losses might be quite low in the spring if the soil temperature is cold.

The chemical reaction is as follows:

$$\underset{\text{(urea)}}{CO(NH_2)_2} + H_2O + \text{urease} \rightarrow 2NH_3 + CO_2$$

The problem is the NH_3, because it's a gas, but if incorporated the NH_3, acts the same as incorporated anhydrous ammonia. Also, half of 28% liquid N is urea and the same thing happens with this half as with regular urea **(**Curtis J. Overdahl et al., 1991).

1.3 Objectives of the study

Main objectives of this study are:

1. **To study the effect of blending the tapioca starch and cellulose.**
2. **To study the effect of cross linking to tapioca starch-cellulose blend**

1.4 Scope of the study

The study of controlled-release fertilizer is widely developed by scientists all over the world. From numbers of fertilizers either organic or chemical fertilizers, this study will focus on developing urea fertilizer by experimenting it with tapioca starch and cellulose blend to see the effect in its rate of release to the soil.

1.4.1 Significant of the study

The main idea of the project is to develop a new form of fertilizer which is released to the soil with the characteristics of environmental-friendly by the use of tapioca starch (biodegradable substance) and having the ability to slow down the release to the soil by introducing cross linking (with Borax) and coating (with cellulose).

1.4.2 Relevancy of the project

This project is relevant enough to be executed based on these factors:

- Tapioca starch has been studied as **potential biodegradable polymer.**
- Urea fertilizer is used since it composes the **highest percentage of Nitrogen** (46%) compare to other nitrogenous fertilizer
- Cellulose can be easily obtained from various sources for example empty fruit bunch, wood residues and rice husk. It is **cheap and exhibit good coating property.**

1.5 Feasibility of the study

This project will start by collecting the reading material such as the books, journals, related website, and thorough discussion with project supervisor about the topic. At the end of Final Year Project (FYP) 1, it is expected that the writer have carry out the literature survey on selected important aspects of the study which cover the information of urea fertilizer as base substance, cellulose as coating material, sodium borate (Borax) as cross linking agent and tapioca starch as potential biodegradable substance.

From the research done, the writer will have to come out with few choices of available methodologies that are suitable to be applied to develop the cellulose-modified cross linking tapioca starch to slow the release of fertilizer.

The next phase will be testing proposed experimental methods for developing the fertilizer. The best method will be selected and the test will be done experimentally in the lab. A few set of experiments will be conducted including the preparation of the tapioca starch-cellulose blend film, swelling test, solubility test, chemical structure observation and tensile test.

The result from the experiment will be collected after it is being conducted repeatedly to ensure its validity and reliability. The best condition for the blend films in terms of water absorbency and biodegradability in soil will be determined based on the result and observation. Finally, these conditions will be applied to the test subject to produce the new controlled-release urea fertilizer.

CHAPTER 2: LITERATURE REVIEW

2.1 Cellulose

2.1.1 Properties and characteristic

Cellulose was discovered in 1838 by the French chemist Anselme Payen, who isolated it from plant matter and determined its chemical formula (Crawford, R. L., 1981). Cellulose was used to produce the first successful thermoplastic polymer, celluloid, by Hyatt Manufacturing Company in 1870. Hermann Staudinger determined the polymer structure of cellulose in 1920. The compound was first chemically synthesized (without the use of any biologically derived enzymes) in 1992, by Kobayashi and Shoda (Klemm et al., 2005).

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1,4 glycosidic bonds) linked D-glucose units (Updegraff DM, 1969). Cellulose is the structural component of the primary cell wall of green plants, many forms of algae and the oomycetes. Some species of bacteria secrete it to form biofilms. Cellulose is the most common organic compound on Earth. About 33% of all plant matter is cellulose (the cellulose content of cotton is 90% and that of wood is 40–50%) (Britannica Encyclopaedia: Cellulose, 2008).

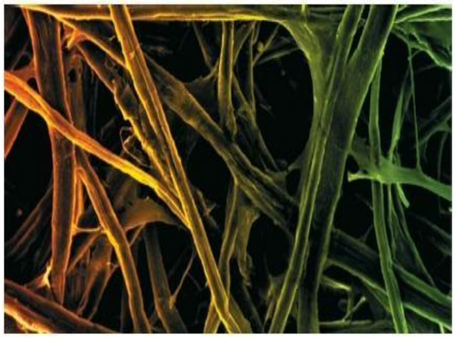

Figure 1: Scanning electron micrograph of wood cellulose

Cellulose has no taste, is odourless, is hydrophilic with the contact angle of 20–30, is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. (Charles A. Bishop, 2007). Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bonds. This linkage motif contrasts with that for α (1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbour chain, holding the chains firmly together side by side and forming microfibrils with high tensile strength. This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells.

Compared to starch, cellulose is also much more crystalline. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60-70 °C in water (as in cooking), cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water (Deguchi et al., 2006). Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial celluloses have chain lengths ranging from 800 to 10,000 units. (Klemm et al., 2005).

2.1.2 Application and potential as coating material

Cellulose is one of the most widely used natural substances and has become one of the most important commercial raw materials. The major sources of cellulose are plant fibers (cotton, hemp, flax, and jute are almost all cellulose) and, of course, wood (about 42 percent cellulose). Since cellulose is insoluble in water, it is easily separated from the other constituents of a plant. Cellulose has been used to make paper since the Chinese first invented the process around A.D. 100. Cellulose is separated from wood by a pulping process that grinds woodchips under flowing water. The pulp that remains is then washed, bleached, and poured over a vibrating mesh. When the water finally drains from the pulp, what remains is an interlocking web of fibers that, when dried, pressed, and smoothed, becomes a sheet of paper. (www.scienceclarified.com)

Raw cotton is 91 percent cellulose, and its fiber cells are found on the surface of the cotton seed. There are thousands of fibers on each seed, and as the cotton pod ripens and bursts open, these fiber cells die. Because these fiber cells are primarily cellulose, they can be twisted to form thread or yarn that is then woven to make cloth. Since cellulose reacts easily to both strong bases and acids, a chemical process is often used to make other products. For example, the fabric known as rayon and the transparent sheet of film called cellophane are made using a many-step process that involves an acid bath. In mixtures if nitric and sulfuric acids, cellulose can form what is called guncotton or cellulose nitrates that are used for explosives. However, when mixed with camphor, cellulose produces a plastic known as celluloid, which was used for early motion-picture film. However, because it was highly flammable (meaning it could easily catch fire), it was eventually replaced by newer and more stable plastic materials. Although cellulose is still an important natural resource, many of the products that were made from it are being produced easier and cheaper using other materials (www.scienceclarified.com).

Cellulose-based coatings are among the possibilities that offer a variety of gas and moisture permeability characteristics have extended the realm of potential uses for the materials. Oxygen barrier films are needed to prevent vitamin degradation, lipid oxidation and other oxidative reactions. Flavor-exchange barriers are needed to retain the sensory individuality of different components. Light barrier films could be used to protect pigments, flavors and nutrients from photodegradation. For instance, nuts stored for a long time-up to about a year-can rapidly become stale unless they are kept frozen. (www.thefreelibrary.com).

2.2 Tapioca starch

2.2.1 Properties and characteristic

Starch is one of the most abundant substances in nature, a renewable and almost unlimited resource. Starch is produced from grain or root crops. It is mainly used as food, but is also readily converted chemically, physically, and biologically into many useful products to date, starch is used to produce such diverse products as food, paper, textiles, adhesives, beverages, confectionery, pharmaceuticals, and building materials. Tapioca starch has many remarkable characteristics, including high paste viscosity, high paste clarity, and high freeze-thaw stability, which are advantageous to many industries (Integrated Cassava Project, 2005).

Starch is mainly composed of two homopolymers of D-glucose which are amylase, a mostly linear α-D(1, 4')-glucan and branched amylopectin, having the same backbone structure as amylose but with many α-1, 6'-linked branch points (Pareta R et al., 2006)

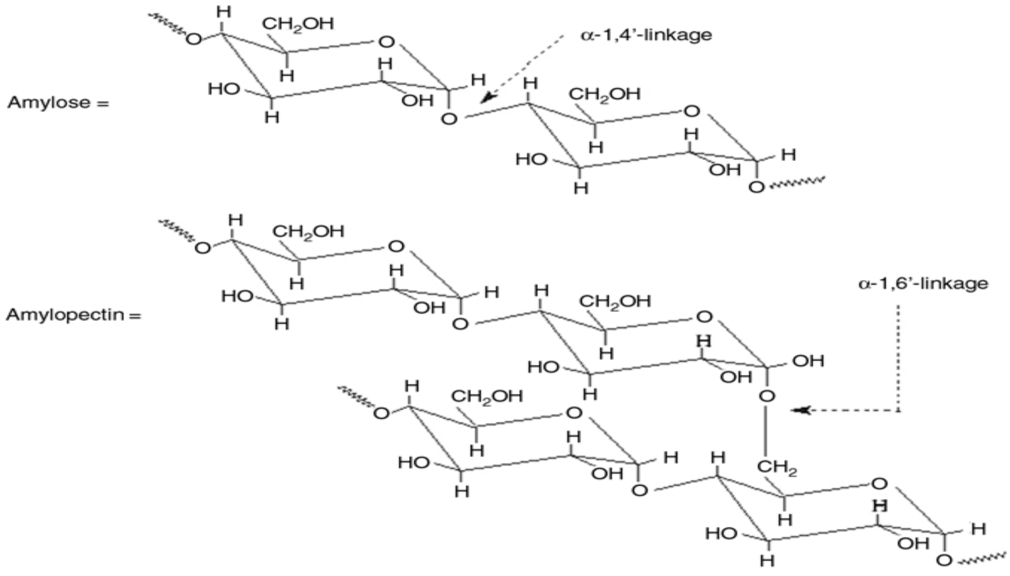

Figure 2: Molecular structure of starch

There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked. Evidently, starch is hydrophilic. The available hydroxyl groups on the starch chains potentially exhibit reactivity specific for alcohols. In other words, they can be oxidized and reduced, and may participate in the formation of hydrogen bonds, ethers and esters (Tomasik P. et al., 2004).

2.2.2 Modification of tapioca starch and its potential

For tapioca, the process of starch extraction is relatively simple as there are only small amounts of secondary substances, such as protein, in the roots. When tapioca roots are harvested or selected for starch extraction, age and root quality are critical factors. Tapioca roots need to be processed almost immediately after harvest, as the roots are highly perishable and enzymatic processes accelerate deterioration within 1-2 days. A first-rate quality starch can be obtained from tapioca using only water, and this makes the processing of tapioca starch and flour particularly suitable for developing countries and rural industries. Below are some advantages of using tapioca in producing tapioca starch:

- High level of purity.
- Excellent thickening characteristics.
- A neutral (bland) taste.
- Desirable textural characteristics.
- A relatively cheap source of raw material containing a high concentration of starch (dry-matter basis) that can equal or surpass the properties offered by other starches (maize, wheat, sweet potato, and rice).

Tapioca starch is easy to extract using a simple process (when compared to other starches) that can be carried out on a small-scale with limited capital. It is also often preferred in adhesive production as the adhesives are more viscous, work more smoothly, and provide stable glues of neutral pH. Moreover, it has clear paste.

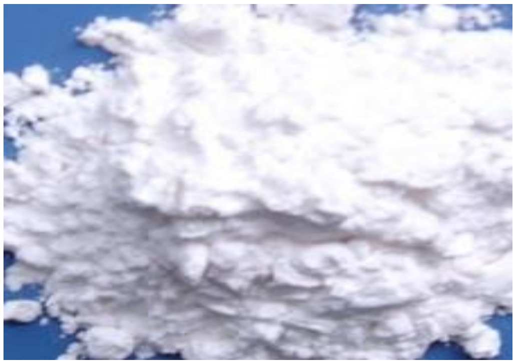

Figure 3: Tapioca starch

The different ways of modifying native starch consist in altering one or more of the following properties: paste temperature, solids/viscosity ratio, starch paste resistance to reduction of viscosity by acids, heat and or mechanical agitation (shear), retrogradation tendencies, ionic and hydrophilic nature. Modifying starch is important to provide the following properties: thickening, gelatinization, adhesiveness and/or film-formation, to improve water retention, enhance palatability and sheen and to remove or add opacity (Integrated Cassava Project, 2005).

The reasons why native starch is modified are:

- To modify cooking characteristics (gelatinization).
- To reduce retrogradation.
- To reduce paste’s tendency to gelatinize.
- To increase paste’s stability when cooled or frozen.
- To increase transparency of pastes and gels.
- To improve texture of pastes and gels.
- To improve adhesiveness between different surfaces, such as in paper applications.

Modification can be as simple as sterilizing products required for the pharmaceutical industry or highly complex chemical processes to confer properties totally different from the native starch. A simple modification process is represented by washing, air classification, centrifugation, and pre-gelatinization (Integrated Cassava Project, 2005)

2.3 Urea Fertilizers

Urea fertilizer, also known as carbamide, is the most important nitrogenous fertilizer. It is a white crystalline organic chemical compound containing about 46 percent nitrogen. It is a waste product formed naturally by metabolizing protein in humans as well as other mammals, amphibians and some fish. Synthetic urea is produced commercially from ammonia and carbon dioxide. Urea is widely used in the agriculture sector both as a fertilizer and animal feed additive, which makes the production of urea considerably high in comparison to other fertilizers. In the United States alone, approximately one million pounds of urea is produced every year. (Curtis J. Overdahl et al., 1991).

Urea was first discovered by a French scientist, named Hillaire Rouelle in 1773. But, synthetic urea was started to produce in 1828, about 55 years after its discovery. Currently, urea is manufactured industrially by the dehydration of ammonium carbamate in a process involving elevated temperature and pressure. Normally, a high pressure reactor is used within which all these reactions are carried out. **(**Harvey L. Meredith et al., 1991).

Figure 4: Urea fertilizer in pellet form

Below are some of the advantages of the urea fertilizer:

- Urea can be applied to soil as a solid or solution or to certain crops as a foliar spray.
- Urea usage involves little or no fire or explosion hazard.
- Urea's high analysis, 46% N, helps reduce handling, storage and transportation costs over other dry N forms.
- Urea manufacture releases few pollutants to the environment.
- Urea, when properly applied, results in crop yield increases equal to other forms of nitrogen. (Curtis J. Overdahl et al., 1991)

However, urea fertilizer posses a few disadvantages**.** Nitrogen from urea can be lost to the atmosphere if fertilizer urea remains on the soil surface for extended periods of time during warm weather. The key to the most efficient use of urea is to incorporate it into the soil during a tillage operation. It may also be blended into the soil with irrigation water. A rainfall of as little as 0.25 inches is sufficient to blend urea into the soil to a depth at which ammonia losses will not occur (W.Rehm et al., 1991).

If properly applied, urea and fertilizers containing urea are excellent sources of nitrogen for crop production. After application to the soil, urea undergoes chemical changes and ammonium (NH_4 +) ions form. Soil moisture determines how rapidly this conversion takes place. When a urea particle dissolves, the area around it becomes a zone of high pH and ammonia concentration. This zone can be quite toxic for a few hours. Seed and seedling roots within this zone can be killed by the free ammonia that has formed. Fortunately, this toxic zone becomes neutralized in most soils as the ammonia converts to ammonium. Usually it is just a few days before plants can effectively use the nitrogen (Harvey L. Meredith et al., 1991).

Although urea imparts an alkaline reaction when first applied to the soil, the net effect is to produce an acid reaction. Urea or materials containing urea should, in general, be broadcast and immediately incorporated into the soil. Urea-based fertilizer applied in a band should be separated from the seed by at least two inches of soil. Under no circumstances should urea or urea-based fertilizer be seed-placed with corn (W. Rehm et al., 1991).

Urea and fertilizers containing urea can be blended quite readily with monoammonium phosphate (11-52-0) or diammonium phosphate (18-46-0). Urea should not be blended with superphosphates unless applied shortly after mixing. Urea will react with superphosphates, releasing water molecules and resulting in a damp material which is difficult to store and apply (K.C. Nicolaou et al., 2008).

2.4 Studies of Controlled-Released Fertilizer (CRF)

Use of conventional fertilizers may lead to concentration levels that are too high for effective action. A high concentration may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment (K. El Refaie et al., 1996).

One method of reducing nutrient losses involves the use of controlled-release fertilizers (CRF). These fertilizers can be physically prepared from the granules of the soluble fertilizers by coating them with materials, which reduce their dissolution rate. CRF demonstrate many advantages over the conventional type, such as decreased rate of removal of the fertilizers from the soil by rain or irrigation water, sustained supply or minerals for a prolonged time, increased efficiency of the fertilizer, lower frequency of application in accordance with normal crop requirement, minimized potential negative effects associated with over dosage, and reduced toxicity (K. Byung-Su et al., 1996)

Starch-based biodegradable polymers have found three major applications in agriculture: the covering of greenhouse, mulch film and fertilizers controlled-release materials (Dilara P.A. et al., 2000). The consumption of agriculture films is abundant. Generally, the disposal methods of tradition films are landfill, recycling or burning. But they are time-consuming, not economic and lead to environmental pollution (Bohlmann G. et al., 2004).

On the other hand, the utilization efficiency of fertilizers is the key element of the development of agricultural productions. However, due to surface runoff, leaching and vaporization, the fertilizers escape to environment to cause diseconomy and environmental problems (Guo M. et al., 2005).

The development of starch-based biodegradable polymers offers a possibility to overcome the mentioned problems. They can be used as the fertilizers controlled release matrices to release the fertilizers slowly or in controlled way. As a result, the loss of fertilizers and environment pollution can be avoided or reduced (Chen L. et al., 2008).

After using, starch-based films can be ploughed into soil and disposed directly. Moreover, no toxic residues formed after the degradation of starch based biodegradable polymers (Malinconico M. et al., 2002).

Polymer coated controlled release fertilizers look promising for widespread use in agriculture because they can be designed to release nutrients in a more controlled manner by manipulating properties of polymer coating. Application of controlled release fertilizers (CRFs) at the time of planting offers a means to improve the establishment of forest tree seedlings. As compared to conventional fertilizer, the gradual release of nutrient release from CRFs may better coincide with plant needs, minimize leaching and improve fertilizer use efficiency. Many different CRFs types are available and products differ in both the technologies by which nutrients are contained and the environment stimulus for a nutrient release. The coming years represent a critical time in this field as commercial applications are being explored. In near future, CRFs with their ability to provide efficient and desirable controlled release will revolutionize agriculture industry. The advantages of CRFs are numerous which make further study in this field extremely important (Sunil K. Jain., 2007).

A CRF is composed of a semipermeable membrane surrounding water-soluble nitrogen and other nutrients. Water passes through the membrane, eventually causing enough internal pressure to disrupt the membrane and release the enclosed nutrients. Because, the thickness of the coating varies from one pellet, or prill, to another, nutrients are released at different times from separate prills. Release rate of these fertilizers is dependent on temperature,moisture, and thickness of the coating (Sunil K. Jain., 2007).

The coating materials used should be inexpensive and exhibit a good coating property. In addition, they should undergo testing for degradation in soil which might form any toxic substance that could affect the crop. The type of coating is responsible for the mechanism of release elements from encapsulated fertilizers (M. Tomaszewska et al., 2002)

Based on those criteria, starch-cellulose blend can potentially be developed since they are both are cheap, renewable, non- toxic and biodegradable. By increasing the content of the cellulose component, the rupture strength is increased, whereas the elongation at break and the permeability of films for water vapor are decreased. Starch can form thermodynamically compatible blend films with water-soluble carboxymethylcellulose (CMC) when the starch content is below 25 mass% (Suvorova A.I. et al., 2000).

CHAPTER 3: PROJECT METHODOLOGY

3.1 Research Methodology

For Final Year Project 2, the project activities are more focusing on completing the experiment which includes preparation of starch-cellulose blend films, swelling test, solubility test, tensile test, Thermo Gravimetric Analysis (TGA) and Fourier Transform Infra Red (FTIR) spectra.

3.1.1 Preparation of starch-cellulose blend films

- Starch is dispersed in purified water to form starch slurry
- Borax and urea are dissolved separately in purified water
- Starch slurry is heated until gelatinized, mixed with borax and urea, and then stirring is continued until 30 minutes.
- Microcrytalline cellulose (MCC) is dissolved in water and added to the gelatinized starch mixture.
- Stirring is continued until 1 hour
- The mass formed is spread on a leveled plate and dried at 50 °C for 8 hours.
- The ratio of each component to prepare the film sample are determined to be as the following :

  Starch: Urea: Borax =50:25:2.5
- The following table is representing the percentage and mass of components to be mixed :

Sample	starch		urea		Borax		MCC	
	(%)	(g)	(%)	(g)	(%)	(g)	(%)	(g)
1	64.52	5	32.26	2.5	3.226	0.25	0	0
2	61.29	5	30.65	2.5	3.065	0.25	5	0.408
3	58.06	5	29.03	2.5	2.903	0.25	10	0.861
4	54.84	5	27.42	2.5	2.742	0.25	15	1.368
5	51.61	5	25.81	2.5	2.581	0.25	20	1.937

Table 1: Percentage and mass of components to be mixed

3.1.2 Swelling Test

- A slice (square) of film by the size of 2cm x 2cm is taken
- The square is weighed and the initial weight is recorded.
- The square is immersed into water for 24 hours
- After 24 hours, the water is removed and the weight of the swollen film is recorded
- The swollen film is reinserted into the oven for another 24 hours
- After 24 hours, the film is taken out from oven and the final weight of the film is taken.

3.1.3 Solubility Test

- A slice of film by the size of 2cm x 2cm is taken
- The film is immersed into water for 30 days
- The condition of the film after 30 days is recorded.

3.1.4 Chemical structure observation

- Use Fourier transform infrared spectra (FTIR) to determine the bonding introduced by cross linking between starch-urea polymer chains

Figure 5: Fourier Transform Infrared spectra (FTIR)

3.1.5 Thermo Gravimetric Analysis (TGA)

- Analysis is carried out by raising the temperature of the sample gradually and plotting weight (percentage) against temperature. The temperature in this test is increased up to 800 °C. After the data are obtained, curve smoothing and other operations may be done to find the exact points of inflection.

3.2 Project Gantt chart

No	Detail / week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project work continues	▨	▨	▨	▨	▨	▨	Mid-Semester Break								
2	Submission of progress report								●							
3	Project work continues								▨	▨	▨	▨	▨			
4	Pre-EDX											●				
5	Submission of Draft Report												●			
6	Submission of Dissertation (soft bound)													●		
7	Submission of Technical Paper													●		
8	Oral Presentation														●	
9	Submission of Project Dissertation (hard bound)															●

Table 1: Project Gantt Chart

3.3 Key Milestone:

- 13 July 2011 : Progress Report Submission
- 4 August 2011 : Pre-EDX
- 22 August 2011 : Dissertation Submission
- 12 September 2011 : Oral Presentation (viva)

3.4 Tools and equipment

Lab equipment and apparatus will be required to perform the experiment. For example conical flasks, leveled plate, patry dish, spatula, water bath, and glass rod. These apparatus are available in Universiti Teknologi Petronas Chemical Engineering Department's laboratory.

Other equipments that may be needed are Fourier Transform Infra Red (FTIR) spectra, and Thermo Gravimetric Analysis (TGA) equipment after a few series of experiment to prepare the blend films is done.

CHAPTER 4: RESULT AND DISCUSSION

4.1 Results for Swelling Test

sample	Initial weight (g)	Final weight (g)	% of difference	Weight after drying (g)
0%	0.17	1.22	617.65	0.09
5%	0.17	1.22	617.65	0.12
10%	0.16	1.11	593.75	0.09
15%	0.17	1.07	529.41	0.12
20%	0.18	1.01	461.11	0.11

Table 2: Percentage and mass of components to be mixed

4.1.1 Discussion on Swelling Test result

The percentage of difference between the initial weight of film and the final weight is given by this formula:

$$\% \text{ of difference} = \frac{\text{Final weight (g)} - \text{Initial weight (g)}}{\text{initial weight}} \times 100\%$$

Based on the result obtained, it shows that the higher the percentage of cellulose, the lower the percentage of difference between the initial weight of the film (before swelling) and the final weight of the film (after swelling). Higher percentage of cellulose in a sample will reduce the water permeability through the film as well as reducing the water absorbency of the film. In general, the addition of Borax as cross linker plays a significant role in reducing the water absorbency of the films. Starch-urea blend films cross linked by Borax have led intermolecular and intermolecular linkage of –OH between starch and cellulose molecules and therefore the hydrophilic groups were reduced. So this experiment also proves that water absorbency of blend films decreased with the application of Borax. The film with the highest percentage of cellulose (20%) is deduced to be the least swollen film compared to the others.

4.2 Results for Solubility Test

For this experiment, the test is conducted by observing the condition of the films immersed in water for 30 days. The results obtained are as below:

1) Day 1:

Figure 6: Sample film of 0% mcc

Figure 7: Sample film of 5% mcc

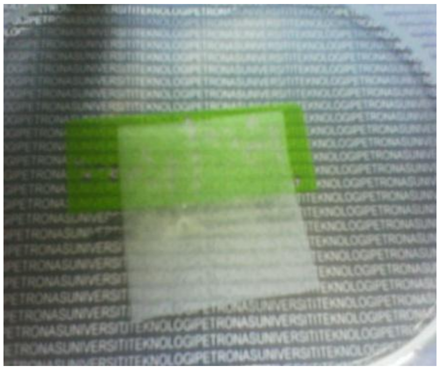

Figure 8: Sample film of 10% mcc

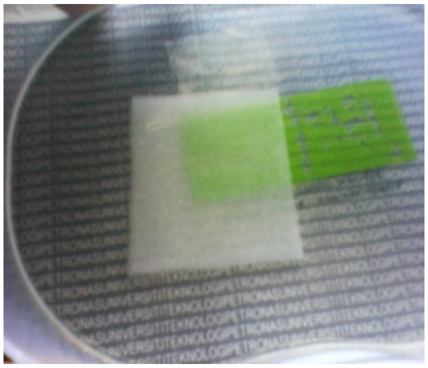

Figure 9: Sample film of 15% mcc

Figure 10: Sample film of 20% mcc

2) After 5 days

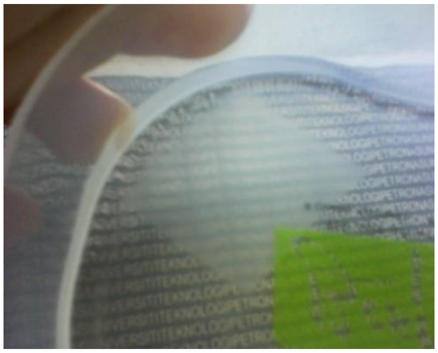

Figure 11: Sample condition after 5 days (0% mcc)

Figure 12: Sample condition after 5 days (5% mcc)

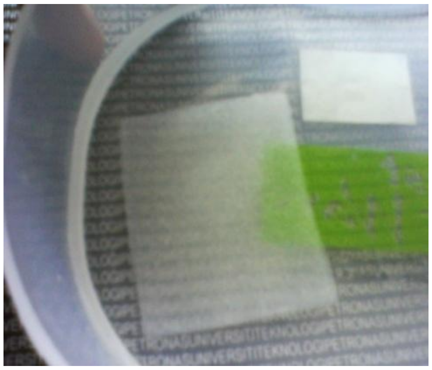

Figure 13: Sample condition after 5 days (10% mcc)

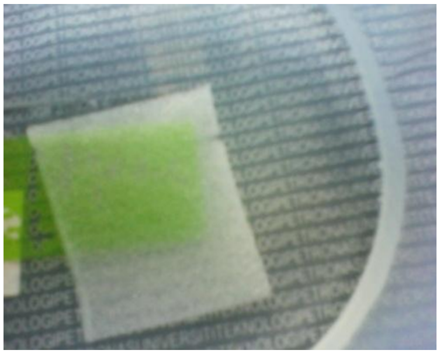

Figure 14: Sample condition after 5 days (15% mcc)

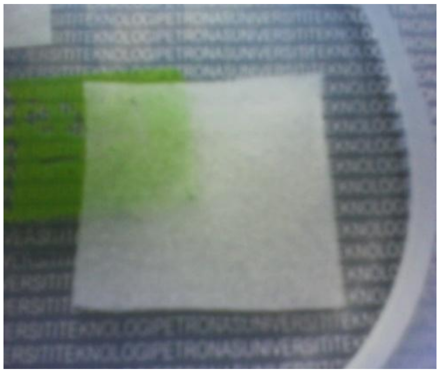

Figure 15: Sample condition after 5 days (20% mcc)

3) After 20 days

Figure 16: Sample condition after 20 days (0% mcc)

Figure 17: Sample condition after 20 days (5% mcc)

Figure 18: Sample condition after 20 days (10% mcc)

Figure 19: Sample condition after 20 days (15% mcc)

Figure 20: Sample condition after 20 days (20% mcc)

4.2.1 Discussion on Solubility Test result

Different samples with different micro crystalline cellulose (MCC) content are immersed in water to observe the solubility of the samples. Observation is conducted for 30 days and the condition of each film is recorded. As being observed, the films had gradually swollen and became greater in size as the films take in the water. As the time goes by, as shown on the fifth day, the size of the films starts to become constant. After 20 days, obvious changes can be seen on each film. The sample with 20% cellulose content maintain its shape after 20 days compared to the sample with 0% cellulose which is observed to be fully soluble in water. Some others for example, the sample with 10% cellulose broke into pieces. Therefore, it can be concluded that the film with higher MCC content exhibits lower solubility in water.

4.3 Result for Thermo Gravimetric Analysis (TGA)

1) 0% mcc

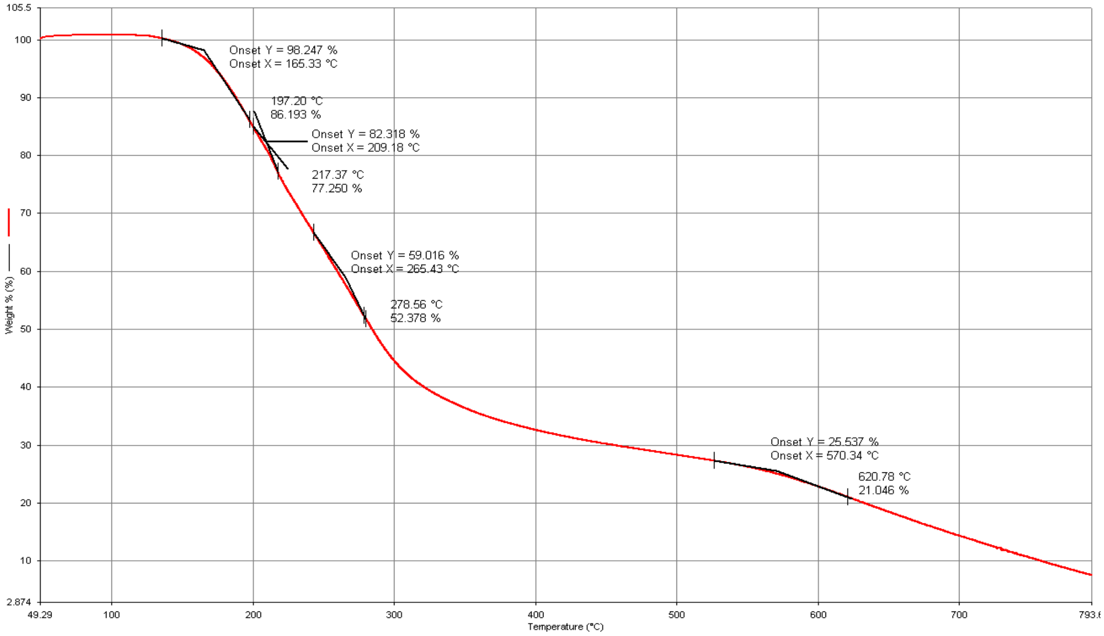

Figure 21: TGA curve for 0% mcc

2) 5% mcc

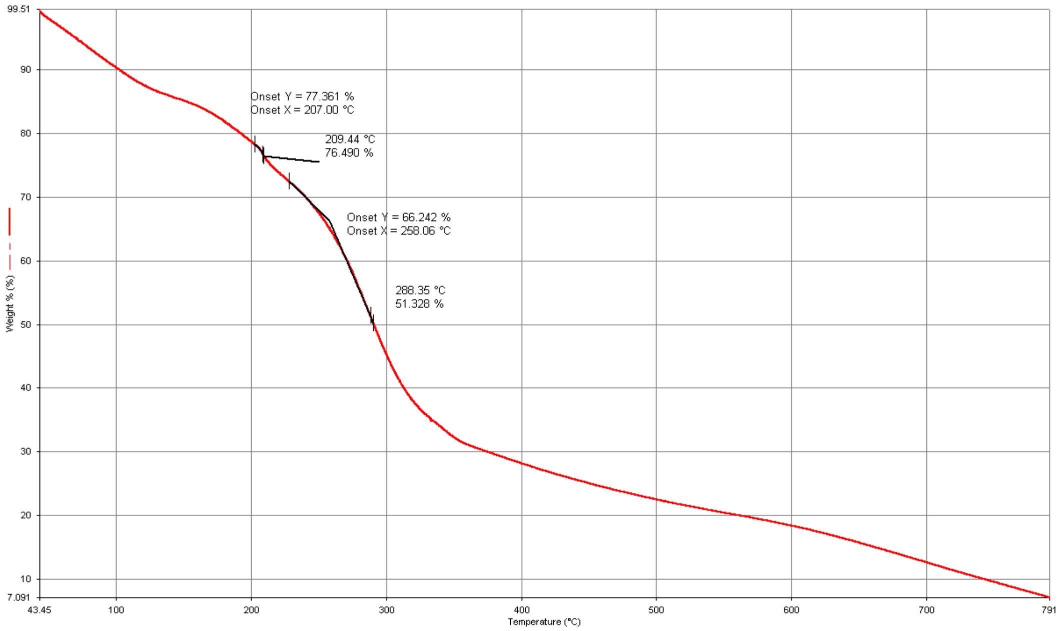

Figure 22: TGA curve for 5% mcc

3) 10% mcc

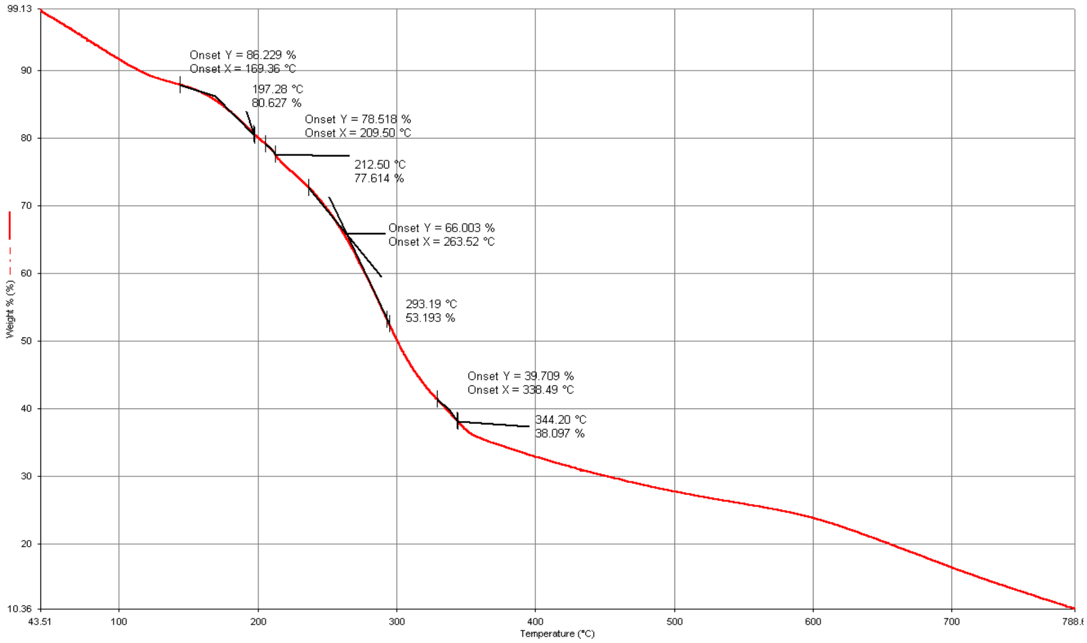

Figure 23: TGA curve for 10% mcc

4) 15% mcc

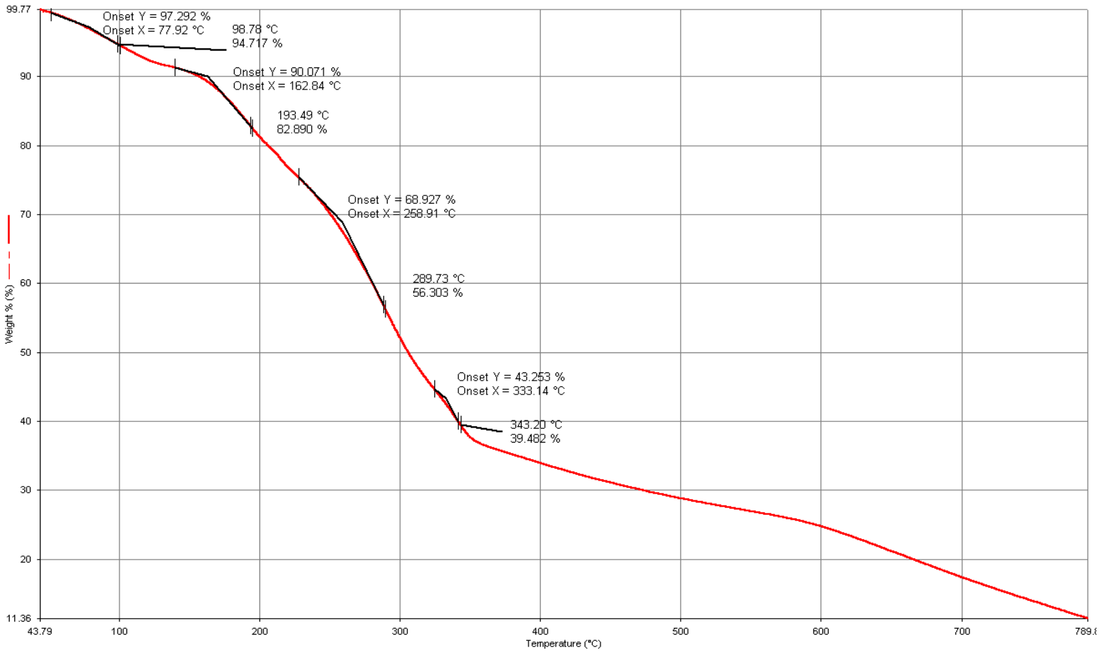

Figure 24: TGA curve for 15% mcc

5) 20% mcc

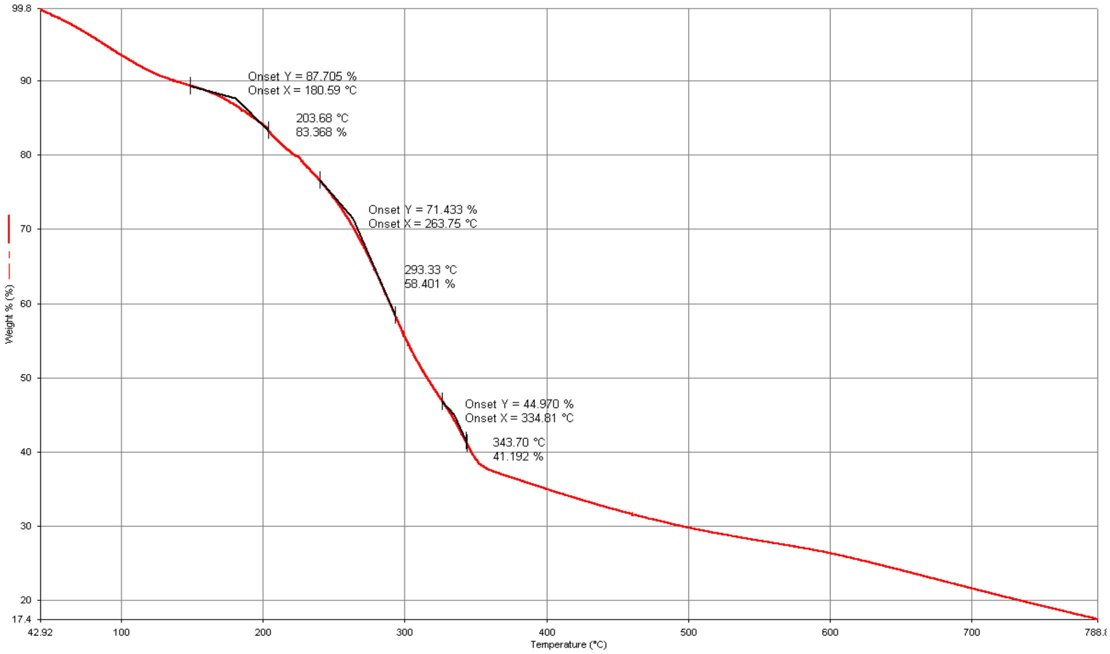

Figure 25: TGA curve for 20% mcc

4.3.1 Discussion for TGA result

Thermo gravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. TGA is conducted to determine the characteristic of materials or components. One of characteristic that can be determined by TGA is degradation or decomposition temperature of one component. Based on the result, as the percentage of cellulose is increased, the decomposition temperature of the film will also increase. For example, sample with 10% mcc has 66.003% left (not decompose) at 263.52 ^{o} C while the sample with 20% mcc has a slightly higher composition (71.433%) at about the same temperature (263.75 ^{o} C). This finding proves that the higher the percentage of cellulose in a sample, the higher the thermal stability it has. In application, when this property is used to develop a new modification to control release fertilizer, it will results in further resistance to the high temperature. In other words, the fertilizer will not easily decompose at high temperature.

4.4 Result of Fourier Transform Infra Red (FTIR) spectra

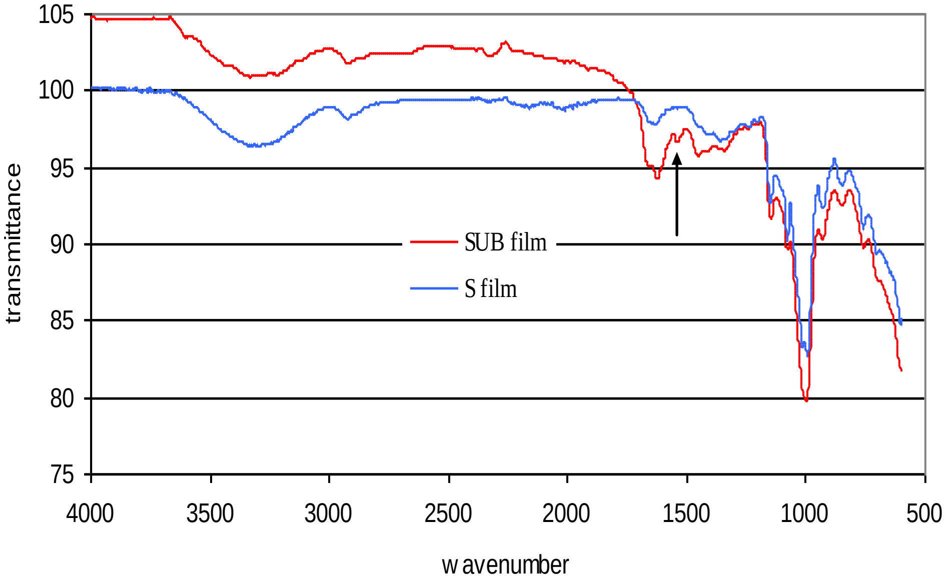

Figure 26: FTIR result

4.4.1 Discussion for FTIR result

After conducting FTIR analysis for starch sample and starch-urea-borate sample, it appears that both generate a quite similar curve but slightly different in terms of peak values in certain wavenumbers. The peaks for starch-urea-borate sample are shifted down from the original value where starch sample alone is tested. The weakness, disappearance and shift of the characteristic absorption bands may result from the interaction of different –OH groups in the starch and urea molecular chains. Secondary amide is formed. This proves that the cross linking mechanism occurs within the sample. So it may be deduced that from these results that the starch was linked with urea by chemical bonding introduced by sodium borate. This kind of linkage has great effect on the improvement of compatibility.

CHAPTER 5: CONCLUSION

A starch-cellulose blend film for coating the conventional urea fertilizer has been prepared. The water absorbency and water permeability of the starch-cellulose blend films cross linked by sodium borate (Borax) decreased with the existence of cross linking mechanism since it can lead the intermolecular and intramolecular linkage of –OH between starch and cellulose molecule and therefore the hydrophilic groups were reduced. Based on those criteria, starch-cellulose blend can potentially be developed since they are both are cheap, renewable, non- toxic and biodegradable. By increasing the content of the cellulose component, the rupture strength is increased, whereas the elongation at break will be decreased. These characteristics are highly favorable to develop the newly modified control release fertilizer in the future.

REFERENCES

1. O.A. Salman, Polythylene-coated urea. l. Improved storage and handling properties, Ind. Eng. Chem. Res., 28 (1989) 630-632.

2. O.A. Salman, J. Hovakeemian and N. Khraishi, Polyethylene-coated urea. 2. Urea release as affected by coating material, soil type and temperature. Ind. Eng. Chem. Res., 28 (1989) 633-638.

3. K. El-Refaie and Al.A. Sakran, Controlled release formulation of agrochemicals from calcium alginate, Ind. Eng. Chem. Res., 35 (1996) 3726-3729.

4. K. Byung-Su, C. Young-Sang and H. Hyun-Ku,Controlled release of urea from rosin-coated fertilizer particles, Ind. Eng. Chem. Res., 35 (1996) 250-257.

5. M. Tomaszewska, A. Jarosiewicz and K. Karakulski, Physical and chemical characteristic of polymer coatings in CRF formulation, Desalination, 146 (2002) 319323

6. Curtis J. Overdahl, George W. Rehm and Harvey L. Meredith, University of Minnesota, 1991.

7. Britannica Encyclopedia: Cellulose, 2008

8. Suvorova A. I., Tyukova I. S., Trufanova E. I.: Biodegradable starch-based polymeric materials. Russian Chemical Reviews, 69, 451–459 (2000)

9. Integrated Cassava Project, www.cassavabiz.org, 2005

10. Sunil K. Jain: Controlled Release Fertilizers: Trends and Technologies, 2007.

11. Pareta R., Edirisinghe M. J.: A novel method for the preparation of starch films and coatings. Carbohydrate Polymer, 63, 425–431 (2006).

12. Tomasik P., Schilling C. H.: Chemical modification of starch. Advances in Carbohydrate Chemistry and Biochemistry, **59**, 175–403 (2004).

13. Deguchi, Shigeru; Tsujii, Kaoru; Horikoshi, Koki (2006). "Cooking cellulose in hot and compressed water". *Chemical Communications*: 3293.

14. Charles A. Bishop, ed (2007), *Vacuum deposition onto webs, films, and foils, Volume 0, Issue 8155*. p. 165.

15. Klemm, Dieter; Brigitte Heublein, Hans-Peter Fink, Andreas Bohn (2005). "Cellulose: Fascinating Biopolymer and Sustainable Raw Material". *ChemInform* **36** (36).

16. Crawford, R. L. (1981). *Lignin biodegradation and transformation*. New York: John Wiley and Sons.

17. Updegraff DM (1969). "Semimicro determination of cellulose in biological materials". *Analytical Biochemistry* **32** (3): 420–424.

18. Dilara P. A., Briassoulis D.: Degradation and stabilization of low-density polyethylene films used as greenhouse covering materials. Journal of Agricultural Engineering Research, **76**, 309–321 (2000).

19. Bohlmann G., Toki G.: Chemical economics handbook. SRI International, Menlo Park (2004).

20. Guo M., Liu M., Zhan F., Wu L.: Preparation and properties of a slow-release membrane encapsulated urea fertilizer with superabsorbent and moisture preservation. Industrial and Engineering Chemistry Research, **44**, 4206–4211 (2005).

21. Chen L., Xie Z. G., Zhuang X. L., Chen X. S., Jing X. B.: Controlled release of urea encapsulated by starchg- poly(L-lactide). Carbohydrate Polymers, **72**, 342–348 (2008).

22. Malinconico M., Immirzi B., Massenti S., La Mantia F. P., Mormile P., Petti L.: Blends of polyvinylalcohol and functionalised polycaprolactone. A study on the melt extrusion and post-cure of films suitable for protected cultivation. Journal of Materials Science, **37**, 4973–4978 (2002).

23. "Molecules That Changed the World"; K.C. Nicolaou, Tamsyn Montagnon, 2008.

24. "Cellulose" at www.scienceclarified.com

25. "Cellulose coating extends shelf life of nutmeats at room temperature" at www.thefreelibrary.com

26. www.sciencedirect.com

27. www.icis.com