



Department of Chemical Engineering
King Mongkut's Institute of Technology
Ladkrabang



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The Thai Institute of Chemical Engineering
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(RSCE 2015)**

**“Embracing the Opening of AEC Incorporating with Education,
Research, and Industries in Chemical Engineering”**

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The Effect of Methods in Synthesizing a Controlled-Release Fertilizer based on the graft copolymer of *Canna edulis* Ker.

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Abstract — Nowadays the excessive use of fertilizer causes a serious problem to the environment. A system for controlled retaining and release of fertilizer components would be a great improvement. The goal of this research is to study the synthesis of controlled-release fertilizer (CRF) based on *Canna edulis* Ker. (ganyong) starch. This product is derived from the 3-D matrix copolymer of acrylic acid grafted onto starch backbone. The variables observed are the method used in synthesizing the CRF and the amount of crosslinker added to the copolymer (1.5% and 2.5% - wt. of monomer). The CRF is synthesized by two different methods, (1) soaking the prepared copolymer into the fertilizer solution and (2) addition of the fertilizer solution during the grafting reaction. The 2nd method produces a higher amount of fertilizer released (409.9 mg urea/g CRF) compared to the 1st method (\approx 300 mg urea/g CRF). On the other side, the highest % add-on (46%) is obtained from the 1st method with 1.5% crosslinker added. It was observed that in the 2nd method, a part of the urea is grafted onto starch during the grafting reaction.

Keywords: *Canna edulis* Ker. (ganyong) starch, controlled-release fertilizer (CRF), cross linker, grafting reaction, loading and release fertilizer.

I. INTRODUCTION

Fertilizers are important for crops since they provide additional nutrients like nitrogen, phosphorus, and potassium. In poor or depleted soils these are needed for crop growth and cultivation. The most used synthetic fertilizer in Indonesia is urea (its molecule structure can be seen in figure 1). In 2013 the demand has reached 13,659,930 tons and based on the report from the Indonesian Fertilizer Industry Association, the yearly increase in demand approaches 7% [1]. This is much larger than the increase of production land.

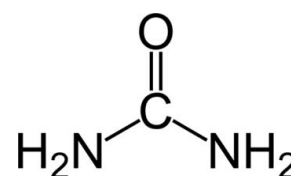


Figure 1. Urea molecular structure

A major part of these fertilizers is usually lost into the environment by denitrification, leaching, run-off, and evaporation. That's why the excessive use of fertilizer can cause problems, like soil dispersion, decrease of pH and making soil particles negatively charged. Such negatively charges cause soil particles to repel each other thereby hardening the structure and surface of soil. One of the methods to improve the efficiency of fertilizer use is by using fertilizer which can release the nutrients periodically to the environment (controlled-release fertilizer).

The definition of controlled-release fertilizer (CRF) based on the Association of American Plant Food Control Officials (AAPFCO) is "A fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference 'rapidly available nutrient fertilizer' such as ammonium nitrate or urea, ammonium phosphate or potassium chloride" [2]. Most of the CRF is developed by coating the fertilizer with polymeric material [3-9].

Liang et al. developed CRF based on superabsorbent composites made from wheat straw-g-poly (acrylic acid) [10]. The problem is wheat straw cannot be easily degraded by nature and also the release cannot be controlled. Whereas Liu et al. [11] developed CRF based-on the surface cross-linked superabsorbent material. They found that surface crosslinking could improve the slow release and water retention properties.

From our previous study [12-13] it was found that by developing a grafting reaction onto cassava starch, a three dimensional (3-D) matrix was obtained. This structure showed superabsorbent properties which can be utilized as

a template for fertilizer components. The addition of crosslinker in the synthesis of the matrix will improve the fertilizer loading capacity and the stability of CRF.

In this work instead of using cassava starch, the starch comes from *Canna edulis Ker.* (ganyong) rhizomes (figure 2). It can grow in diverse soil condition and temperature. In Java. Its productivity is 30 tons/ha, while its production can reach 44.5-49.40 tons/ha. This rhizomes has no economic value as a food.



Figure 2 *Canna edulis Ker.* (ganyong)

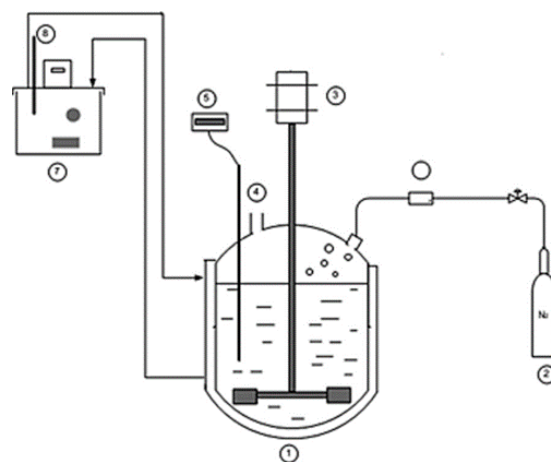
II. MATERIAL AND METHODS

1. Materials

The canna starch used in this experiment was produced by the community based organization “Mekar Sari”, Kulon Progo – Yogyakarta, Indonesia. Acrylic acid was kindly supplied by BASF PETRONAS Chemicals, Sdn. Bhd., Malaysia) and used without further purification. Ferrous ammonium sulfate (FAS), hydrogen peroxide (H₂O₂), sodium hydroxide (NaOH), N,N'-methylene- bisacrylamide (MBAM), hydroquinone (HQ), acetone, urea, Erlich reagent was reagent grade chemicals, purchased from Sigma Aldrich, Singapore and used as received. All solutions were prepared with distilled water.

2. Controlled-Release Fertilizer (CRF) Synthesis

The copolymer of canna starch-graft-(poly) acrylic acid was produced by a grafting reaction in a 1 L isothermal batch reactor. The set up of the equipment can be seen in figure 3 [9].



1. Stainless steel (jacketed) isothermal reactor with turbine blade stirrer
2. Nitrogen gas tank
3. Overhead stirrer
4. Gas outlet / reactant inlet
5. Thermocouple connected to the temperature control
6. Thermometer
7. Water heater with the temperature control

Figure 3 The set-up of grafting copolymerization equipment.

The detailed procedure can be found in our previous paper [9], but in general the procedure can be seen in the following diagram (figure 4).

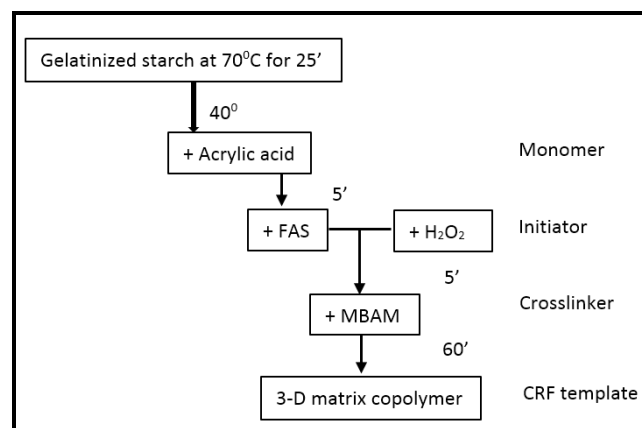


Figure 4 The scheme of grafting reaction

Then, the CRF template was synthesized with 2 different methods. The 1st method was done by soaking dry copolymer in various concentration of fertilizer solution (10,000; 15,000; 20,000; 25,000 and 30,000 ppm), while the 2nd method was done by adding 65 ml (0.25 v/v) of the fertilizer solution (the same concentration as 1st method) during the reaction. Then the side product (homopolymer) was separated using acetone.

3. Water Absorption Capacity (WAC)

Water absorption capacity was observed only on the

CRF template which does not contain fertilizer. The sample was soaked in distilled water at room temperature. Then the swollen sample was filtered and weighed every period of time until the weight was constant. The water absorption capacity was calculated using the following equation:

$$WAC \left(\frac{g}{g} \right) = \frac{m_1 - m_0}{m_0} \quad (1)$$

Where m_0 and m_1 are the weights of the dry copolymer sample and the swollen sample respectively. Water absorption capacity was calculated as grams of water per gram of dry sample [9].

4. Fertilizer loading capacity (FLC)

The measurement of the fertilizer loading capacity for the 1st method was done by soaking the dry copolymer in various concentrations of fertilizer solution for 24 hours. After that, the swollen sample was separated from the solution and dried in the oven at 40°C until it has a constant weight. Whereas the measurement for 2nd method should be done by NMR (still in progress). The fertilizer loading capacity for the 1st method was calculated using the following equation:

$$FLC \left(\frac{g}{g} \right) = \frac{m_3 - m_2}{m_2} \quad (2)$$

Where m_2 and m_3 are the weights of the unloaded and loaded dry copolymer sample respectively.

5. % add-on

The grafting add-on is a common parameter to measure the efficiency of the grafting reaction. It represents the amount of monomer that has actually been grafted onto starch, while the rest of the reacted monomer ends up as by-product homopolymer. The amount of acrylic acid grafted was measured using a carboxyl content analysis (titration method). 25 ml HCl (0.1N) was added into 1 g dry sample and stirred for 30 minutes. The sample was filtered and 30 ml distilled water was added and then it was heated to 85°C for 2 hours. The mixture was then titrated with NaOH (0.01N) with phenolphthalein indicator. The carboxyl content (COOH) was calculated using the following equation:

$$COOH (\%) = \frac{100 \times N \times V}{(1000 \times m_4) - 1} \quad (3)$$

Where N is NaOH normality, V is the titrated volume of NaOH, m_4 is the weight of sample.

While % add-on was calculated using the following equations:

$$m_5 = COOH (\%) \times m_4 \quad (4)$$

$$m_6 = \frac{m_5}{m_4} \times m_7 \quad (5)$$

$$\% \text{ add-on} = \frac{m_5}{m_5 + m_6} \times 100 \quad (6)$$

Where m_5 and m_6 are the total weight of grafted copolymer starch and weight of starch respectively.

6. Fertilizer release capacity (FRC)

The fertilizer release capacity was determined by soaking the copolymer that has contained urea in 1000 mL distilled water. Samples of 2,5 mL were taken from the solution periodically and Ehrlich reagent was added in order to get a yellow complex compound of urea. Then the concentration of urea can be determined using a spectrophotometer at 430 nm wave length.

III. RESULTS AND DISCUSSION

1. Water absorption capacity

The water absorption capacities of copolymer with 1.5% and 2.5%, crosslinker are 9.9 and 9.2 g H₂O/g dry copolymer, respectively (see figure 5). It can be seen that the capacity slightly decreases at higher crosslinker concentration. This condition is in parallel with our previous observation that the crosslinker helps in the formation of 3-D matrix but at a certain level it generates a stiff structure instead of flexible network [8]. Therefore, the available space within the superabsorbent is reduced and water absorption capacity decreases. This is confirmed also by Omidian et al. [14]. But to get a quantitative relation between the crosslinker concentration and the specific properties of the material needs further study.

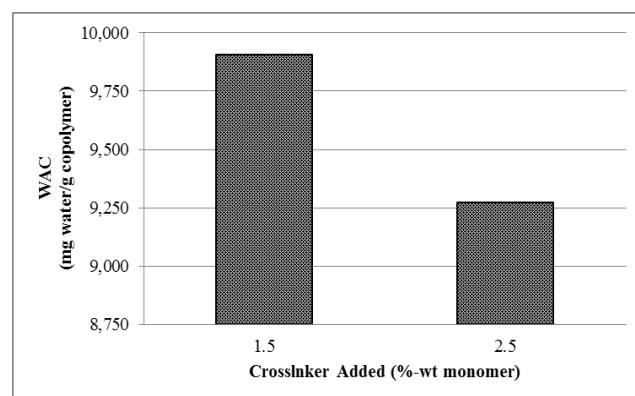


Figure 5 Water absorption capacity

Since urea is soluble in water, this copolymer property gives a benefit on the CRF, especially for loading fertilizer into the copolymer synthesized using 1st method. This properties has been utilized as well by Bortolin et al [15] in their CRF product based on hydrogel.

2. Fertilizer loading capacity

Fertilizer loading capacity at various crosslinker concentration for the 1st method copolymer can be seen in figure 6.

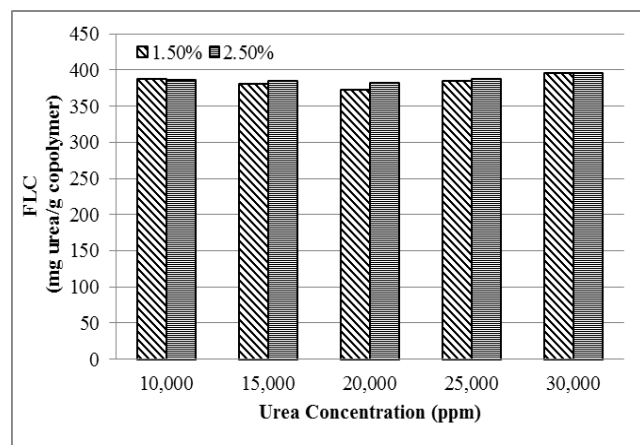


Figure 6 %-loading of fertilizer (1st method)

The fertilizer loading capacities with 1.5% crosslinker in 10,000; 15,000; 20,000; 25,000; and 30,000 ppm urea concentration are 387.8 mg; 380 mg; 372.8 mg; 384.5 mg and 394.9 mg urea/g copolymer, For the material with 2.5% crosslinker these amounts are 385.3 mg; 384.7 mg; 382.1 mg; 388 mg and 396.1 mg urea/g copolymer, respectively.

From this figure it can be observed that the amount of crosslinker added and fertilizer concentration do not have a significantly effect on the fertilizer loading capacity. But it cannot be concluded yet that there is no effect of these variables. Because from our previous study [16], there is a tendency of increase of the loading capacity with the increase of the fertilizer concentration (up to 2,000 ppm) and a decrease with the increase of the amount of crosslinker added. It seems that a semi-permeable membrane was formed on the surface of copolymer which affects the diffusion of fertilizer into the copolymer. In fact, loading capacities as found in the present study can be considered too low. In order to improve that we tested another method for loading fertilizer into the copolymer, where the loading of fertilizer is integrated with the grafting reaction This is further referred to as the 2nd method.

3. % add-on

Carboxyl content of copolymer at various crosslinker concentrations and various fertilizer concentrations is shown in figure 7. The % add-on values for the 1st copolymerization method (no fertilizer added during reaction) with 1.5% and 2.5%, crosslinker are 46.3% and 40.4%. For the 2nd method with 1.5% crosslinker with 10,000; 15,000; 20,000; 25,000; and 30,000 ppm urea concentration the respective values of the add-on are 26.9%; 26.3%; 23.3%; 20.3%; and 17.8%, At 2.5% crosslinker with the same urea concentration the add-

on values are 21.1%; 16.4%; 11.4%; 9.7%; and 8.8%.

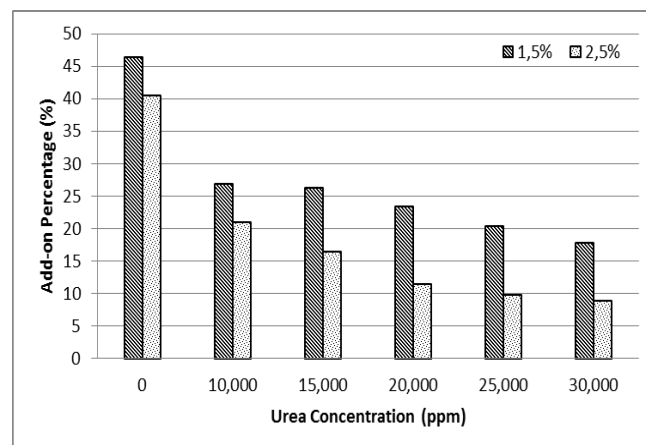


Figure 7 % add-on for 1st method (urea concentration 0 ppm and 2nd method (in various concentration of fertilizer added)

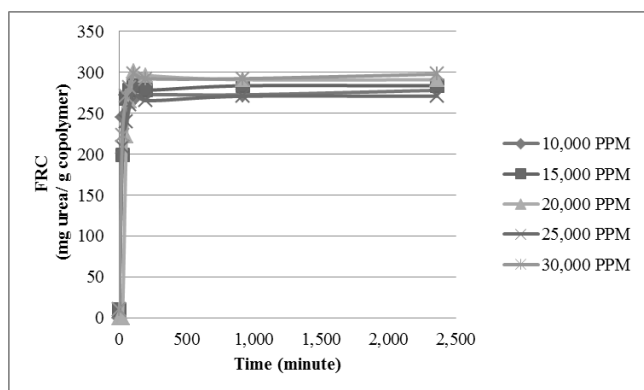
It can be observed that the copolymer without fertilizer added (1st method) has higher % add-on either with 1.5% or 2.5% crosslinker added than the copolymer with the addition of fertilizer during reaction (2nd method). There is a possibility that initiator reactions lead to the urea radical formation, since urea has double bond in its molecule structure which is easily attacked by radicals. It may explain why the higher urea concentration added during reaction gives the lower % add-on, as observed by the titration method. Since some of the urea molecules then also may get attached to the grafted product this can influence the measurement. So, perhaps it is better to regard the measured value as a pseudo-add on.

4. Fertilizer release capacity

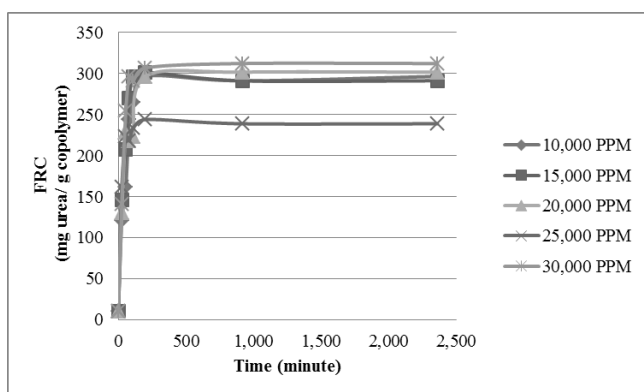
For a better accuracy of release observations, in this work we used water as a medium instead of soil. The validity of results we obtained has no doubt, since Adams, C. et al [17] have indicated in their study that there is no significant difference in nutrient-release rates in water and a moist solid substrate. This means that release rates determined in water can be used to model fertilizer release in moist soil or soilless media.

The amount of urea release vs. time for products made with the 1st method can be seen in figure 8. In equilibrium condition for 1st copolymer method with 1.5% crosslinker in 10,000; 15,000; 20,000; 25,000 and 30,000 ppm urea concentration are 262.2 mg; 273.6 mg; 291.7 mg; 266.2 mg and 287.6 mg urea/g copolymer. While for the CRF from the 1st method with 2.5% crosslinker 291.9 mg; 299.1 mg; 293.8 mg; 240.1 mg and 304.9 mg urea/g copolymer.

In general 75% of fertilizer loaded in CRF was released into aqueous medium. And the rest can be expected to release in the long term, when the material is biodegraded. In this part the amount of fertilizer release has been closed to our expectation.



(a)



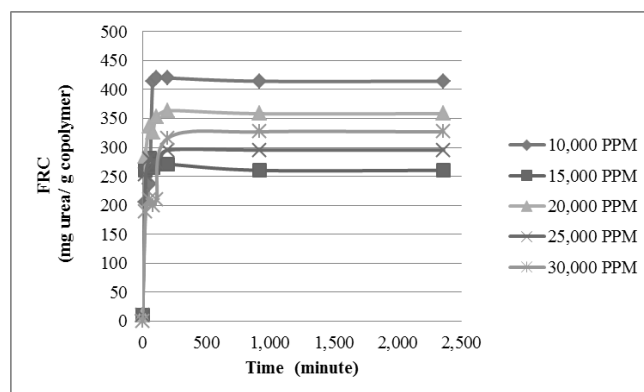
(b)

Figure 8 urea release as function of time, 1st method copolymer (a) 1.5% MBAM and (b) 2.5% MBAM

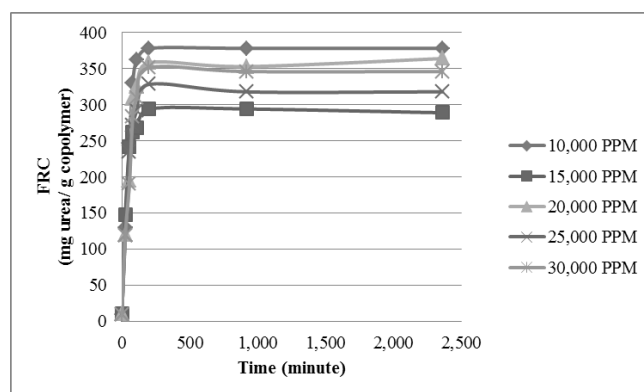
CRF derived from 2nd method (as it shown in figure 9) with 1.5% crosslinker in 10,000; 15,000; 20,000; 25,000 and 30,000 ppm urea concentration released 409.9 mg; 260.9 mg; 353.8 mg; 285.4 mg and 317.1 mg urea/ g copolymer while with 2.5% crosslinker are 368.4 mg; 284.3 mg; 348.2 mg; 318.7 mg and 341.7 mg urea/ g copolymer. The ratio of fertilizer release towards to amount loaded from the 2nd method is similar to value found for the 1st method \approx 75%. The absolute values of urea release from the 2nd method are higher compare to those obtained from the 1st method. This result confirms that in the 2nd method which fertilizer is added directly during grafting reaction, some of the fertilizer is also grafted onto starch beside it is entrapped. Therefore the total amount of fertilizer inside the matrix is higher.

For practical purposes, the time release is still too fast. CRF with 1.5 % crosslinker neither from the 1st method or 2nd method released urea rapidly until 80 minutes, then slow down up to reach the equilibrium in 110 minutes. Whereas CRF with 2,5% crosslinker released urea rapidly until 110 minutes, then urea release rate will decrease dan reach the equilibrium in 200 minutes. It means that CRF with 2,5% crosslinker already has the ability to prolonge urea release, compared to 1,5% crosslinker. The stiffer stucure obtained in this product caused more diffusion resistance. A low fertilizer release rate must be obtained for application in

agriculture in order to effectively prevent ‘fertilizer burn’ in plants and to decrease the amount of urea contaminant in the environment.



(a)



(b)

Figure 9 urea release as function of time, 2nd method copolymer (a) 1.5% MBAM and (b) 2.5% MBAM

IV. CONCLUSIONS

The graft copolymer based on *Canna edulis* Ker. starch has a potency to be controlled-release fertilizer (CRF). The use of different methods for the CRF as well as the amount of crosslinker used is factors that determine the product properties. These involve both the fertilizer loading capacity (FLC) and the fertilizer release capacity (FRC). The highest amount of fertilizer released (807.7 mg/g CRF) is obtained when the fertilizer was added during reaction. It is likely that part of fertilizer is then grafted as well, instead of just being physically entrapped.

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collection of the *Canna edulis* Ker. Rhizome, and BASF PETRONAS, Malaysia which supplies acrylic acid. We also like to thank Inge-Willem Noordergraaf from Groningen University for his valuable comments during the finalizing of the manuscript.

REFERENCES

- 1 A.P.P.I., the Statistic of Urea Fertilizer Consumption 2006-2015. Jakarta, Indonesian Fertilizer Producers Association, 2009.
- 2 Trenkel, M. E., Definitions of slow- and controlled-release fertilizers and nitrification and urea inhibitors Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrients Use Efficiency in Agriculture Paris, France. International Fertilizer Industry Association (IFA), 2010, p.14.
- 3 Han, X., Chena, S., Hub, X., Controlled-Release Fertilizer Encapsulated by Starch/Polyvinyl Alcohol Coating. *Desalination* 240, 2009, p.21-26.
- 4 Li, Q., Ma, Z., Yue, Q., Gao, B., Li, W., Xu, X., Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers. *Bioresources Technology* 118, 2012, p. 204-209.
- 5 Liang, R., Liu, M., Preparation and Properties of a Double-Coated Slow-Release and Water-Retention Urea Fertilizer. *Journal of Agricultural and Food Chemistry* 54, 2006, p. 1392-1398.
- 6 Noppakundilokrat, S., Pheatcharat, N., Kiatkamjornwong, S., Multilayer-coated NPK compound fertilizer hydrogel with controlled nutrient release and water absorbency. *Journal of Applied Polymer Science*, 132(2), 2015, p. n/a-n/a.
- 7 Tao, S., Liu, J., Jin, K., Qiu, X., Zhang, Y., Ren, X., Hu, S., Preparation and characterization of triple polymer-coated controlled-release urea with water-retention property and enhanced durability. *Journal of Applied Polymer Science*, 120(4), 2011, p. 2103-2111.
- 8 Wu, L., Liu, M., Liang, R., Zhan, F., Liu, Z., Niu, A., Preparation and characterization of cellulose acetate-coated compound fertilizer with controlled-release and water-retention. *Polymers for Advanced Technologies*, 19(7), 2008, p.785-792.
- 9 Yamada, D., Ebato, M., Shibuya, T., Fertilizer efficiency of two types of coated urea in a pasture. *Grassland Science*, 60(1), 2014, p. 36-44.
- 10 Liang, R., Yuan, H., Xi, G., Zhou, Q., Synthesis of Wheat Straw-g-poly(acrylic acid) Superabsorbent Composites and Release Urea from it. *Carbohydrate Polymers*, 77(2), 2009, p.181-187.
- 11 Liu, M., Liang, R., Zhan, F., Liu, Z., and Niu, Z., Synthesis of a Slow Release and Superabsorbent Nitrogen Fertilizer and its Properties. *Polymer for Advance Technologies*, 17, 2006, p.430-438.
- 12 Witono, J. R., Noordergraaf, I. W., Heeres H. J. and Janssen, L. P. B. M., Water Absorption, Retention and the Swelling Characteristics of Cassava Starch Grafted with Polyacrylic Acid. *Carbohydrate Polymers* 103, 2014, p.325-332.
- 13 Witono, J.R., Noordergraaf, I.W., Heeres, H.J. and Janssen, L.P.B.M., Graft Copolymerization of Acrylic Acid to Cassava Starch-Evaluation of The Influences of Process Parameters by An Experimental Design Method. *Carbohydrate Polymer*, 90, 2012, p.1522-1529.
- 14 Omidian, H., Hashemi, S.A., Sammes, P.G. and I.G., Meldrum, modified acrylic-based superabsorbent polymer. Effect of temperature and initiator concentration. *Polymer*, 39(15), 1998, p 3459-3466.
- 15 Bortolin, A., Aouada, F. A., de Moura, M. R., Ribeiro, C., Longo, E., Mattoso, L. H. C., Application of polysaccharide hydrogels in adsorption and controlled-extended release of fertilizers processes. *Journal of Applied Polymer Science*, 123(4), 2012, p. 2291-2298.
- 16 Witono, J.R., Wijaya, L., Tan, D., Miryanti, A., Santoso, H. The Controlled-release Fertilizer (Urea and Potassium Phosphate) Based on *Canna edulis* Ker. Starch Copolymer. in CHEMECA 2014. 2014. Perth, Australia.
- 17 Adams, C., J. Frantz, and B. Bugbee, Macro- and micronutrient-release characteristics of three polymer-coated fertilizers: Theory and measurements. *Journal of Plant Nutrition and Soil Science*, 176(1), 2013, p. 76-88.