

LAYERED AGGLOMERATION OF UREA GRANULES

by

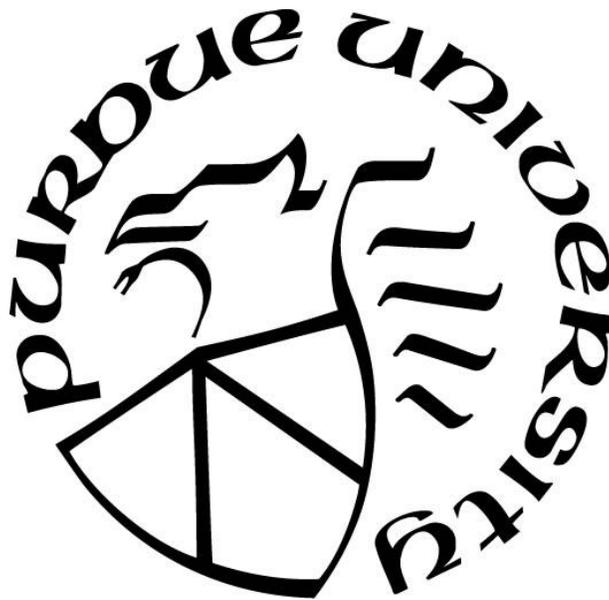
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LIST OF ABBREVIATIONS

ESN-Environmental Smart Nitrogen

Florikan- Florikan plus controlled release fertilizer (14-14-14)

Osmocote- Scotts Osmocote slow release fertilizer (14-14-14)

Everris- Osmocote Everris slow release fertilizer (17-3-6)

The Andersons A- The Andersons slow release fertilizer (12-6-6)

The Andersons B- The Anderson slow release fertilizer (18-6-12)

DL- Double Layer granules form drum granulation

DLControl- Double layer granules with no binder added in the second layer

DL PEG- Double layer granules with 5% PEG4000 added in the second layer

DL Hydrogel- Double layer granules with 5% corn starch added in the second layer

ABSTRACT

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Title: Physical & Chemical Properties of Granule Fertilizers and Layered Agglomeration of Urea Granules

Committee Chair: Bernard Engel

Urea has been widely used as a crop fertilizer to increase crop yield. The low nutrient use efficiency (NUE) of urea, however, is a challenge. Coated fertilizers are considered a solution not only for enhancing the NUE but also for alleviating soil and water pollution. In this paper, the physical properties of coated fertilizers were analyzed, including their particle size distribution, fracture force, thermal behavior, envelope density, and apparent density (regular fertilizer: pure urea and the Anderson 12-6-6; slow release fertilizer: Osmocote 14-14-14, the Anderson 18-6-12; controlled release fertilizer: Environmentally smart nitrogen (ESN), Florikan 14-14-14, Everris 17-3-6). The granules' closed and open pore number, pore volume, and total porosity were analyzed using X-ray micro-tomography (XRCT). The results demonstrated that pure urea and Florikan have a similar median particle size, around 4 mm, while ESN and Osmocote have a similar median particle size of around 3 mm. Finally, Everris, the Andersons 18-6-12, and the Andersons 12-6-6, have a similar median particle size of roughly 2.5 mm. The fracture pressure of ESN (4.58 ± 0.98 MPa) and the NPK combination fertilizers (Florikan: 9.40 ± 1.46 MPa and Osmocote: 8.94 ± 2.09 MPa) were higher than pure urea. The envelope and apparent density of pure urea (envelope: 1.22 ± 0.02 kg/m³ and apparent: 1.27 ± 0.01 kg/m³) and ESN (envelope: 1.26 ± 0.03 kg/m³ and apparent: 1.27 ± 0.00 kg/m³) are similar, while all NPK fertilizers have a significantly higher density (envelope: 1.68 – 1.87 kg/m³ and apparent: 1.83 – 2.09 kg/m³). ESN had higher internal pore space and a higher total pore volume than pure urea, while NPK combination fertilizer showed lesser pores and significantly smaller pore volumes. The physical properties were also significantly different when comparing urea and NPK compound fertilizers, mainly because of the differences in their nutrient coatings and manufacturing methods. The coating of the urea increases the granule strength but does not alter the thermal properties; however, the overall porosity of the granules is influenced by the coating. In this thesis core, different binders were used to alter the internal structure of the urea granule to control the dissolution behavior and to make it a slow-

release fertilizer. The layered agglomeration technique was used to manufacture the granules. The core of the granule was made by granulating technical urea powder in a drum granulator, with corn starch as the binder. A second layer of urea was added to the core by drum granulation in order to obtain a nutrient release pattern that matches with the crop demand. Corn starch, PEG 4000, and corn starch hydrogel were used as binders for the second layer. The density, thermal properties, strength, and internal porosity were measured to compare with market urea and coated slow-release fertilizer granules. All the dissolution rates of the double layer granules were slower than for market urea. Among these granule types, the dissolution rate curve of the granule with starch hydrogel in the second layer better matched the crop demand curve than those of the other two types of granules. Moreover, the strength of the double layer granules with hydrogel was the greatest of the three double layer granules. So, overall, the double layer granule manufactured with corn starch in the core and starch hydrogel in the second layer performed the best. Although the pattern of dissolution of the double layer granule was similar to the crop nitrate demand curve, a soil-based study is needed to verify the nitrate release characteristics.

CHAPTER 1. INTRODUCTION

The first part of this thesis presents a study on the physical and chemical characterization analysis of nitrogen (market urea granule and ESN) and NPK compound slow and control-release fertilizers (Osmocote, Florikan, Everris, the Andersons A and B). In the second part, a layered agglomeration of urea granules manufacturing is presented. Different binders (corn starch, corn starch hydrogel, PEG 4000) and granulation parameters (granulation rpm, granulation time and granule size) were tested and optimized. The overall goal of this thesis was to develop a double layer controlled-release urea granule.

This chapter provides a description of urea, slow-release urea and NPK compound slow-release fertilizers and outlines the objectives of this thesis.

1.1 Problem Statement

Fertilizers are widely used to release the nutrients necessary for plants to grow better (Tomaszewska & Jarosiewicz, 2002). Of all fertilizers, urea is the most widely used in the world, mainly because of its high nitrogen content (up to 46%) and low price (Ibrahim et al., 2014; Xiao et al., 2017). However, around 70% of applied urea is reported to be lost in regions with high, intermittent precipitation (Allison, 1955; Lundt, 1971). The loss of urea to leaching leads not only to major economic loss, but also to severe environmental pollution (Diez et al., 1994; Li & Yang, 2004). To mitigate this problem, an effective solution is to develop slow-release urea fertilizers (Ni et al., 2013). Adding coating material to fertilizer granules is one useful way of achieving this. There are many different materials available that can be used for coating, such as sulfur, and various types of polymers, including, but not limited to; low density polyethylene (LDPE) (Salman, 1998), ethyleneacrylic acid copolymers (Goertz, Timmons, & Mcvey, 1993), and polyurethane (Du, Zhou, & Shaivi, 2006). Meanwhile, this coating method is used not only for urea fertilizer, but it is also widely used to enhance the performance of NPK compound fertilizers. Some studies have focused on the dissolution behavior of fertilizer samples and the properties of coating films (Wei et al., 2017; Zhang et al., 1994). Hofstee & Huisman (1990) reviewed some of the physical properties of fertilizer, including particle size and particle size distribution, coefficient of friction, coefficient of restitution, aerodynamic resistance and particle strength, along with their

relationship to particle motion. The physical properties of fertilizer granules, such as crush strength, can be affected by the process parameters and are optimized by changing process variables (Walker et al., 2003; Rodrigues et al., 2017). However, there is no published study on the physical and mechanical properties of commercially available urea granules, coated urea granules and coated compound NPK fertilizers.

Coated urea does extend the release time and increase the efficiency of nutrient use; however, coated urea use is limited to developed countries because of its high price (Ni et al., 2013). In order to create a cheaper slow-release urea fertilizer, many different biodegradable materials, such as starch (Ni et al., 2013) and hydrogel (Ni et al., 2011), have been added to urea granules to extend the release time. However, so far, there is no layered granule, made by the drum granulation technique, available. Thus, the overall goal of this thesis is to develop a two-layer urea granule with a slower dissolution rate. The objectives of this thesis are listed below:

1.2 Objectives

The objectives of this study are:

- To characterize the physical and chemical properties of market urea, ESN, Osmocote, Florikan, Everris, and the Andersons A and B fertilizers.
- To design a two-layer slow-release urea granule and to characterize its physical and mechanical properties and its dissolution behavior.

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CHAPTER 2. REVIEW OF LITERATURE

2.1 Fertilizer Demand

An adequate supply of food is the most important factor for human health and wellbeing; however, over the last 50 years, a significant proportion of the global population has suffered from malnutrition (Long et al, 2015). Global food demand is increasing rapidly. For instance, when measured by the content of all crops' caloric value or protein content, the global crop demand for the period 2005 – 2050 is forecasted to increase by 100 – 110% (Tilman et al., 2011). When measured according to the number of people, the global population is expected to increase by 35%, from 7 billion today to 9.5 billion by 2050 (USCB, 2015). Thus, the rates of increase in global food demand differ according to whether that demand is measured by crop yield or global population; one reason for this is the demand for high quality animal products from a global population that is increasingly urban (Ray et al., 2013). Meanwhile, the yield rates of wheat, rice and cassava (the three main food crops in the world) will not be able to meet the demand if the crop yield improvement per hectare remains constant (Figure 2.1; Ray et al., 2013). In order to increase the crop yield, agricultural fertilizers are widely used and usually over-applied because fertilizer is a leading source of crop nutrients (Sheriff, 2005). Thus, the application of fertilizer is one of the indispensable approaches to increasing crop yield (Cakmak, 2002).

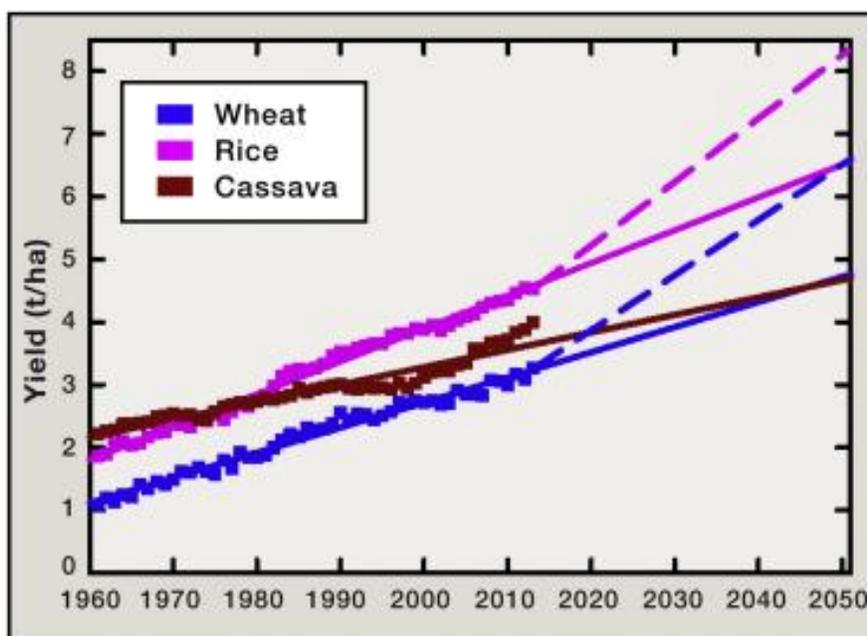


Figure 2.1 Annual average global yields of cassava, rice and wheat from 1961 to 2013. The bold solid lines are the actual production, the solid lines are the expected yield based on the current yield increase rate and the dashed lines are the required yield based on the global population (Ray et al., 2013).

2.2 Urea Production and Use

Urea ($\text{CO}(\text{NH}_2)_2$) is a white, crystalline, water-soluble solid with a molecular mass of 60.07 g/mol. For mammals and other ureotelic animals, urea is the major end product of nitrogen extraction in the urea cycle (Hine & Martin, 2015). In addition to its use as a fertilizer in agriculture, urea has many other applications, including; as a stabilizer in nitrocellulose explosives, as animal feed, as a raw material for manufacturing of plastics, as an ingredient in cigarettes and dish soap, as a flame-proofing agent, and as a cream to soften skin (Chauhan, 2011).

Eighty to 85 percent of global urea production is allocated for use as fertilizer, making urea the most popular solid nitrogen fertilizer in the world, and especially in developing regions. Over 40% of all food grown globally is fertilized by urea (HIS Markit, 2016). The main advantages of using urea as a nitrogen source are that it has a lower risk of explosion, a high nitrogen content (46%), its manufacture releases fewer pollutants into the environment, it has greater crop yield increases and it can be used in multiple ways (solid or solution) (Chauhan, 2011).

Ammonia and carbon dioxide are required to produce urea (Eq. 2.1) (EFMA, 2000).



where the first part of the reaction is fast and exothermic, while the second part of the reaction is slower and endothermic and does not reach the ending point. In the second part, the conversion rate (on a CO₂ basis) can be increased with a higher temperature and a higher NH₃/CO₂ ratio, and can be decreased by increasing the H₂O/CO₂ ratio (EFMA, 2000).

The price of urea increased from \$64.63 per metric ton in 1999 to \$770 per metric ton in 2008. Then, because of the global financial crisis, the price of urea began to decrease. By May 2018, the price was \$217.7 per metric ton (index mundi, 2018).

2.3 Urea prilling process

Significant attention has been paid to the urea prilling process, mainly because this is the method by which most urea is produced and because the final urea prills are of relatively good quality, being almost spherical, relatively hard, and nonporous with no fragmented shells (Rahmanian et al., 2013). As shown in **Figure 2.2**, the two main steps in the prilling process are: a. a liquid spray is applied to produce drops of molten urea; b. with the influence of surface tension, drops are turned into crystallized, spherical particles (by falling through the cooling medium where the temperature is below urea's solidification temperature) (Rahmanian et al., 2013). Depending on the heat transfer mechanisms, the prilling towers can be classified into two types: forced and natural convection heat transfer. The dimensions of the prilling tower can directly affect the urea plant's capacity. For instance, a 500, 000 tons/year urea capacity needs a prilling tower with a diameter of 17 m, a fall height of 60 m, and a total height of 77 m (Hashemi & Nourai, 2006).

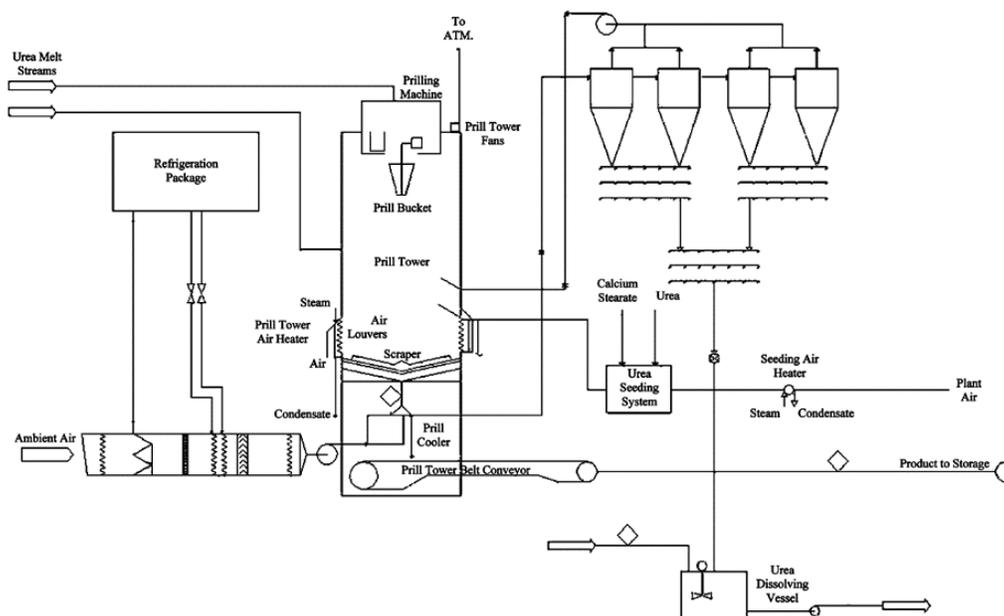


Figure 2.2 Urea prilling process flow diagram. (Hashemi & Nourai, 2006).

Ruskan (1976) detailed some characteristics of prilling towers, including large air flow, requirement height (45–60 m), accompanied dust-recovery problem with high capacity (more than 800 metric tons per day) and high fixed costs. The prilled urea particle size distribution is shown in **Figure 2.3**. The particle size range is 0.5–2mm (Salman, 1988) and a detailed urea processing model was studied by Hashemi & Nourai (2006). The larger sized prills were formed mainly because of the formation of a quiescent zone, which results in a lower air velocity (Saleh et al., 2015). In order to get a narrow prill particle size distribution and to obtain relatively mono-dispersed droplets, a spray-type showerhead was recommended by Saleh (2015).

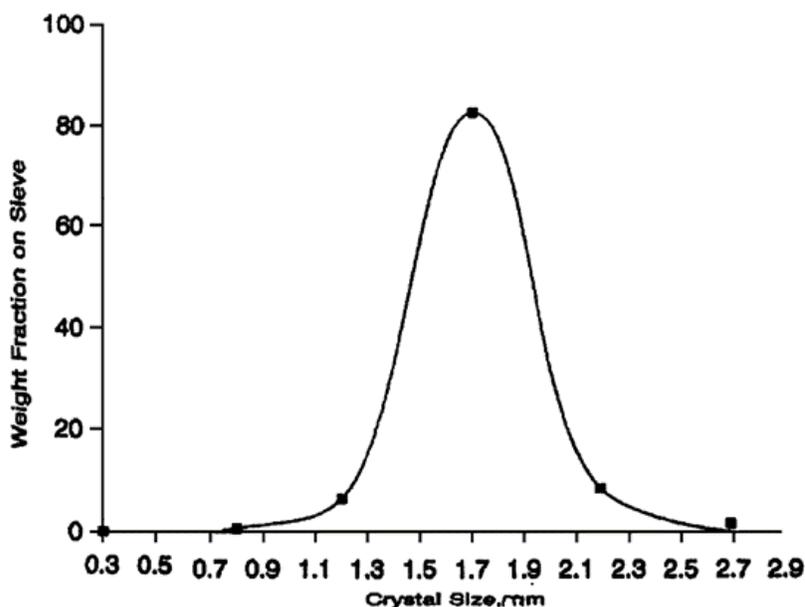


Figure 2.3 Particle size distribution of prilled urea granules. (Hashemi & Nourai, 2006).

The moisture content of urea obtained by prilling was 0.29% and the fracture pressure is 29 Kg/cm^3 , 27 Kg/cm^3 and 32 Kg/cm^3 for urea prills with a diameter of 1.4 mm, 1.7 mm and 2 mm, respectively (Salman, 1988).

2.4 Urea granulation

The granulation process is used to increase the physical properties of urea granule, such as flow property, strength, rate of dissolution, resistance to segregation, in order to get a better handling performance (Cape, 1980; Pietsch, 1991; Ennis & Lister, 1997; Lister & Ennis, 2004; Rahmanian et al., 2011). The common granulation technique used by the urea industry are pan granulation, drum granulation, spheroidizer granulation, spouted-bed granulation, and fluidized-bed granulation (Young & Mccamy, 1967; Bertin et al., 2007; Bertin et al., 2011; Rahmanian et al., 2013; Bertin et al., 2013). Meanwhile, these granulation-techniques are also commonly used for NPK fertilizer, coating of urea and slow-release fertilizer processing (Weiss & Meisen, 1983; Ramachandran et al., 2008; Villa et al., 2016). The urea granulation technology patent is considered to be high (Chauhan, 2011), and thus a few, large Japanese, North European and U.S. companies (including Netherland NSN, Japanese MTC-TEC, U.S. TVA) are the leaders of this technology.

Figure 2.4 shows a spout fluid bed granulator used for large urea granule production (Bertin et al., 2013). In this process, highly concentrated urea solution (about 96%) and the small urea seed particles are fed into the granulator where the granules are dried and cooled simultaneously (Niks et al., 1980; Chauhan, 2011). The purpose of this unit is to let small urea granules grow in a coating process, which consists of urea liquid droplets being deposited onto seeds, water evaporation, and the solidification of the sprayed urea (Bertin et al.; 2013). The fluidized bed unit is the most important part of the urea granulation circuit (Knight, 2004; Wang et al., 2007). Normally, there are several growth chambers in the fluidized bed unit and the small urea particles (seeds) are fed into one solid chamber of air. Meanwhile, the concentrated urea solution is sprayed from the bottom (Bertin et al., 2011). While in the cooling chamber, in order to meet specific granule requirements, no urea solution is added and the streams are often placed down-stream of the growth beds (Kayaert et al., 1997). Even though urea granules from the fluidized bed are larger and stronger than those from the prill tower, currently, industrial urea fluidized bed granulators are usually operated by trial and error (Litster & Liu, 2004; Cameron et al., 2005; Fung et al., 2006).

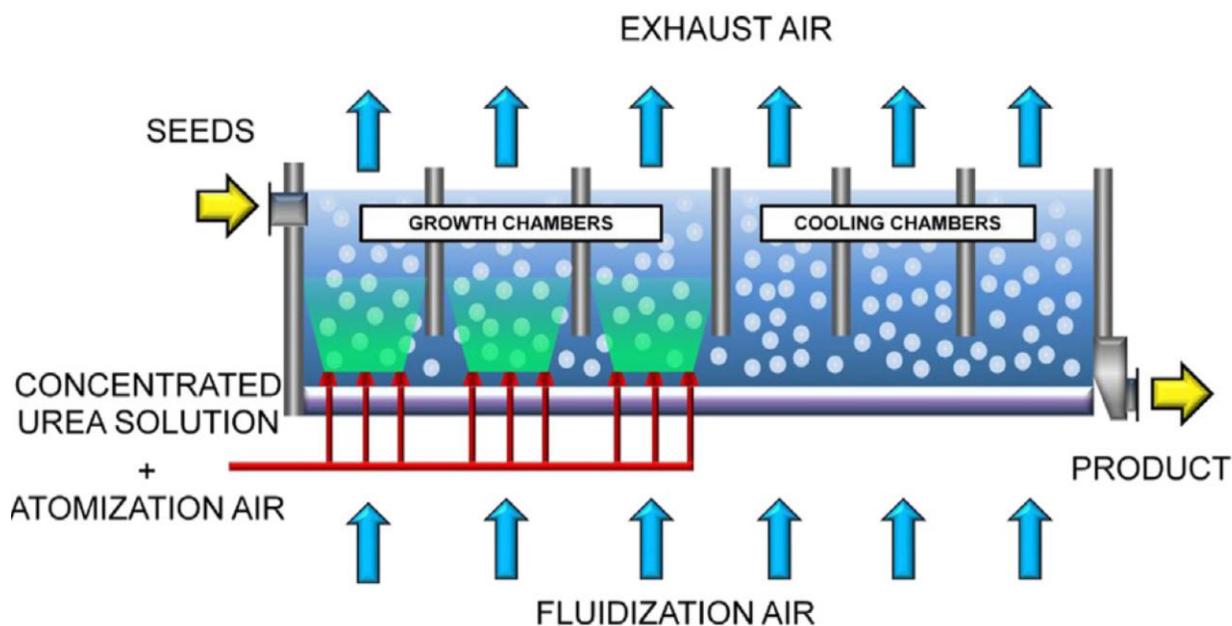


Figure 2.4 Schematic representation of a multi-chamber fluidized-bed granulator for urea production.

2.5 Slow release and controlled release fertilizers

Fertilizer can help to increase crop yields but some environmental hazards are caused by the use of large amounts of fertilizer. There are several ways to increase the nutrients, and especially the efficient use of nitrogen, including: a) by using controlled-release fertilizers (CRFs) or slow-release fertilizers (SRFs); b) by placing urea granules deeper in the ground; c) by using inhibitors to reduce nitrate leaching, denitrification and ammonia volatilization in urea (Chien et al., 2009).

Using CRF or SRF is the better way to improve nutrient use efficiency while reducing environmental hazards (Hauck, 1985; Shaviv, 2001). As shown in **Figure 2.5** (Ebelhar, University of Illinois, DATE?), the nitrogen needed during wheat growth is not constant, so nutrient use efficiency can be increased by extending the nutrient release time. The use of SRF/CRF is only about 0.15% of the total use of fertilizers and they are mainly used in developed countries, such as United States, Canada, Japan, and European countries (Trenkel, 1997).

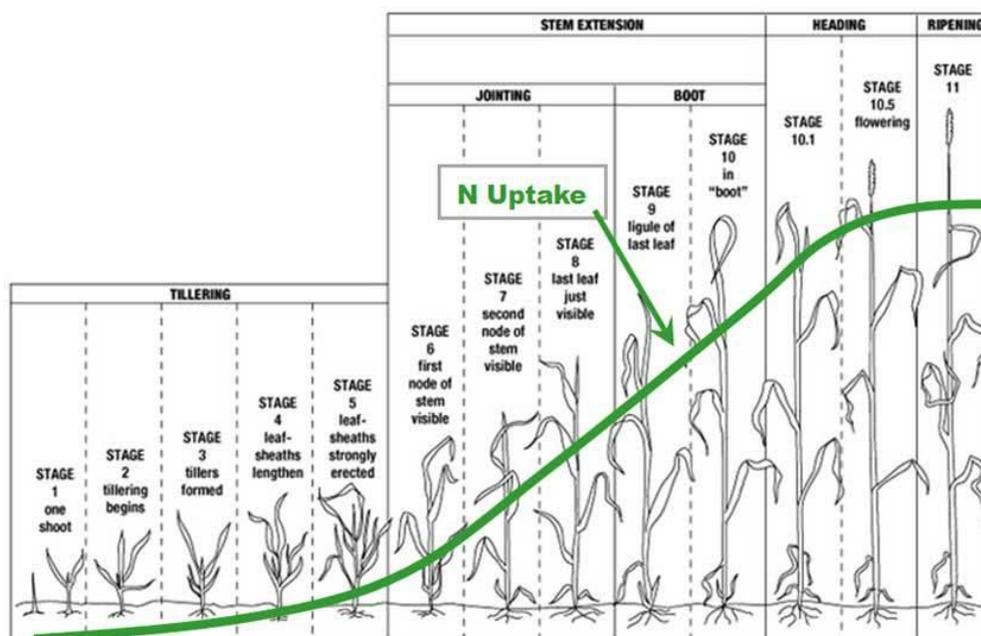


Figure 2.5 Wheat growth staging and nitrogen use. Source: S.A. Ebelhar, University of Illinois.

According to the Association of American Plants Food Control Officials (AAPFCO) (1995), SRF/CRFs are fertilizers that can either delay nutrient availability for plant uptake or prolong it for a significantly longer period than the “rapidly available nutrient fertilizers, such as

ammonium nitrate or urea, ammonium phosphate or potassium. There is no official differentiation between slow and controlled release fertilizer and AAPFCO uses both in its Terms and Definitions (AAPFCO, 1997). In order to quantify the slow release fertilizer, a standard is provided by the European Standardization Committee (CEN):

A fertilizer can be named as a slow release fertilizer if it releases the nutrients into the soil under the following criteria: no more than 15% release of the nutrients (available in plant useable form) from the fertilizer in 24 h, no more than 75% release in 28 days, and at least about 75% release of the available nutrients during the stated release time (Naz & Sulaiman, 2016).

There are many methods being used to manufacture SRF/CRFs, including: a) slow-releasing organic-N compounds; b) coated fertilizers; c) matrix-based slow-release fertilizers; and d) low-solubility inorganic fertilizers (Shavis, 2000). Slow-releasing organic-N compounds include urea-formaldehyde condensation products (Trenkel, 1997; Shaviv, 1999) and other urea-aldehyde and synthetic nitrogen compounds (Goertz, 1991; Landels, 1994; Trenkel, 1997). Coated fertilizers include fertilizers coated with nonorganic coatings (Weiss & Meisen, 1983; Landels, 1994), polymer coating of sulfur-coated fertilizers (Blouin et al., 1971; Goertz, 1995) and fertilizer coated with organic polymers such as resin coated and thermoplastic polymer coated, which have not been widely studied until now (Suri, 2000; Saleh & Hemati, 2003; Donida & Rocha, 2007; Kantheti et al., 2013). Matrix-based slow-release fertilizer is made of a mixture of different materials that can reduce the dissolution rate of nutrients. For example, Hepburn and Arizal (1989) used rubber, Mikkelsen (1994) used gel-based materials, Zhou et al. (2013) and Qiao et al. (2016) used starch based superabsorbent polymers. Finally, low-solubility inorganic fertilizers have a limited use because of low N content and poor release control (Shaviv, 2001).

2.6 Conclusion

Fertilizer is widely used globally to increase crop yields. Of all fertilizers, urea is the most important nitrogen source. In order to extend the dissolution time and maintain the physical properties of urea, different methods have been applied. Slow or controlled-release fertilizer has been studied since the 1970s. Recently, a variety of different materials and processing methods

are being used in the production of SRF/CRF, with the aim of making them more environmentally friendly, with longer dissolution times and better handling properties. The aim of this section has been to review the characteristics of both common urea and SRF/CRFs. The next section presents my effort to make a double layer slow-release urea granule using drum granulation.

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CHAPTER 3. PHYSICAL AND MECHANICAL PROPERTIES OF GRANULAR FERTILIZERS

ABSTRACT: The low nutrient use efficiency (NUE) of urea is a challenge. Coated fertilizers are considered a solution to not only enhance the NUE but also alleviate the soil and water pollution. In this Chapter, the physical properties including particle size distribution, fracture force, thermal behavior, envelope density, and apparent density of fertilizers (regular fertilizer: pure urea and the Anderson 12-6-6; slow release fertilizer: Osmocote 14-14-14, the Anderson 18-6-12; controlled release fertilizer: Environmentally smart nitrogen (ESN), Florikan 14-14-14, Everris 17-3-6) were analyzed. The granules' closed and open pore number, pore volume, and total porosity were analyzed using X-ray micro-tomography (XRCT). The results demonstrated that pure urea and Florikan have a similar median particle size, around 4 mm, while ESN and Osmocote have a similar median particle size of around 3 mm. Everris, the Andersons 18-6-12, and the Andersons 12-6-6, have a similar median particle size of approximately 2.5mm. The fracture pressure of ESN (4.58 ± 0.98 MPa) and the NPK combination fertilizers (Florikan: 9.40 ± 1.46 MPa and Osmocote: 8.94 ± 2.09 MPa) was higher than pure urea. The envelope and apparent density of pure urea (envelope: 1.22 ± 0.02 kg/m³ and apparent: 1.27 ± 0.01 kg/m³) and ESN (envelope: 1.26 ± 0.03 kg/m³ and apparent: 1.27 ± 0.00 kg/m³) were similar while all the NPK fertilizers had a significantly higher density (envelope: 1.68-1.87 kg/m³ and apparent: 1.83-2.09 kg/m³). ESN had higher internal pore space and a higher total pore volume than pure urea, while NPK combination fertilizer showed lesser pores and significantly smaller pore volumes. Chemical coating of urea increased the granule fracture pressure but didn't not alter the thermal properties. The physical properties were significantly different when compared with urea and NPK compound fertilizers, mainly because of the differences in nutrient content.

Keywords: *Granular fertilizers, fracture pressure, particle density, X-ray micro-tomography.*

3.1 Introduction

In order to feed 6 billion people in the world, the global cereal production has doubled with the help of agricultural fertilizers (Ni et al., 2011). Among the fertilizers, nitrogen is the most important nutrient that limits the crop yields (Ni et al., 2013). Urea is widely used all over the world as a source of nitrogen mainly because of its high nitrogen content (up to 46%) (Xiao et al., 2017). However, due to urea's high water-solubility property, it dissolves quickly once it contacts water, which results in a large amount of urea as waste. In order to make the urea granule release rate slow, an outside coating was added to inhibit the dissolution. Alternatively, binders may also be added to the inside of the urea granule to change the internal structure in order to slow the release. Obtaining slow release fertilizers requires the use of drum granulation, which is commonly used to add coating materials outside of the granule (Ibrahim et al., 2014). There are many different types of slow release fertilizers available in the market. One example includes the Environmental Smart Nitrogen (ESN), a slow release fertilizer with an external polymer coating. The polymer membrane of ESN allows water to enter through the surface and form the urea solution, and then the urea solution diffuses out through the small pores on the polymer membrane. The performance of ESN is influenced by the soil temperature and meanwhile, matches the crop's demanding curve (Nutrien, 2018). Elemental sulfur, polysulfone, and gypsum are also used and analyzed by many researchers as a granular fertilizer coating material (Yasmin et al., 2007; Tomaszewska and Jarosiewicz, 2002). As phosphorous and potassium are also important to crop growth, there are many different NPK combination slow release fertilizers available in the market, such as the Andersons 12-6-6 and Osmocote 14-14-14. For some NPK combination fertilizers, such as the Anderson 12-6-6, each nutrient is granulated separately and then the granules mixed to form the combination fertilizer. While for some NPK fertilizers, such as Osmocote 14-14-14, all nutrients are added in the same granule instead of using multiple granules.

The physical and mechanical properties of these coated urea granules and the NPK combination fertilizers do not appear to be similar due to their difference in structural makeup and the components. Some studies focused on the dissolution behavior of fertilizer samples and the properties of coating films (Wei et al., 2017; Zhang et al., 1994). A review paper by Hofstee & Huisman (1990) discussed and summarized some fertilizer physical properties, including particle size and particle size distribution, coefficient of friction, coefficient of restitution,

aerodynamic resistance, and particle fracture pressure, along with their relationship to particle motion. However; no paper has analyzed the physical properties of the environmental smart nitrogen, which is a widely used commercially available controlled release fertilizer, and other widely used slow release fertilizers such as Osmocote and Florikan. Every fertilizer granule should have a breaking force of at least 15 N and not every fertilizer granule meets this standard (Hofstee & Huisman, 1990). The physical and mechanical properties can be correlated by analyzing the internal porosity and dissolution rate. There is no published study focusing on the internal porosity of fertilizer granules and the relationship between internal porosity and other physical properties. So, the objective of this chapter is to measure and analyze the particle size, density, mechanical fracture pressure, thermal property, internal structure, and porosity of urea and commonly available slow release granular fertilizer samples.

3.2 Materials and methods

3.2.1 Materials

A range of regular, slow release, and controlled release fertilizers were characterized in this study. These include the following: pure urea, Environmentally smart nitrogen (ESN), Florikan 14-14-14, Osmocote 14-14-14, Everris 17-3-6, Andersons 12-6-6 (The Andersons A), and the Andersons 18-6-12 (The Andersons B). The three numbers refers to the percentage of Nitrogen, Phosphorus, and Potassium in the fertilizer. ESN is a coated controlled release fertilizer while the rest are coated NPK combination fertilizer. Pure urea and ESN samples were obtained from the Crop Production Services (Delphi, IN) while all other samples were purchased from the A. M. Leonard Vendor (Piqua, OH.).

As shown in Table. 3.1, there are many different colored granules with different nutrients in Everris and the two types of Andersons fertilizer. For some similar colored granules, it is difficult to differentiate based on color, such as dark brown and black in the Andersons B. And, there are some granules with the same color but different nutrients, such as two dark brown colored granules in the Andersons A fertilizer.

Table 3.1 Fertilizer samples, their color and the respective nutrient content

Fertilizer sample	Granule color	Nutrient
Everris 17-3-6	Orange	Polymer sulfur coated urea
	Black	Ammonium phosphate
	Grey	Minor elements (Mg, S, Fe, Mn Zn, Cu)
The Andersons 18-6-12	Dark brown*	Triple super phosphate/Potassium sulfate
	Shade of blue or light blue*	Urea form
	Light tan or white	Magnesium ammonium phosphate hexahydrate
	Light blue*	Polymer coated sulfur coated urea (XCU)
	Orange or brown	Polymer coated sulfate of potash
	Black	Micro nutrient: Copper, iron, manganese and zinc
	White*	Magnesium
The Andersons 12-6-6	Dark brown*	Triple super phosphate
	Light blue	Methylene urease
	Dark brown*	Potassium sulfate
	Light gray	Limestone

3.2.2 Particle size analysis

The particle size analysis was conducted based on the IFDC S-107 method (Rutland, 1986). A sub-sample of 350 g was obtained using the spin riffler (Retsch, Haan, Germany). The samples were then loaded in a ro-tap model E test sieve shaker (W.S. Tyler, Mentor). Following the IFDC method, a series of US standard sieve: no. 4 (4750 μm), no. 6 (3350 μm), no. 7 (2800 μm), no. 8 (2360 μm), no. 10 (2000 μm), no.12 (1700 μm), no. 14 (1400 μm), no. 16 (1180 μm), no. 18 (1000 μm), no. 20 (850 μm), and no. 25 (710 μm) were used. The particle size distribution was calculated from the weight of samples collected in each sieve.

The mass median diameter was the diameter where the mass of the particles with a diameter smaller than that diameter equal 50% of the total sample mass (Hofstee & Huisman, 1990) and it was calculated using the cumulative size distribution curve.

3.2.3 Density and porosity analysis

AccuPyc II 1340 Gas Pycnometer (Micromeritics, Norcross, GA), GeoPyc 1360 Envelop, were used to determine the envelope and apparent density of all fertilizer samples. Around 2 g of samples were loaded into a 3.5 cm³ chamber for apparent density measurement and the same samples were used for envelope density measurement.

3.2.4 Fracture testing

MTS Criterion (MTS System Corporation, Eden Prairie, MN) was used to determine the fracture force and fracture pressure of fertilizer granules. Most of the fertilizer granules are very close to spherical shape but still the variation in shape was wider. So, the granules that were close to an “ideal” spherical shape were used in the compression tests. To overcome the shape variability, 30 replicates were performed for granules from each fertilizer sample. A 500 N load cell was applied and the test rate was set at 0.02 mm/s. The peak force and peak pressure were derived from the equipment. More specifically, the length and width of the sample granule were measured using a digital caliper. The maximum peak value during compression was considered the fracture force.

$$\text{Fracture pressure} = \frac{\text{Force}}{\text{length} \times \text{width}} \quad (3.1)$$

3.2.5 Internal structure analysis

Select granules from all fertilizer samples were scanned using a Skyscan X-ray micro CT (Micro Photonics Inc., Allentown, PA) at 3.5 μm scan resolution. All image analysis, which included the number of pores, area, and volume of pores and porosity, were performed using the Skyscan software that included Skyscan CTvox, CTAn, and CTvol (Micro Photonics Inc., Allentown, PA). More specifically, no filter was added for both market urea and ESN, as their density were similar and relatively low, however; for Florikan and Osmocote, the 0.5 mm Aluminum filter was applied as density was relatively higher. Other parameters were maintained the same: frame averaging was set at 4 and random movement was set at 10. In order to obtain the porosity, after the samples were scanned, those scanned images need to be reconstructed and then with the reconstructed images, following by volume of interest (VOI) determination, region

of interest (ROI) determination, ROI cropping, binary image conversion, thresholding, white and black despeckle, and then 3D analysis for porosity. Open porosity means that the amount of pores inside the granule that are connected with the outside environment, while closed porosity is defined as the amount of pores inside the granules which are inhibited and isolated from the outside environment.

3.2.6 Thermal analysis

Thermogravimetry (TG) analysis was performed using the ThermoGravimetric Analyzer 4000 (PerkinElmer, Waltham, MA). Samples were heated from 35 °C to 700 °C at a heating rate of 10 °C/min under a nitrogen flow rate at 20 ml min⁻¹. The data recording frequency was every 10 s and the raw data includes sample temperature and sample weight. Then the raw data was analyzed and derivative thermogravimetry curves were obtained using OriginPro 2015 (OriginLab Pro) with “50 pts SG smooth” setting.

3.2.7 Dissolution measurement

The dissolution rate of the fertilizer granules were measured using Cary 60 UV vis spectrometer (Agilent, Clara, CA) by using the following steps: 200 mg samples were loaded on a 250-mesh stainless steel coffee maker filter sieve with a thickness of 0.4 mm, an outer diameter of 615 mm, and an inner diameter of 515 mm. The sieve was glued with three long nails and placed into a 200 ml beaker and a magnetic stirrer (The 75RPM is chosen based on experiment results as the performance was better than 50 rpm and 100 rpm) was additionally added at the bottom, as shown in the Figure 3.1.

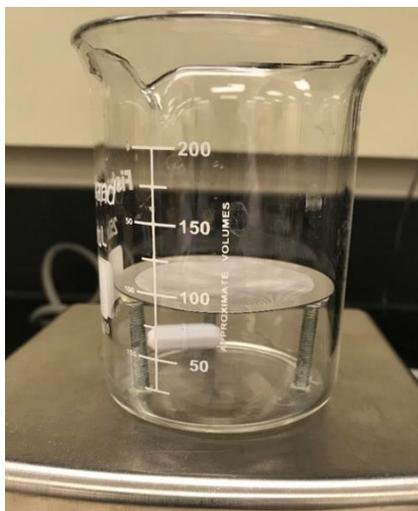


Figure 3.1 Experimental set up for fertilizer granule dissolution measurement

To prepare sample solution for UV spectrometer, a 10 ml urea sample solution was mixed with 10 ml of 20 g/L Paradimethylaminobenzaldehyde (PDAB) ethanol solution, following a 4 ml of 2 mol/L H₂SO₄, and 1 ml of distilled water were added to the solution. The solutions were added together to reach a final volume of 25 ml that is required for UV measurement (Xiao et al., 2017).

Xiao (2017) has measured the urea concentration using the para-dimethyl-amino-benzaldehyde colometry with the target wavelength at 422 nm. However, the peak wavelength for the technical urea sample was measured at 421 nm. As technical urea is in a higher purity compared with market urea. So, the peak wavelength chosen for technical urea is 421 nm and 200, 400, 600, 800, 1000 ml/L technical urea solution was prepared to establish a relationship between the UV absorbency and urea (as shown in Figures 3.2 and 3.3). During the ESN fertilizer granule dissolution measurement, sub-sample solutions were removed every 1 minute. For urea granules, sub-samples were obtained every 8 min. As urea dissolved at a much quicker rate, visual observation was also used as an end point measurement. The time of complete dissolution of urea granules (visual disappearance of solid particles within the solution) signified the fully dissolved concentration within the solution.

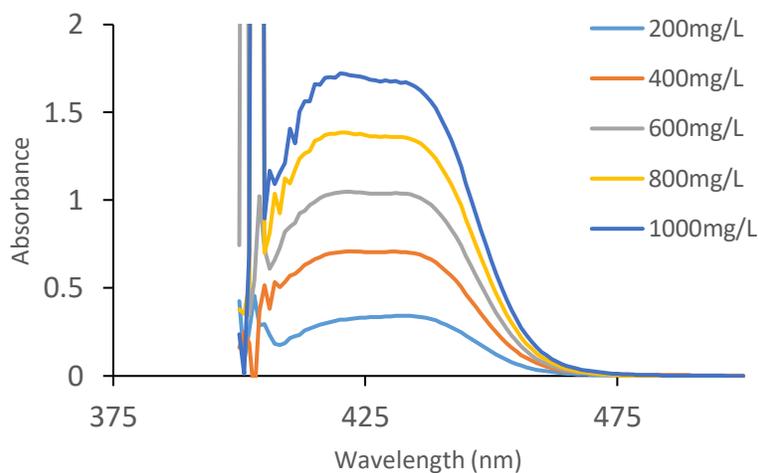


Figure 3.2 UV-Vis wavelength absorbance of different urea concentrations

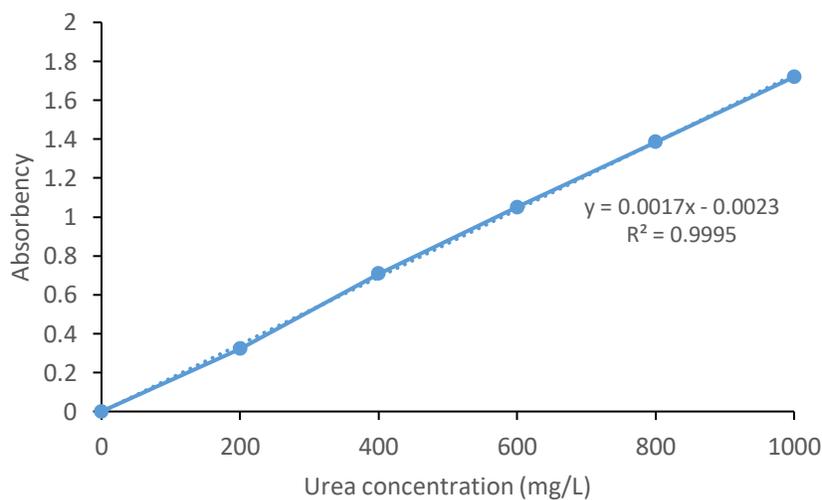


Figure 3.3 Relationship between urea solution concentration and UV absorbency

3.2.8 Statistical Analysis

All density and particle size measurements were performed in triplicate and the fracture pressure measurement were performed in 30 replicates. Statistical analysis was conducted using SAS software (SAS Institute, Cary, NC). Significant difference for comparison was determined based ANOVA Tukey's Studentized Range (HSD) Test ($\alpha=0.05$).

3.3 Results and Discussions

3.3.1 Particle size

The particle size distribution data was classified and presented based on the type of fertilizer in Figures 3.4-3.6. For pure urea, the cumulative coarse fraction decreased sharply starting at 3075 μm and ending at 4375 μm , which means that the majority of the size of the granules ranged between 3075 and 4375 μm (Figure 3.4.a). However, for ESN, the majority of sample particle size ranged between 2580 and 3675 μm . The frequency distribution of pure urea is a typical left-handed skewness (skewness <0), meaning that the mean sample size is larger than the median while the frequency distribution of ESN is a typical right-handed skewness (skewness >0) (Figure 3.4.a & b). Figure 1 shows that pure urea tends to have more larger granules compared with ESN.

As discussed by Watson & Kilpatrick (1991) and Prins & Rauw (1989), the nutrient use efficiency of larger urea granules was not significantly higher unless the larger granules were applied in puddled soil. And Hofstee & Huisman (1990) claimed that all fertilizer particle size distribution had great effect on the fertilizer spread pattern in the air so that those granules with a size smaller than 1 mm should be removed to minimize the side effect on spread pattern. In addition, in order to avoid segregation, the particle size distribution should be as narrow as possible and larger granules can lead to uneven spatial distribution of nutrient (Hofstee & Huisman, 1990).

From Figure 3.4, it can be seen that urea and ESN granules were smaller than 1 mm, and with a relatively narrow distribution, not too many large granules to cause the uneven nutrient distribution. However, for urea and ESN, as the particle size distribution is different, the spread pattern would be different and the projected spread distance should be recalculated when applying urea and ESN. Florikan and Osmocote from Figure 3.5, with a narrow particle size distribution and no granules less than 1 mm, will lead to a good spread pattern without segregation. However, the size distribution of these two samples were different and the projected spread distance would be quite different.

For Everris and the two types of the Andersons Figure 3.6, there were some granules less than 1 mm, which would result in uneven spreading. And all these three samples showed wide distribution, which meant that special attention would be required to avoid segregation. However, as all these three samples showed similar particle size distribution, the projected spread distance may be similar.

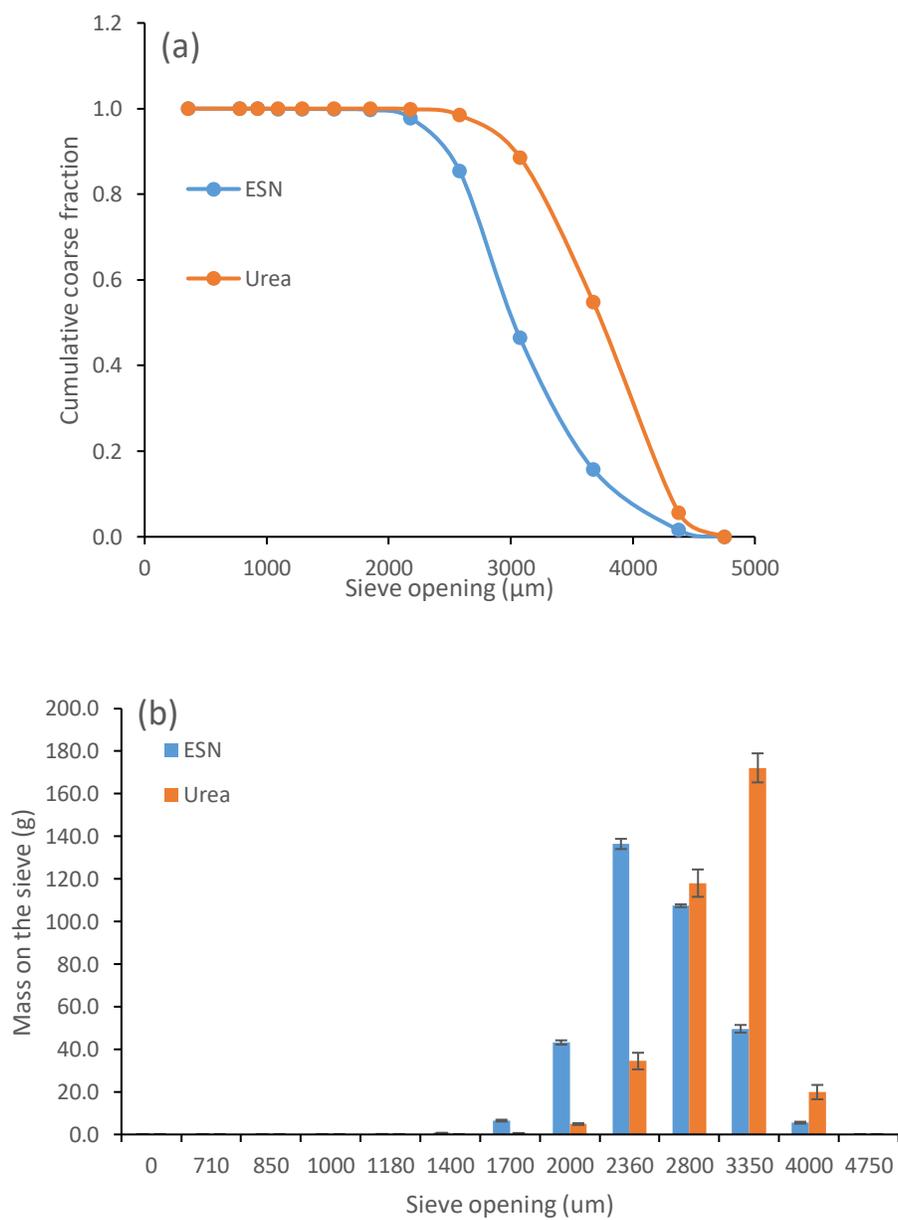


Figure 3.4 (a) Particle size distribution of pure urea and ESN fertilizer samples; (b) Frequency distribution by mass.

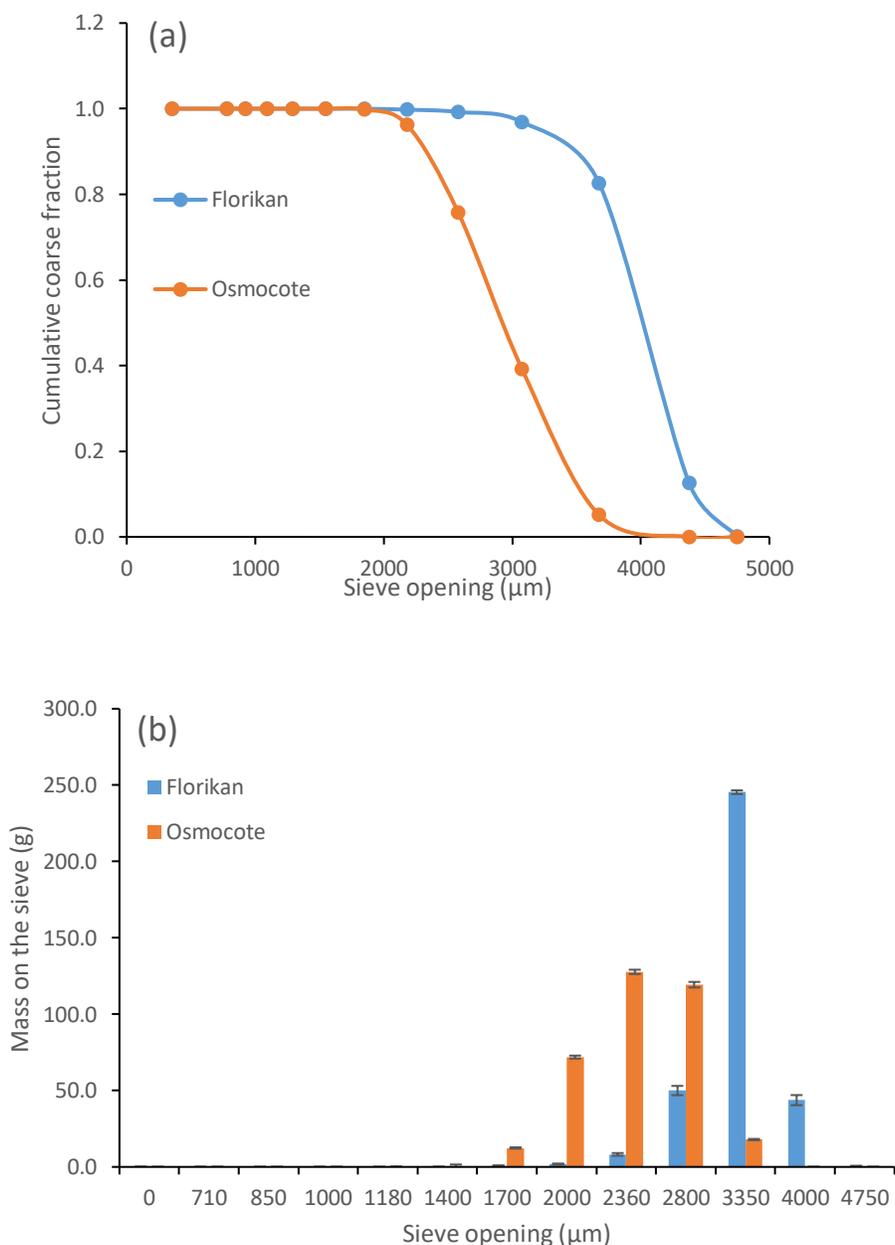


Figure 3.5 (a) Particle size distribution of Florikan and Osmocote granules; (b) Frequency distribution by mass.

Everris, the Andersons B and the Anderson A are all NPK combination fertilizers and the NPK related nutrients are made into individual granules. The particle size distribution of Everris, the Andersons 18-6-12, and the Anderson 12-6-6 samples are presented in Figure 3.6. For all three samples, cumulative coarse fraction decreased sharply starting at 2180 μm and ending at 3075 μm , meaning that the majority of sample size ranged between 2180 μm and 3075 μm . The frequency

distribution of the Everris presented a left-handed skewness (skewness <0), whereby the mean sample size is larger than the median, while the skewness of two Anderson fertilizers' frequency distribution is almost zero, whereby the mean sample size is almost identical to the median.

Most of the Anderson B sample mass ranged between 2800 μm and 2000 μm , while the majority of the Everris sample mass ranged between 3350 μm and 2000 μm and the majority of the Anderson A sample mass ranged between 3350 μm to 1700 μm (Figure 3.6.b). Figure 3 provides evidence to demonstrate that the Everris 17-3-6 sample tend to have larger granules compared with the two types of the Anderson samples.

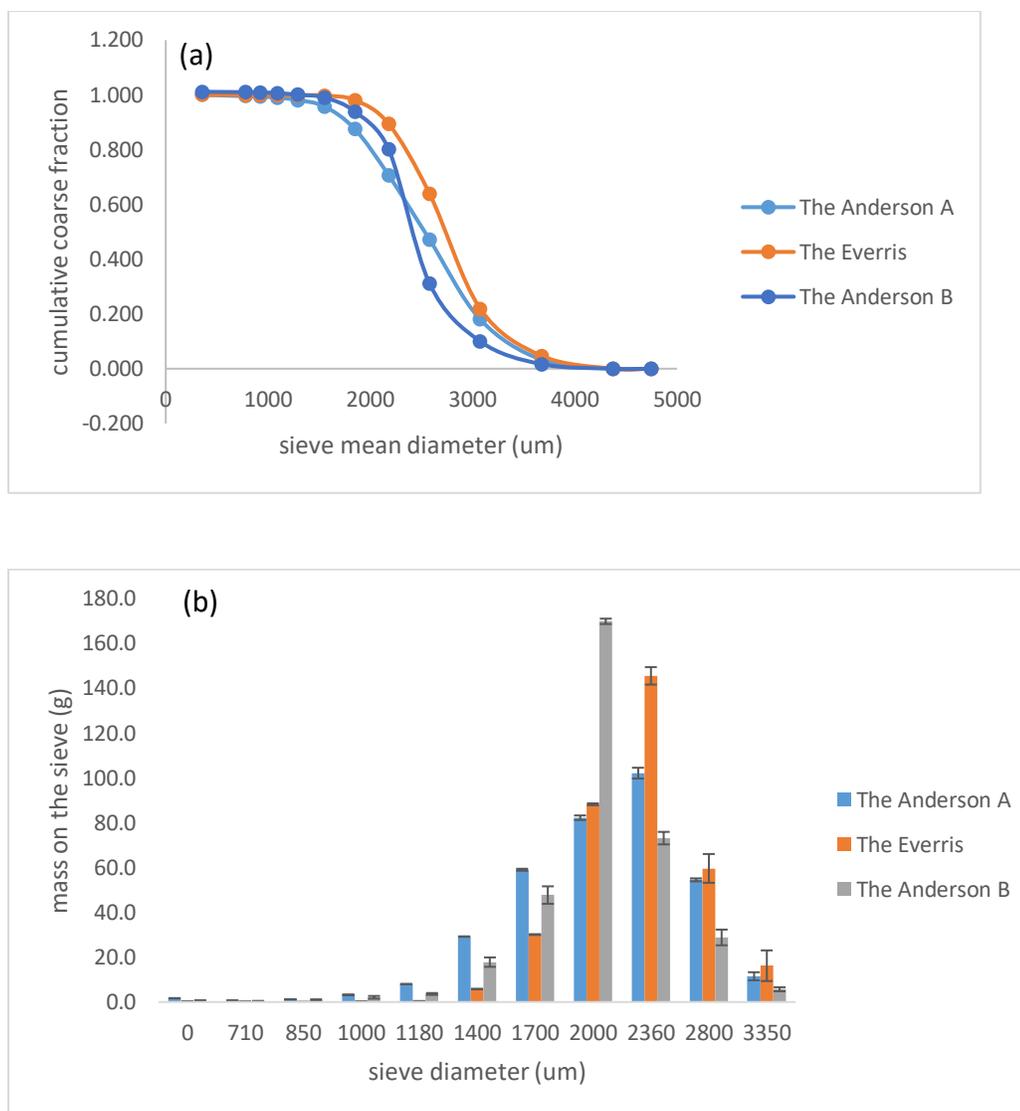


Figure 3.6 (a) Particle size distribution of Everris, the Andersons A, and the Andersons B; (b) Frequency distribution by mass.

According to [Table 3.2.](#), with respect to granule size, Florikan had the largest granule size, while the Andersons B had the smallest granule size. Since the nutrients in The Andersons fertilizers were granulated as different particles, the overall size was smaller compared with the other fertilizer samples.

Table 3.2 Mass median diameter of all samples

	d50 (mm)
Urea	3.68
ESN	3.08
Florikan	4.00
Osmocote	2.95
Anderson A	2.58
Anderson B	2.40
Everris	2.25

3.3.2 Density

The NPK combination fertilizers showed a much higher density compared with urea and ESN, mainly because of the phosphorus and potassium compounds (Table 3.3). Within all the NPK combination fertilizers, the density differences were not significant. For Everris and the two types of the Andersons, as shown in Table 3.1, there are many different colored granules with different nutrients. Their physical properties are also quite different. For Everris, it is easy to distinguish each granule by color. For the two Andersons, however, it was challenging to separate the granules based on color with different nutrients. For this reason, the Retsch rotary sample divider was used to sub-sample from the bulk for conducting density measurement. Based on the porosity calculated from apparent and envelope density, the fertilizers can be grouped as: Osmocote with the smallest porosity; Everris and the Anderson A with high porosity; and the remaining fertilizer granules categorized as granules with medium porosity.

Table 3.3 Physical properties of fertilizer samples

Sample	Envelope density (Kg/m ³)	Apparent density (Kg/m ³)	True density (Kg/m ³)	Porosity %	% ₅₀ Particle size (µm)	Fracture pressure (MPa)
Urea	1.22± 0.02 ^c	1.27±0.01 ^d	1.30±0.01 ^d	5.67±0.17 ^b	3760.0±193.4 ^a	2.73±0.54
ESN	1.26± 0.03 ^c	1.27±0.00 ^d	1.31±0.00 ^d	3.95±0.17 ^b	2983.7±45.0 ^{bc}	4.58±0.98
Florikan	1.72±0.06 ^b	1.80± 0.01 ^c	1.82± 0.01 ^c	5.56±0.50 ^b	4003.3±30.9 ^a	9.40±1.46
Osmocote	1.81±0.02 ^{ab}	1.77± 0.01 ^c	1.82± 0.01 ^c	0.54±0.15 ^c	2997.2±152.2 ^b	8.94±2.09
Everris	1.68± 0.03 ^b	1.83± 0.04 ^c	1.87± 0.02 ^c	10.26±0.91 ^a	2691.0±96.7 ^{cd}	XXX
The Andersons A	1.86± 0.05 ^a	2.09± 0.07 ^a	2.04± 0.05 ^a	8.90± 2.35 ^a	2475.2±78.1 ^d	XXX
The Andersons B	1.87± 0.09 ^a	1.95±0.08 ^b	1.95±0.01 ^b	3.90±0.60 ^b	2445.9±24.7 ^d	XXX

* The same letter in the same column for a given sample indicates no significant differences ($p < 0.05$) based on ANOVA Tukey's Studentized Range (HSD) Test.

3.3.3 Fracture pressure

The Florikan and Osmocoe granules showed higher fracture pressure than urea and ESN (Figure 3.7). The differences in fracture pressure between Florikan and Osmocote are mainly because of their compositional differences. The fracture pressure of ESN is higher than normal urea granules, mainly due to the presence of coating surface. For Everris, the fracture pressure of differently colored granules measured separately, and the calculated average is presented here. The average fracture pressure of Everris is slightly higher than ESN. As shown in Figure 3.8, differently colored granules in Everris showed quite a difference in fracture pressure. Within the granule, the black colored Ammonium Phosphate showed the highest fracture pressure.

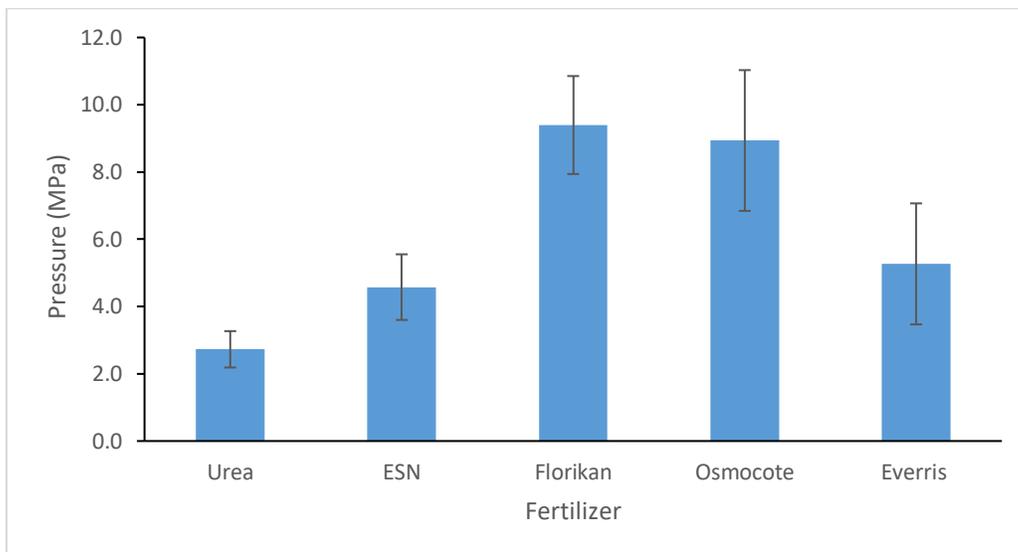


Figure 3.7 Fracture pressure of select granular fertilizer samples

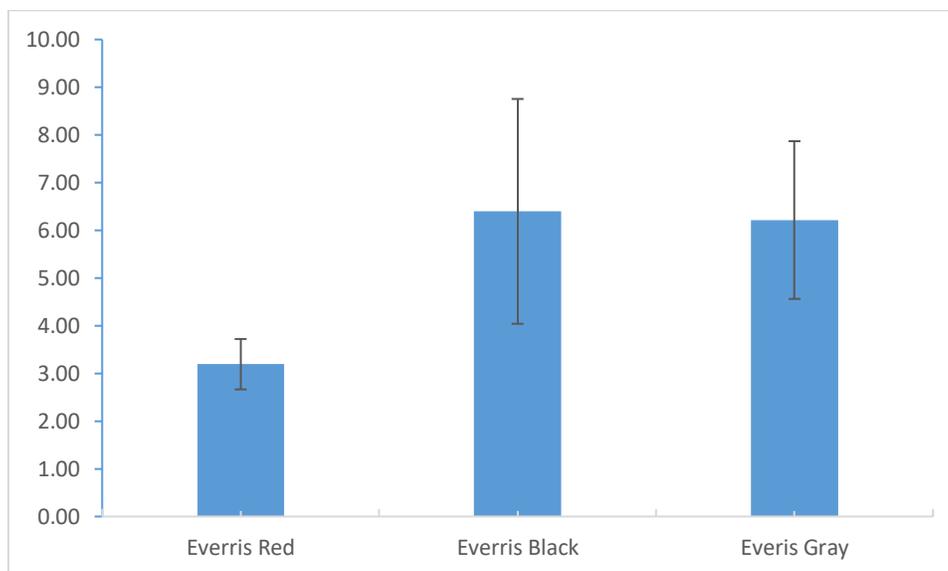


Figure 3.8 Fracture pressure of colored granules present in the Everris fertilizer mix

3.3.4 Thermal Property

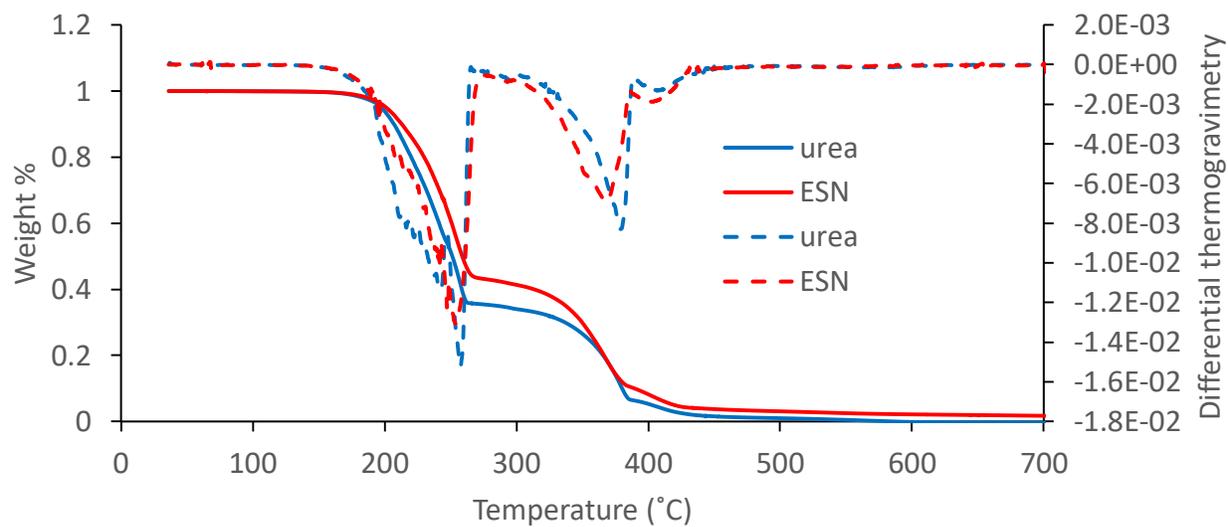


Figure 3.9 Thermal properties of urea and ESN.

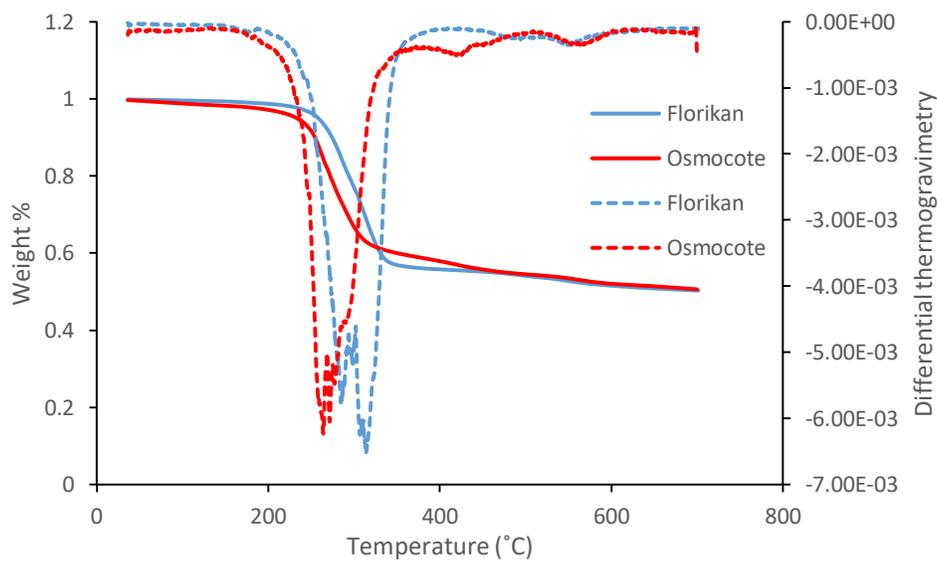


Figure 3.10 Thermal properties of Florikan and Osmocote.

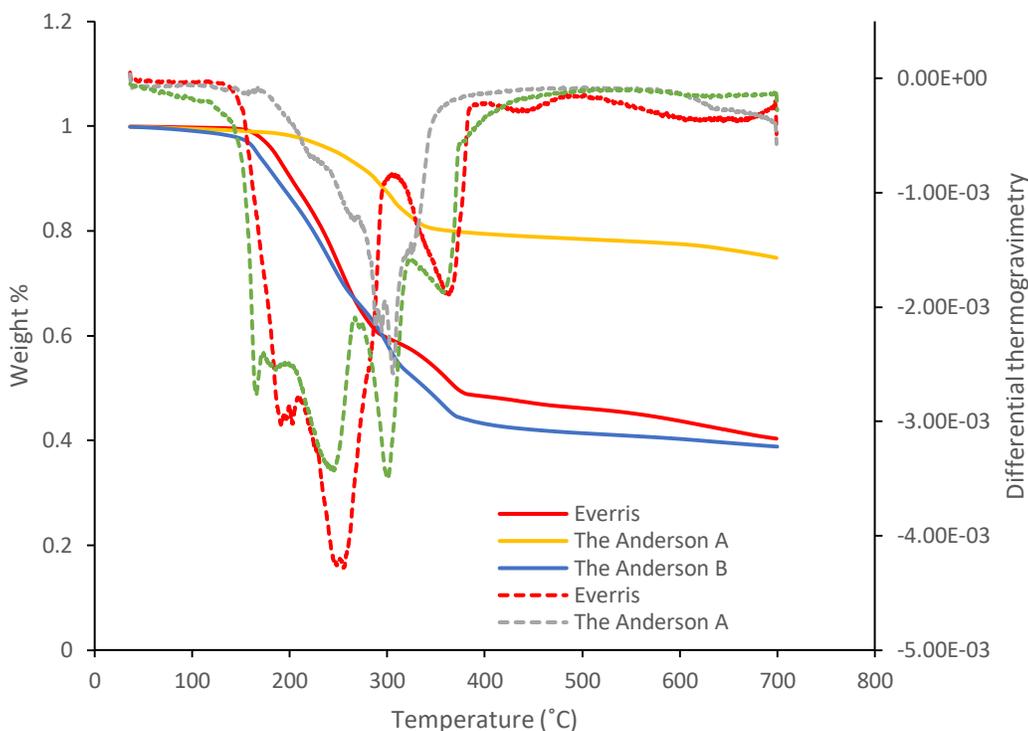


Figure 3.11 Thermal properties of Everris and the Andersons fertilizer granules.

The urea decomposition process can be explained from Figure 3.9: step 1; urea melts at 133 °C; step 2, at 233 °C, two urea molecules were converted into a biuret molecule, releasing ammonia gas; step 3, biuret molecule decomposed at 262 °C; step 4, three biuret molecules were converted into two melamine molecules, thereby releasing water. Finally, melamine decomposed at 380 °C. It is clear that the thermal properties of urea and ESN did not change much with the addition of coating materials. The DTG trends are similar (Figure 3.10), however, Osmocote demonstrated a faster rate of mass loss than Florikan, at a temperature range of 200 to 300 °C. This is mainly because of the differences of NPK components within the granules. On the other side, the final residues after burning were 50.28% and 50.61 % for Osmocote and Florikan, respectively. NPK combination fertilizers cannot be completely decomposed under 700 °C and have a much higher burning residue. The NPK combination fertilizers, with granules separated based on color, demonstrate different thermal properties (Figure 3.11). The Anderson A had a large burning residue at 74.83%, while the Anderson B had a smaller residue at 38.82%. This is mainly due to Anderson A's NPK ratio being 12-6-6, while the Anderson B's NPK ratio is 18-6-12. However, the Everris and the Andersons B show similar decomposing trend and similar

amounts of burning residue, despite the NPK ratio being 17-3-6 and 18-6-12, respectively. When comparing the thermal property results, it seems that phosphorus and potassium chemical components play an important role, which affects the decomposition curve and the residue after burning, especially potassium.

3.3.5 Internal Structure

A raw scanned image of urea granule is presented in Figure 3.12. The black dots indicate the internal pores in the granule. The internal pores are distributed throughout the granule, almost uniformly. A similar internal structure was noticed for ESN granule (Figure 3.13a) with internal pores throughout the granule. But, the sectional image of Osmocote and Florikan fertilizer granules indicated the presence of smaller sized granules within the larger granule (Figure 3.13b, c). The difference in the color of smaller internal granules are due to their differences in density.

Table 3.4 The average closed pore volume of market urea, ESN, Florikan and Osmocote

Sample	Average closed pore volume, μm^3
Urea	10.15
ESN	4.06
Florikan	12.71
Osmocote	14.10

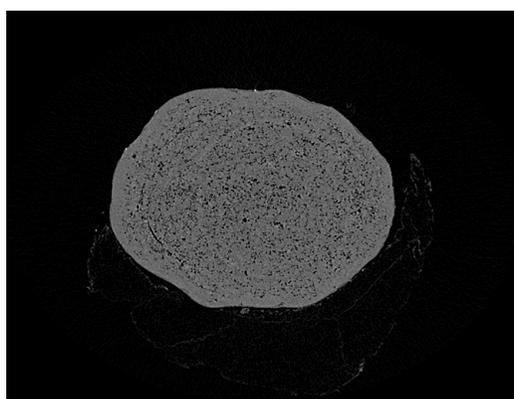


Figure 3.12 XRCT scanned image of urea granule

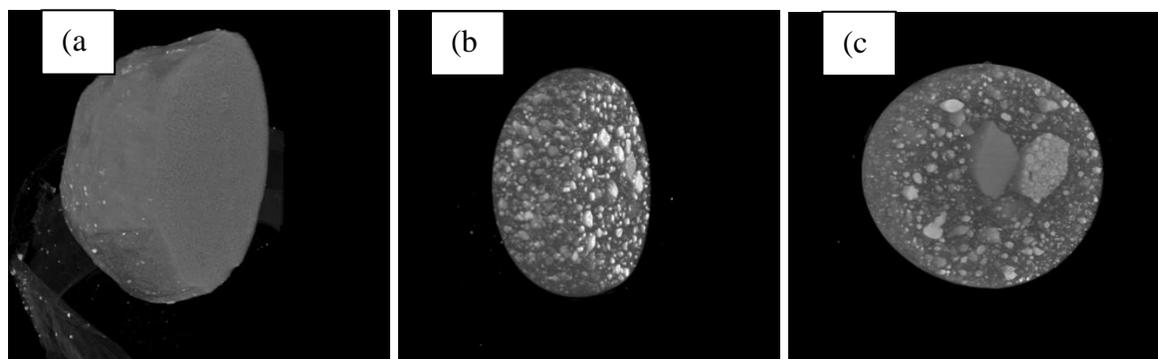


Figure 3.13 3D reconstructed sectional image of a select a) ESN granule, b) Osmocote, and c) Florikan fertilizer granules.

Granule porosity is a very important parameter for fertilizers. As discussed by Rieck (2015), the granule porosity, along with surface structure, will alter the fertilizer dissolution behavior. The porosity shows a negative correlation with the drying potential, meaning a low drying potential process condition led to a high formed coating porosity (Rieck, 2015). As reported by Wang & Cameron (2002), granule porosity affects the probability of coalescence by controlling granule deformability and pore saturation. The internal porosity of the fertilizer granules are presented in Figure 3.14. The NPK combination fertilizers, Florikan and Osmocote, are less porous than market urea and ESN. When comparing market urea and ESN, the open porosity of ESN is 43% higher than market urea which result in a higher total porosity. While for the two types of NPK combination fertilizer, there is almost no open pores, and according to Table 3.4, the average closed pore volumes of Florikan and Osmocote are 20% larger than market urea and almost 3 times larger than ESN. Based on closed porosity data and closed volume data, it can be concluded that the less number of pores inside of the Florikan and Osmocote granules lead to a higher fracture pressure. Even though relatively large pores may result in poor compression, as the pore number is very low, the possibility that the fracture pressure is affected by pores is low, which leads to a higher fracture pressure for Florikan and Osmocote samples.

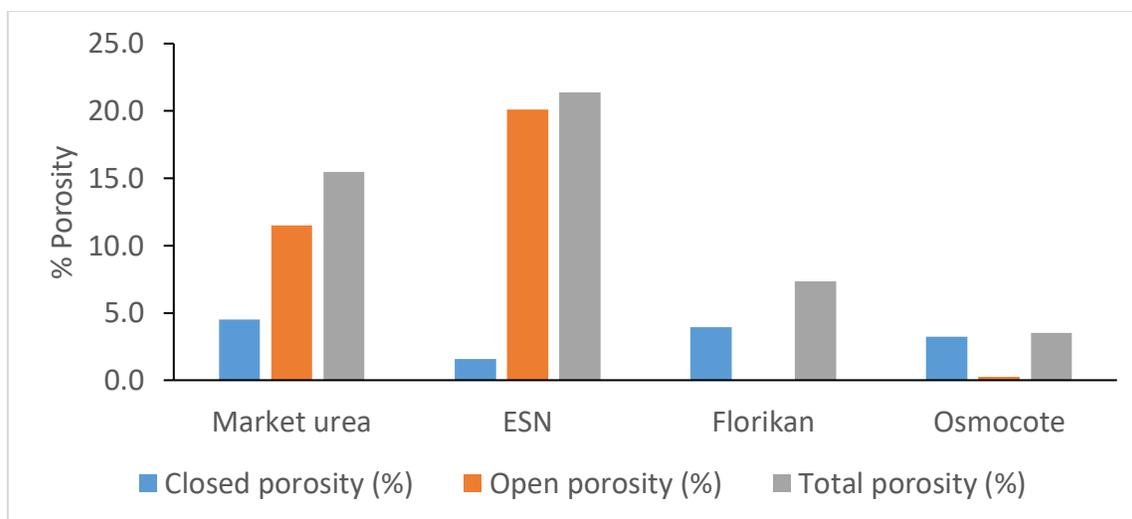


Figure 3.14 XRCT measured porosity of fertilizer samples

3.3.6 Dissolution

ESN dissolves much slower than market urea due to the presence of surface coating (Figure 3.15). According to Hayashi et al. (2007), urea is not a strong structure breaker of water because urea can readily interchange with water in the H-bonding network. In addition, urea doesn't require the presence of disordered phase as urea can easily dissolve in the ordered phase of water. Because of high water soluble property, it is important to measure the urea fertilizer's dissolution rate in water.

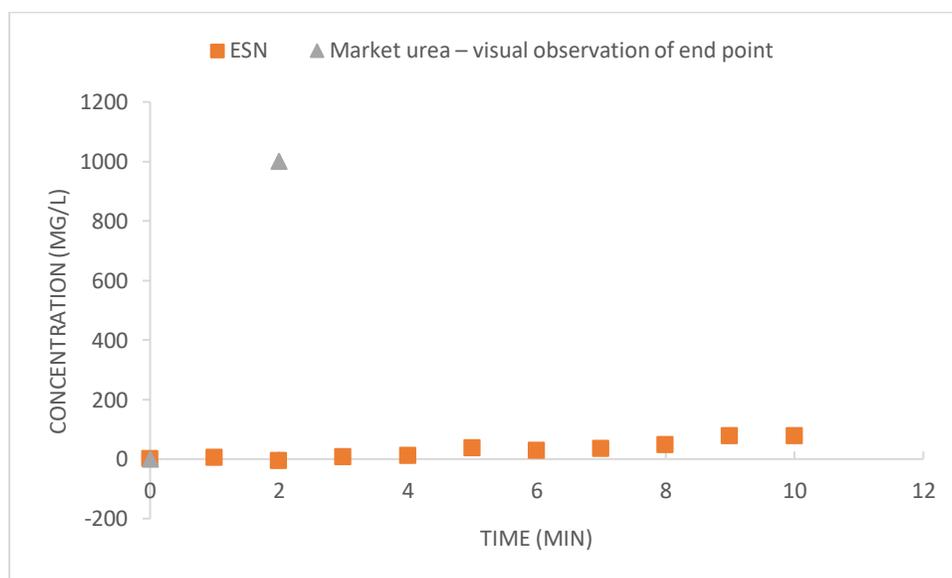


Figure 3.15 Dissolution behavior of urea and ESN fertilizer granules

As shown in Fig. 3.15, the market urea dissolved in water in two minutes, correlating to the findings by Hayashi (2007). For ESN, because of the polymer coating, the diffusion of water into the granule is slowed and then form a nitrogen solution, which slowly moves out through the pores on the coating material. So, the ESN dissolution rate is low and at a constant rate. For some starch based slow release fertilizers, the dissolution time can be up to 45 days (Xiao et al., 2017). So, the dissolution rate of slow release fertilizers are different for different fertilizers but dissolve at a slower rate than urea granules.

3.4 Conclusion

In this work, the particle size, density, mechanical fracture pressure, internal structure, dissolution behavior, and thermal property of market urea, ESN, Florikan and Osmocote, were characterized. The single granule NPK combination fertilizers, had a larger particle size, higher fracture pressure, and higher burning residue, despite lower internal porosity than urea. The NPK combination multiple granule fertilizers presented smaller particle sizes but higher density and higher burning residue than urea fertilizers. The fracture pressure of granules with different nutrient in the NPK combination fertilizers varied with their chemical composition. Using XRCT scanning, it was found that the nutrients in NPK combination single granule fertilizers were not uniformly mixed throughout the granule. As a result, within the granules, they are present as localized nutrient cluster and their internal densities also varied. With the surface coating, the dissolution rate of ESN was much lower than the market urea granules. The mechanical fracture pressure and internal porosity of ESN is higher than market urea. The coating material did not influence the thermal property of fertilizer granules. The physical properties (particle size distribution, density, thermal property, internal porosity, dissolution rate) of fertilizers is very important, as they can greatly affect the handling, storage, transportation process, more importantly, the spread pattern and dissolution rate. Knowledge of physical, mechanical properties and dissolution behaviors will help in improving the performance of fertilizers by modifying the manufacturing process.

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CHAPTER 4. LAYERED AGGLOMERATION OF UREA GRANULES

ABSTRACT: Urea has been widely used as a nitrogen fertilizer due to its high nitrogen content. However, because of its high water-solubility, the nitrate content is lost as surface runoff. In this study, different binders were used to alter the internal structure of the urea granule to control the dissolution behavior and reduce the rate of dissolution. Urea, with binders, was granulated in layers. The core of the granule was manufactured by granulating technical urea powder in a drum granulator, with corn starch as the binder. A second layer was added, by drum granulation, to the core in order to obtain a nutrient release pattern that matches the crop nitrate demand. Corn starch, PEG 4000, and corn starch hydrogel were used as binders for the second layer. The density, thermal properties, fracture pressure, internal porosity, and dissolution rate of the two-layer granules were measured using standard methods. Dissolution rate of the double layer granules were slower than the market urea granules. The mechanical fracture pressure of the double layer granules with hydrogel binder was the highest among these three types of double layer granules. Among these three types of granules, the dissolution behavior of the granule with starch hydrogel on the second layer was identical to the crop nitrate demand curve. Overall, the double layer granule with corn starch binder in the core and hydrogel as the binder in the second layer had a better physical and dissolution properties. Though the pattern of dissolution of double layer granule was similar to the crop nitrate demand curve, but, a soil based study is needed to verify the nitrate release characteristics in the future.

Keywords: urea, drum granulation, X-ray micro-tomography, dissolution rate

4.1 INTRODUCTION

Among all the nutrients that crops need, nitrogen is the most important essential nutrient, and it plays a critical role affecting crop growth and yield (Xiao et al., 2017). Urea is widely used as the nitrogen source, mainly because of its high nitrogen content. However, the nutrient use efficiency of urea fertilizer is very low mainly because of the leaching that tends to occur (Ni et al., 2013).

The prilling tower is widely used to produce urea granules mainly because this process can produce ideal spherical urea particles within a specific size range and with minimal specific surface area in one step (Saleh et al., 2015). In this process, the molten or highly concentrated urea solution is discharged through an orifice nozzle and then the uniform sized droplets will form into urea granules at the bottom of prilling tower (Rahmanian et al., 2013). The urea granule crystalline structure can be affected by the prilling tower height (Saleh et al., 2015).

In order to extend the nutrient release, many methods have been studied such as applying a coating material (Ni et al., 2011) and by adding additional chemical components (Ni et al., 2013, Xiao et al., 2017). As shown in **Fig.2.5**, the nitrogen demand from crop is not constant. A higher nitrogen supply is needed starting from the growth stage and the demand peaks at the flowering stage, and then slowly decreases from the wheat seed development stage till maturity (Croelands, 2014).

An alternate method of manufacturing urea granules is by agglomeration process. The granulation process can be used to agglomerate urea powder into larger granules with the addition of a binder (Xue et al., 2013). Chai et al. (2017) reported that urea powder can be agglomerated by using water as the binder liquid. However, the hardness was relatively low because the raw materials were not mixed evenly and was not bonded uniformly. So, if the solid fraction of the urea granule can be changed by adding different binders, then the urea granule dissolution rate may also be slowed down. The goal of this study is to manufacture urea granules with a larger solid fraction so that the dissolution behavior and the nutrient release characteristic could be controlled. The choice of binder influences the granule fracture pressure and dissolution rate. In this work, a second layer of urea was added to the core layer with an aim to match the nutrient release with the crop nutrient demand curve. The objectives of this study are to i) granulate urea in two layers with an inner core with higher solid fraction than the outer layer, ii) evaluate the physical, mechanical, structural, and dissolution behavior of newly developed urea granules.

4.2 MATERIALS AND METHODS

4.2.1 Experimental Procedure

The procedure used in this study is given in **Figure 4.1**. This process was formalized after many preliminary trails which results are given in appendix. Technical urea powder (Rose Mill Co., West Hartford, CT) that passed through a 212 μm sieve was used for manufacturing granular urea. The urea powder was loaded in a stainless-steel drum (dimensions: 6'' diameter, 4'' height) and mixed with 5% corn starch. Then, 11% distilled water was sprayed into the drum. The granules were then dried for 24 h at 85 °C. Dried granules were sieved and the granules within the size range of 2–3.35 mm were used as the core and used for the second layer agglomeration. For the second layer, binders and technical urea powder were premixed and loaded in the drum following the same procedure as core granules. The wet granules were then dried and sieved. The granules within a size range of 3.35–4 mm were used for characterization studies. This size range was selected since this compares with the average size of market urea granules. The variables tested in this study were: binder type, granulation time (for core and second layer), and drum rpm (for core and second layer). The list of experimental trials used in this study is provided in Table 4.1.

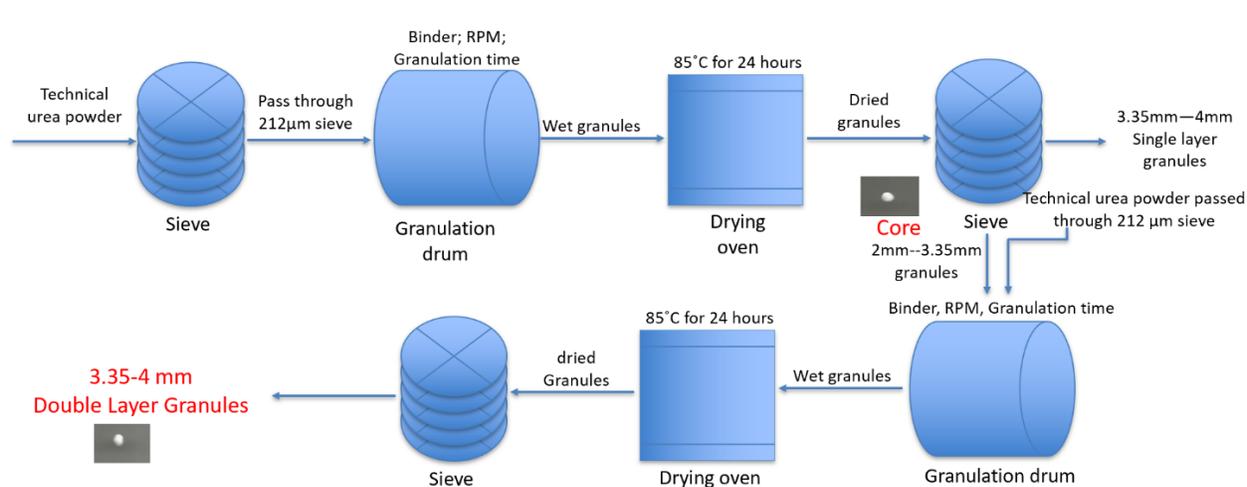


Figure 4.1 Experimental procedure used in the manufacture of double layered urea granules

Table 4.1 Experimental trials

Sample/Parameters	Trials
Urea	Technical urea powder ($\leq 212 \mu\text{m}$)
Temperature	22 °C
Liquid solid ratio	11 %
Binders	<ul style="list-style-type: none"> • Corn starch powder (core) • PEG 4000 (second layer) • Corn starch hydrogel (second layer) • Control (without binder – second layer)
Granulation time (core; min)	<ul style="list-style-type: none"> • 15 (7; 14 rpm) • 20 (7 rpm) • 25 (7; 14 rpm) • 30 (7 rpm) • 35 (7rpm)
Granulation time (second layer; min)	<ul style="list-style-type: none"> • 7 (7; 14 rpm)
	<ul style="list-style-type: none"> • core – 15 min; 14 rpm

4.2.2 Characterization of Two Layered Urea Granules

4.1.1.1. Density and porosity analysis

The envelope and apparent density of all granule samples were measured using AccuPyc II 1340 Gas Pycnometer (Micromeritics, Norcross, GA) and GeoPyc 1360 Envelop and T.A.P. Density Analyzer (Micromeritics, Norcross, GA). Around 0.5 g of samples were put into a 1 cm³ chamber for apparent density measurement, and the same samples were put in a chamber for envelope density measurement.

4.1.1.2. Fracture Pressure

The fracture force and fracture pressure of each sample granule was measured using MTS Criterion (MTS System Corporation, Eden Prairie, MN). Those sample granules with an “ideal” spherical shape were selected to perform the compression tests. Fifteen replicates were measured for each type of granule sample.

4.1.1.3. Internal structure analysis

All sample granules were scanned at 3.5 μm using a Skyscan X-ray micro CT (Micro Photonics Inc., Allentown, PA). All data, including number of pores, area and volume of pores, and porosity were recorded using Skyscan software, including Skyscan CTvox, CTAn and CTvol. During scanning and analyzing, no filter was used; frame averaging setting is 4, random movement setting is 10, and rotation step (deg) setting is 0.200. Select granules from all fertilizer samples was scanned using a Skyscan X-ray micro CT (Micro Photonics Inc., Allentown, PA) at 3.5 μm scan resolution. All image analysis, which included the number of pores, area, and volume of pores and porosity, were performed using the Skyscan software suite that included Skyscan CTvox, CTAn, and CTvol (Micro Photonics Inc., Allentown, PA). Frame averaging was set at 4 and random movement was set at 10. To obtain the porosity, after the samples were scanned, the images were reconstructed. The porosity was obtained from the reconstructed images, following volume of interest (VOI) determination, region of interest (ROI) determination, ROI cropping, binary image conversion, thresholding, white and black despeckle, and then 3D analysis.

4.1.1.4. Thermal analysis

Granule sample thermal properties were analyzed using a TGA 4000 (PerkinElmer, Waltham, MA). All samples were heated from 35 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$ at a heating rate of 10.00 $^{\circ}\text{C}/\text{min}$ with a nitrogen flow rate at 20.00 mL min^{-1} . Thermogravimetry (TG) analysis was performed using the Thermo Gravimetric Analyzer 4000 (PerkinElmer, Waltham, MA). The data recording frequency was set at every 10s and the raw data includes sample temperature and sample weight. Then the raw data was analyzed and derivative thermogravimetry curves were obtained using OriginPro 2015 (OriginLab, Massachusetts) with “50 pts SG smooth” settings.

4.2.2.1 Granulation yield

The granulation yield was calculated using the equation below:

For core:

$$\text{Yield, \%} = \frac{\text{mass of granule in 2 mm} - \text{3.35 mm size range}}{\text{total sample mass used for granulation}} \times 100\%$$

For double layer:

$$\text{Yield, \%} = \frac{\text{mass of granule in 3.35 mm} - \text{4 mm size range}}{\text{total sample mass used for two layer granulation}} \times 100\%$$

4.2.2.2 Dissolution rate measurement

UV spectrometer can be used as an easy and fast way to determine urea concentration (Xiao et al., 2017). The dissolution behavior of all granulated samples was first visually observed to select the granules with better performance. Then, the dissolution of granules manufactured at optimum granulation conditions was measured using UV-Vis spectrometry. To visually observe the dissolution rate, the mass of the single granule was recorded and then the sample was placed in 200 mL of distilled water. The time at which the granule had fully dissolved was noted down. Five replicates were performed for each sample. The dissolution behavior of market urea and ESN samples were also measured to compare the performance with two-layer granules. The dissolution rate was measured using Cary 60 UV vis spectrometer (Agilent, Clara, CA) following these steps:

- a. 200 mg urea granules were placed on a 250-mesh stainless steel coffee maker filter sieve with a thickness of 0.4 mm, outer diameter of 61.5 mm, and inner diameter of 51.5 mm (Podoy, Amazon, https://www.amazon.com/gp/product/B06XSZ1DBY/ref=oh_aui_search_detailpage?ie=UTF8&psc=1).
- b. The sieve was glued with three long nails and placed into a 200 mL beaker. For better mixing of the dissolved nutrients a magnetic stirrer (75 rpm) was placed at the bottom of the beaker (Figure 3.1)
- c. To prepare sample solution for the UV spectrometer, 10 mL of urea sample solution was mixed with 10 mL of 20 g/L Paradimethylaminobenzaldehyde (PDAB) ethanol solution, and then 4 mL of 2 mol/L H₂SO₄ and 1 mL of distilled water were added together to reach a 25 mL solution for UV measurement (Xiao et al., 2017).
- d. The peak wavelength chosen for two-layer granules manufactured using technical urea was 421 nm. In order to get the relationship between the urea concentration and the UV absorbancy, multiple urea solutions were prepared to test under UV. More specifically, 200, 400, 600, 800, 1000 mg/L solution were used and the relationship is shown in Figure 3.2 and Figure 3.3.
- e. During the measurement of urea and ESN dissolution, 10 ml sample solutions were drawn every 2 minute up to 8 and 10 min., respectively.

- f. Then sample solution was mixed with 10 ml of 10 mL of 20 g/L Paradimethylaminobenzaldehyde (PDAB) ethanol solution, and then 4 mL of 2 mol/L H₂SO₄ and 1 mL of distilled water were added together to reach a 25 mL solution for UV measurement.

4.2.2.3 Statistical Analysis

All density measurements were performed in triplicate and the fracture pressure measurement were performed in 15 replicates. Statistical analysis was conducted using SAS software (SAS Institute, Cary, NC). Significant difference for comparison was determined based ANOVA Tukey's Studentized Range (HSD) Test ($\alpha=0.05$).

4.3 RESULTS AND DISCUSSION

4.3.1 Granulation Yield

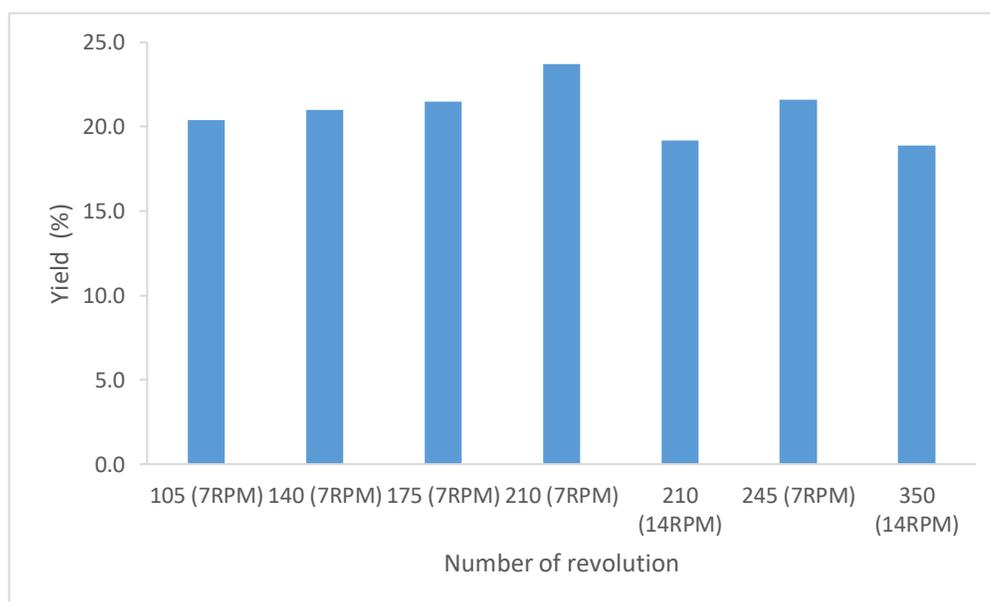


Figure 4.2 Granulation yield for core with a size range of 2mm—3.35mm.

With the increase in the total revolution, the yield increases till a revolution of 210 and then decreased (**Fig.4.2**). As the yield indicates the amount of granules with a size range of 2—3.35 mm, along with the results from **Fig. 4.3**, the results can't predict a clear relationship between revolution and yield at different granulation sizes. Similar like Adetayo (1993) claimed

that the kinetics in determining fertilizer granule size distribution was not completely established.

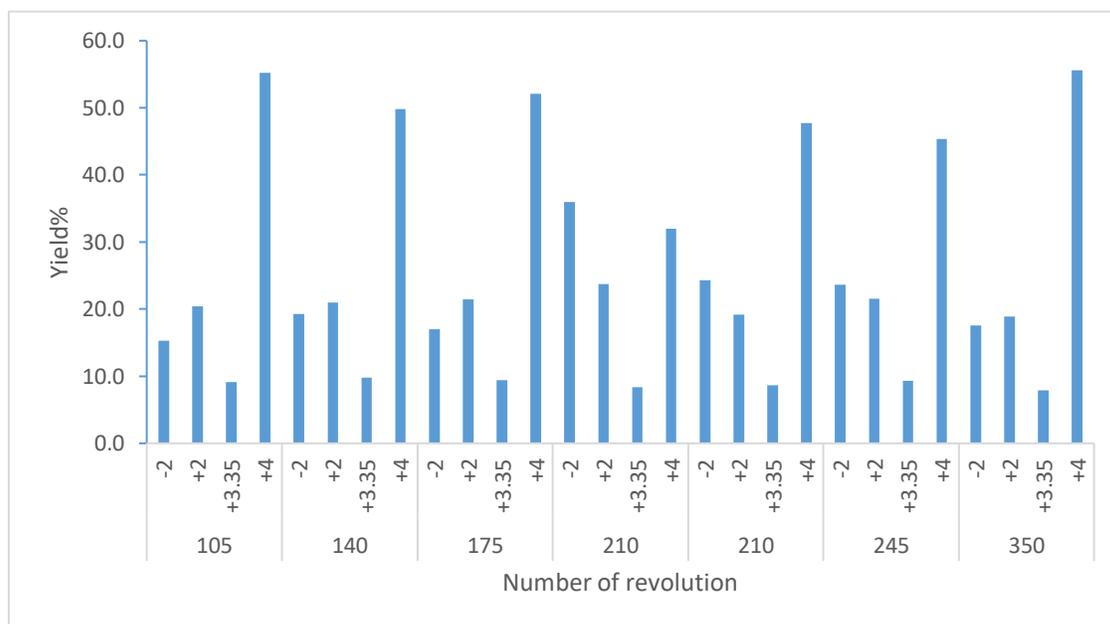


Figure 4.3 Granulation yield for core granules.

4.3.2 Fracture pressure and Dissolution

From Fig. 4.4, it is clear that the granule fracture pressure increased as the number of revolution increased till the revolution of 210, and then with more number of revolutions, the fracture pressure decreased. As discussed by Rodrigues et al. (2017), the granule hardness increased with the increase in granulation time, mainly because the increased granulation time lead to an increase in particle densification. The granule saturation was reached because the pore space reduction by consolidation rather than the filling of the pores (Adetayo et al., 1993). The fracture pressure showed a negative correlation with dissolution (Fig.4.4), which may because of the reduced pore space. According to Braumann (2010), granulation speed showed significant influence on the granule fracture pressure. The fracture pressure of the granule manufactured with 210 revolution (14 rpm) is 23% higher than the granule fracture pressure produced at 210 revolution (7 rpm), indicating higher granulation speed can increase the granule fracture pressure.

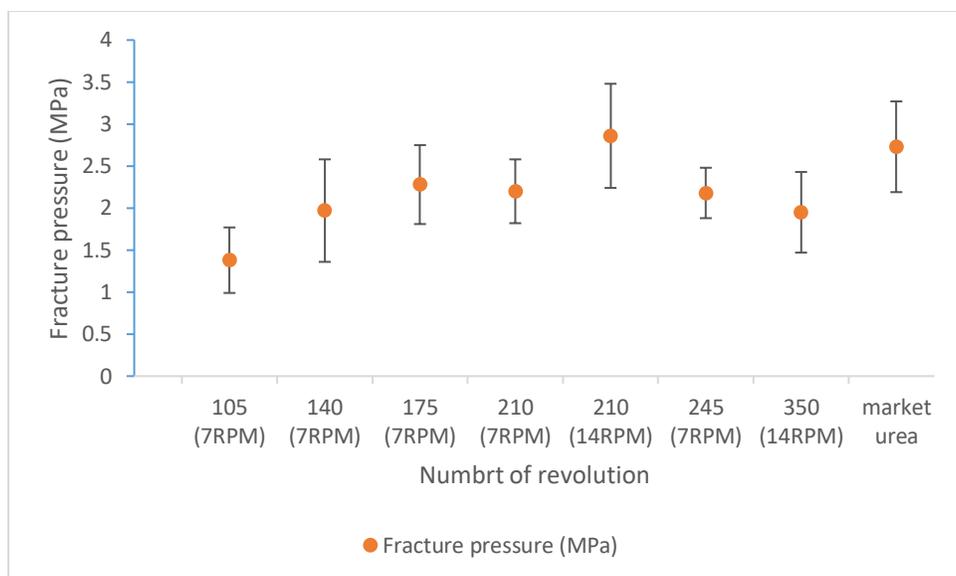


Figure 4.4 Fracture pressure of core granules with a size of 2mm—3.35mm

As this single layer granule will be working as the core for double layers, so higher fracture pressure is preferred. Based on the results in **Fig. 4.4**, the granule manufactured at 14 rpm with 15-minute granulation time was selected as the core for double layer.

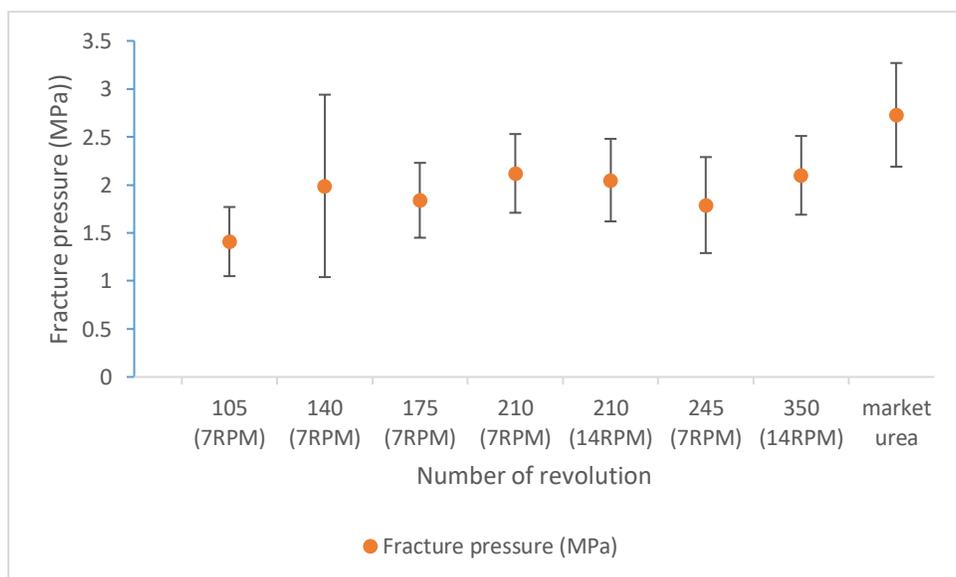


Figure 4.5 Fracture pressure of core granules within the size of 3.35 mm—4 mm

When comparing Fig. 4.4. with Fig. 4.5, it can be concluded that granule fracture pressure is a function of the number of revolution. Higher fracture pressure can be reached no matter for large or small granules, with increased number of revolution. However, from Fig.4.6, it also can be seen that the higher fracture pressure can be found for small granules, which contradicts the findings by Walker (2003). This may be because of the reason that different liquid/solid ratio and granulation speed, or due to the method of binder application (Braumann et al., 2010).

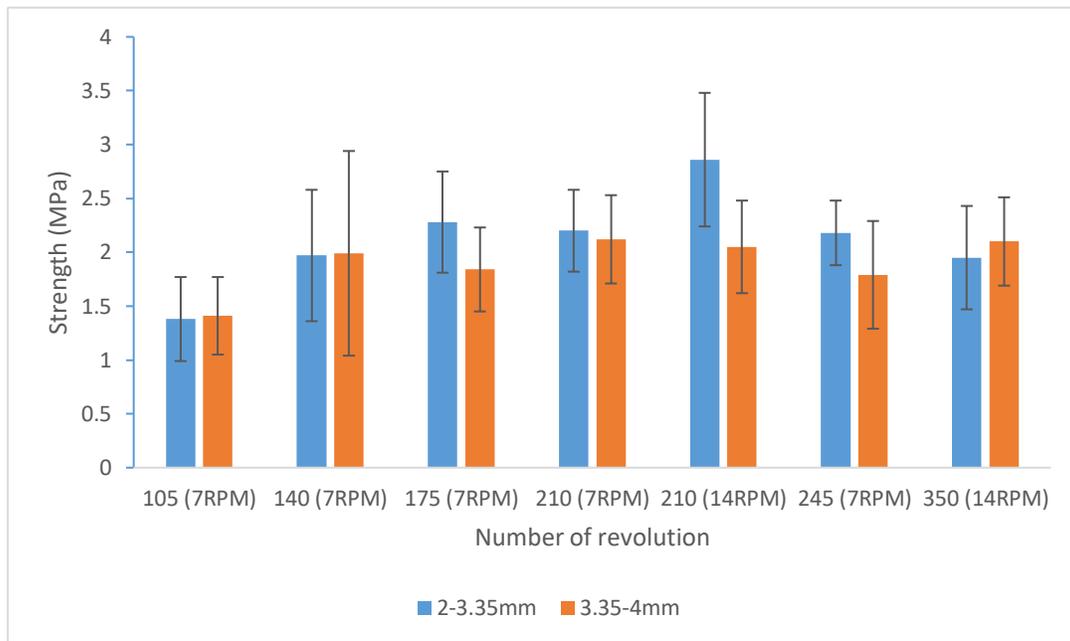


Figure 4.6 The fracture pressure of granules of 2-3.35 mm and 3.35-4 mm

Fig.4.6. The fracture pressure of granules of 2-3.35 mm and 3.35-4 mm

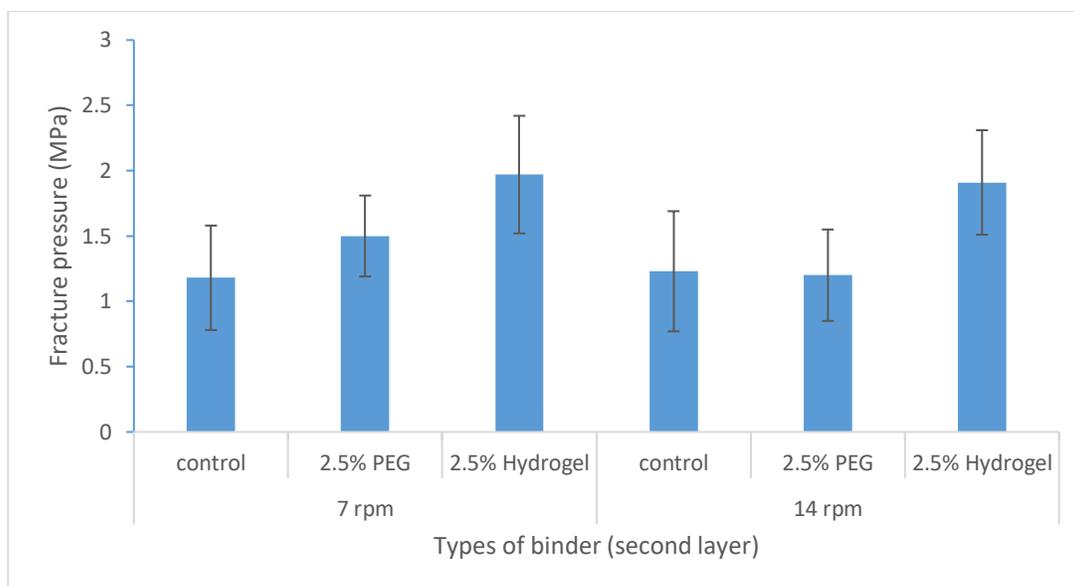


Figure 4.7 Fracture pressure of double layer granules

The binder amount, binder solution viscosity and binder distribution have significant effect on the granule physical properties (Dosta et al., 2016). Lower moisture content and lower binder viscosity tend to reduce the equilibrium size distribution granulation time (Adetayo et al., 1992). The fracture pressure and dissolution rate results of double layer granules are shown in Fig. 4.7. In this figure, control indicates that the second layer is made with urea powder without addition of binder. The 2.5% PEG and 2.5% corn starch hydrogel indicate the different binders used in the second layer. It is clear that for both 7 rpm and 14 rpm, the second layer with hydrogel shows the highest fracture pressure. In terms of dissolution rate, the hydrogel binder had the lowest dissolution rate. Overall, the 7 rpm granulation speed with 2.5% corn starch hydrogel had the best performance regarding the fracture pressure and dissolution rate.

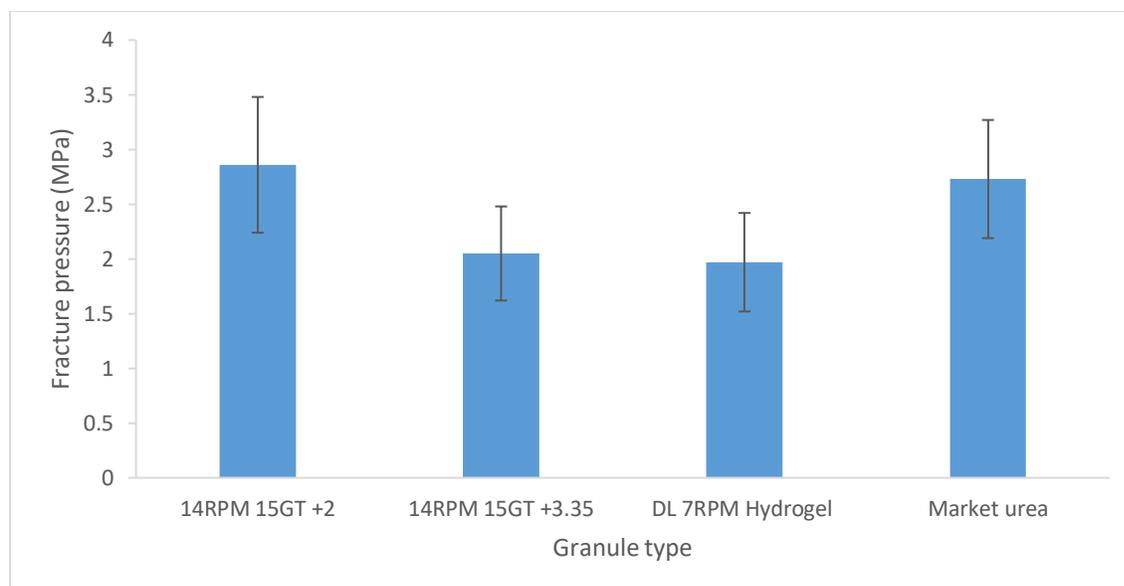


Figure 4.8 Fracture pressure of selected granules

The fracture pressure of two-layered granule with hydrogel as the binder has comparable with market urea (Fig.4.8). For the other two types of granules, the fracture pressures were roughly 25 % lower than the marker urea granules. Meanwhile, the dissolution rate of the double layer core is about 16 % of the market urea. For the single layer granule with a size of 3.35–4 mm, the fracture pressure becomes lower and dissolution rate becomes larger when comparing with the single layer granule with a size of 2–3.35 mm. When comparing the core and the double layer using the core, it is clear that the fracture pressure became 30 % lower and the dissolution rate became almost 20 % higher. However, for all the self-made granules, the dissolution rates are 80 % lower than the market urea, which means the self-made granules become slow-release because of the added binder.

4.3.3 Density and Internal Poros

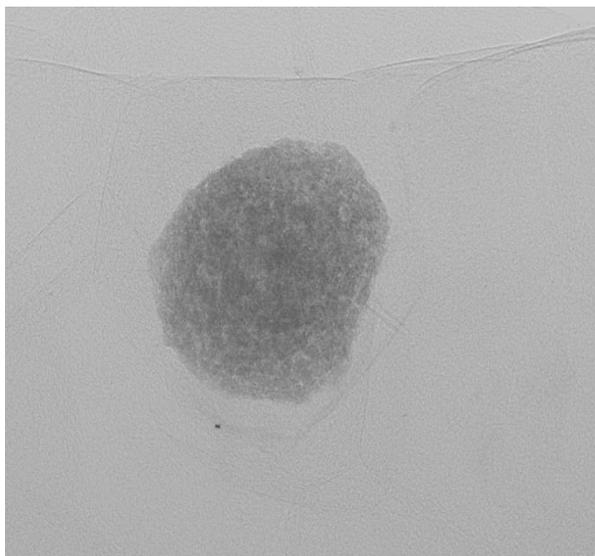


Figure 4.10 XRCT scanned image of core granule (15 minutes granulation, 14 rpm, size 2–3.35mm)

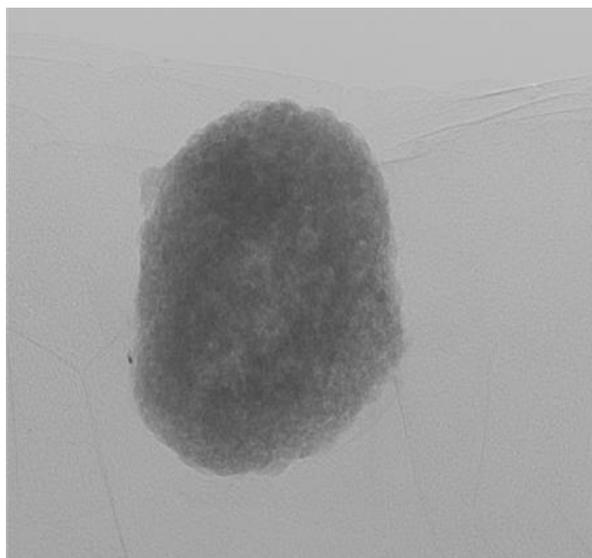


Figure 4.9 XRCT scanned image of double layer granule (with 2.5 % starch hydrogel binder binder)

Fig. 4.9 and Fig. 4.10 are the raw images from XRCT scan. The white spots indicate the air or pore space in the granules. It is clear that there are many small pores inside the core granule. For the two-layer granule, the color of the centered core is different from the outer layer, which is because the density of core was higher than the outer layer.

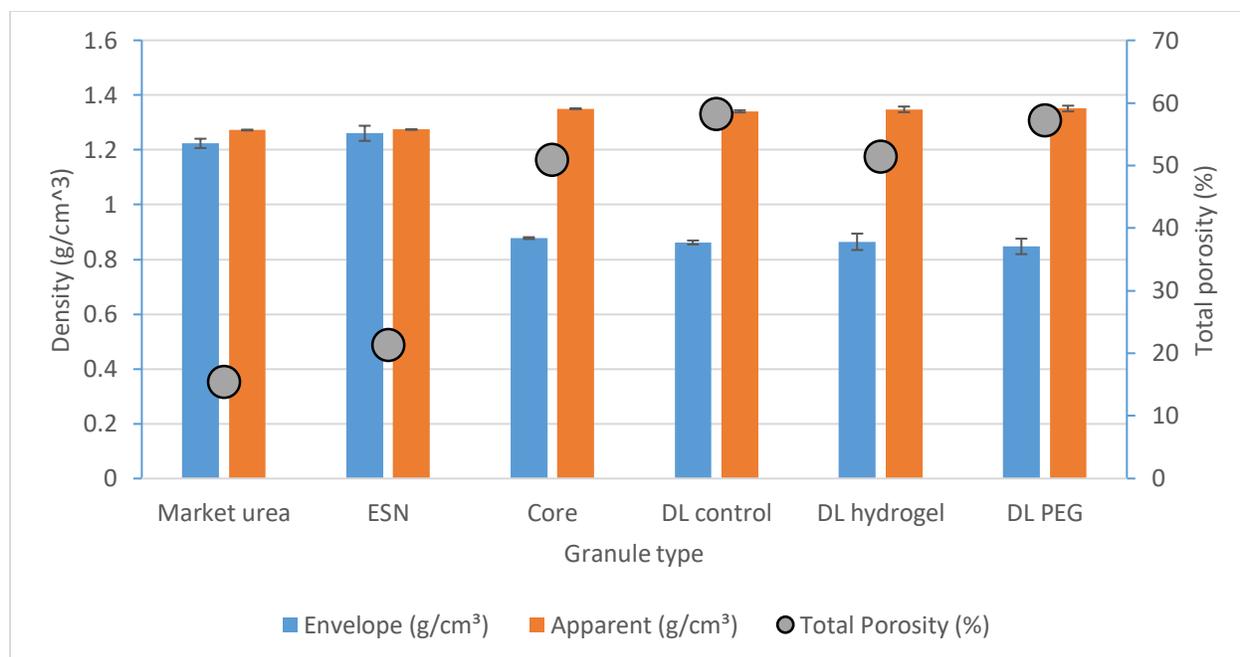


Figure 4.11 Density and internal porosity of selected samples

The target is to make a two layer granule that is similar in size and fracture pressure as market urea but with a much lower dissolution rate. The normal market urea granule, ESN, core, and three types of double layer granules' density and internal porosity are listed in Fig. 4.11 and Table 4.2.

Table 4.2 Density of two-layers granules.

Sample	Envelope density (Kg/m³)	Apparent density (Kg/m³)
Urea	1.22± 0.02 ^a	1.27±0.01 ^b
ESN	1.26± 0.03 ^a	1.27±0.00 ^b
DL Control	0.86±0.01 ^b	1.34± 0.00 ^a
DL Hydrogel	0.86±0.03 ^b	1.35± 0.01 ^a
DL PEG	0.85±0.03 ^b	1.35± 0.01 ^a

For all the self-made granules, there is no statistically significant difference in the envelope and apparent density. However, the core did had a relatively lower internal porosity than the other three types of double layer granules, which is mainly because of the low density of the second layer. Among the three types of double layer granules, the one with starch hydrogel did show relatively low internal porosity, which is similar to the core. Braumann (2010) claimed that more viscous binders tend to led a porous particle ensemble. However, this can't be proved in this experiment as granule porosity is also affected by many other factors, such as surface structure (Rieck et al, 2015), granulation rpm, granulation time, and liquid-solid ratio. For the market urea and ESN samples, the envelope and apparent density are quite similar, while ESN had a higher internal porosity than market urea, mainly because of the added polymer coating. Overall, the two-layer granules showed about 30% lower apparent density and 10% higher envelope density than the market urea and ESN. However, the internal porosity of the two-layer granules was more than 2 times higher than the market urea and ESN. The relatively low fracture pressure of the two layers granules is also a provident of this.

4.3.4 Dissolution Behavior of Two-layer Granules

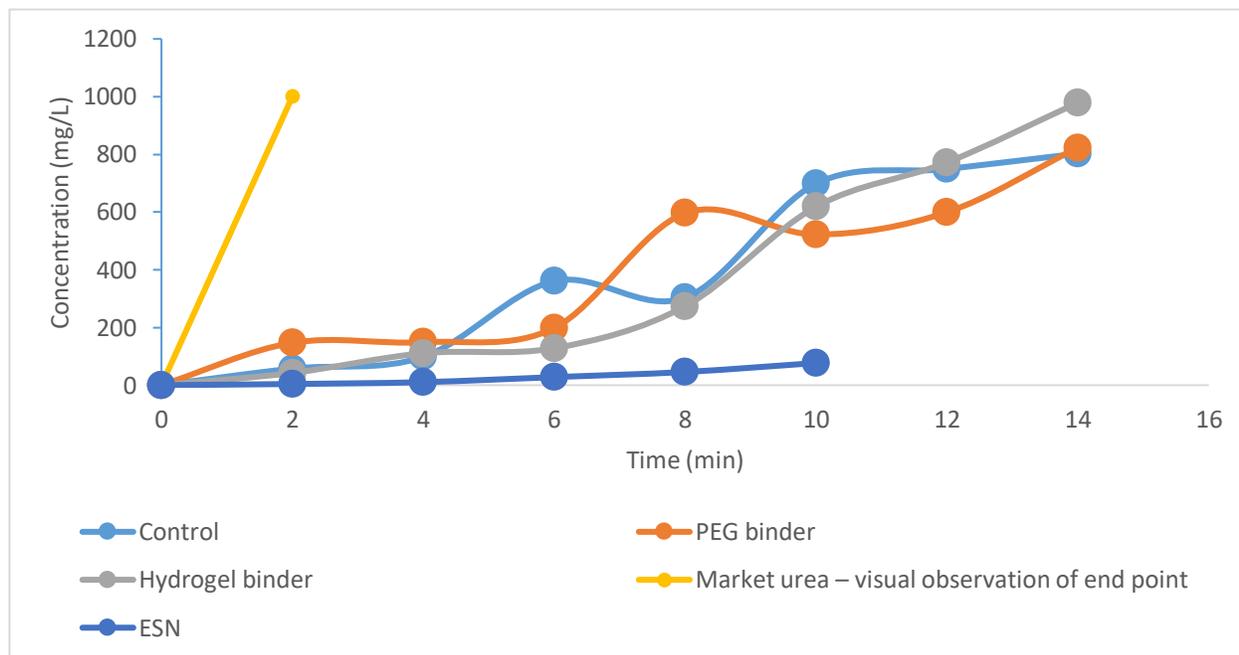


Figure 4.12 Two-layer granule dissolution rate measured using UV spectrometer

The dissolution rate results are shown in Fig. 4.12. It is evident that the ESN shows a very slow dissolution rate with progression of time. On the contrary, the market urea shows a fast dissolution rate. For all the three types of two-layer double layer granules, the dissolution rate was within the range between market urea and ESN. The change in dissolution rate pattern may be because of the sample solution volume accuracy error or due to the sample's dissolution properties. The granule with starch hydrogel binder had a uniform pattern with low fluctuation. Where in the dissolution increased slowly at the beginning and then increased rapidly, that indicated the nutrient release rate is slow at the beginning and then becomes higher with increase in time. The dissolution pattern of this granule was similar to the crop demand curve (Fig. 2.5.).

When comparing Fig. 2.5 and Fig. 4.13, it is clear that the market urea granules dissolve too quickly, while the ESN dissolve too slowly to meet the crop requirement. The two-layer granules manufactured in this work fit the crop demand curve much better than the commercial fertilizers, which means that the granule will release nutrient matching crop needs.

4.4 CONCLUSION

The smaller size of the granule (core) had a similar fracture pressure as the normal market urea, but the dissolution rate was more than 80% lower. For the two-layer granules, the granule with corn starch hydrogel binder in the second layer showed the best performance. The fracture pressure is roughly 28% less than the normal market urea; however, the dissolution rate is 80% lower. The dissolution pattern showed that this granule released nutrients slowly at the beginning. As the added hydrogel has a better holding capacity in the outer layer, the initial nutrient release rate is slow. Then, once the outer layer is fully saturated, the nutrient from the second layer with a starch binder releases the nutrient. At the same time, the total porosity of these double layer granules is higher than market urea.

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CHAPTER 5. SUMMARY OF CONCLUSIONS

5.1 Restatement of Research Objectives and Goals

This thesis work measured the physical property (including particle size distribution, fracture pressure, thermal property, density, internal porosity, and dissolution of urea and ESN granules) of some common fertilizer samples (including urea and ESN granules, Florikan, Osmocote, Everris and the two types of the Andersons). In addition, a two-layer slow release fertilizer was manufactured. The primary objectives of this research, as stated in CHAPTER 1, are:

- To characterize the physical and chemical properties of market urea, ESN, Osmocote, Florikan, Everris, and the Andersons A and B.
- To design a two-layer slow release urea granule and characterize its physical properties and dissolution behavior.

5.2 Major Findings

The particle size distribution of urea and ESN samples, Florikan and Osmocotesamples were relatively narrow, compared with the two types of the Anderson samples. Narrow particle size distribution can avoid segregations during handling and transportation. The added coating materials didn't alter the urea's thermal property, which mainly because of the small amount of coating materials applied. The thermal properties of NPK compound fertilizer and urea granule are quite different, NPK fertilizers had more than 10 times burning residue than urea and ESN, mainly because of the phosphorus and potassium compounds' decomposition temperatures are higher than the testing temperature (700 °C). The coating material didn't result in significant density differences between urea and ESN. The density of NPK compound fertilizers showed significant difference with urea and ESN. The internal porosity of NPK compound fertilizers were lower than urea and ESN while the closed pore volumes were larger, meaning less number of closed pores available in the granule, resulting in a higher density and fracture pressure. The added corn starch did extend the urea dissolution time. And 5% corn starch didn't alter the urea thermal property. With second layer added, among the second layer binders, control (pure

urea powder), 5% PEG 4000 and 5% corn starch, the 5% corn starch hydrogel worked best. The granules with hydrogel as the binder showed a relatively higher fracture pressure and lower porosity. More importantly, the dissolution granules with hydrogel binders showed a slow dissolution at the beginning and faster in the second half, which better fit the crop demand curve. Overall, the fracture pressure of all drum granulated granules is 10-30% lower than urea and ESN. However, as long as the granule strength was enough to prevent any breaking attention during handling. These two-layer granules will be highly applicable for production purposes.

5.3 Future Work

- Increase the drum granulation yield by refining operational variables
- Calculate the economical cost of double layer granules in a pilot scale granulator
- Studying the dissolution of layered granules in soil medium
- An alternative cheaper binder would reduce the production cost

APPENDIX A: GRANULATION TRIALS

1. Effect of Granulation Temperature:

Urea powder with a size range of 212—600 μm were loaded in a 40 ml glass with a magnetic stirrer at the bottom to mix the powder well. The beaker and the urea powder were heated to different temperatures: 22°C, 40°C, 60°C with distilled water. The liquid/solid ratio was maintained at 11%. With the rotation of the magnetic stirrer, the granules were produced. The rotation time was 3 minutes. All the granules were overnight dried and fracture pressure was measured.

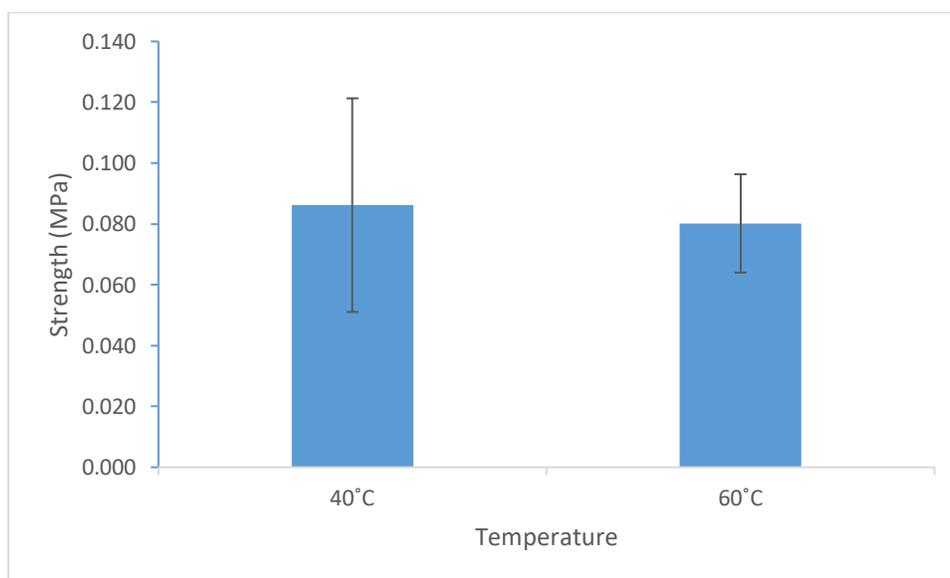


Figure A. 1 Granule fracture pressure at different temperatures.

2. Urea Tablets Manufactured by Compaction:

Pure urea tablets were made using ground urea powder with a size range of 212-600 μm with 40 MPa, 80 MPa and 160 MPa compaction pressure. For compaction, the urea powder was weighed

and loaded in a die followed by compaction at different pressures using the MTS. The dissolution rates were measured by visually operation.

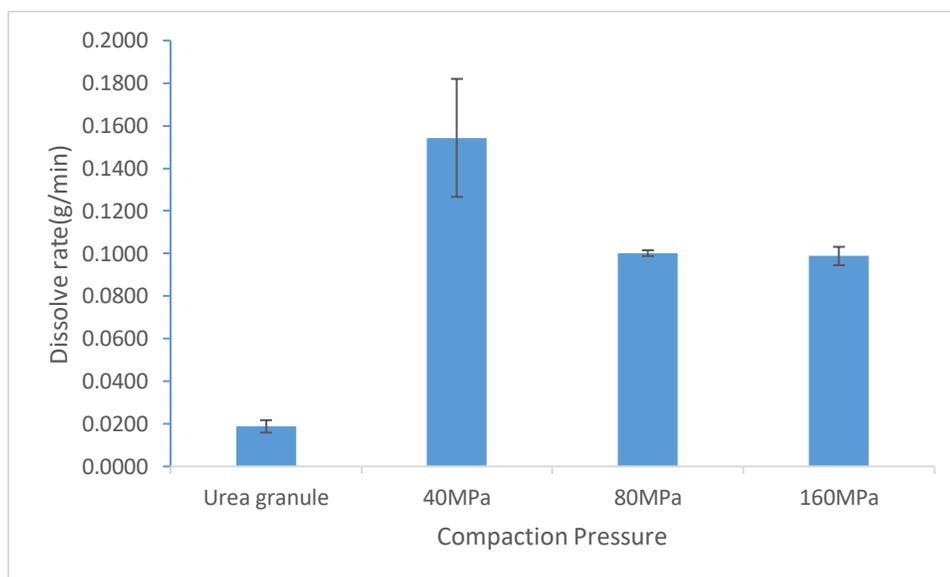


Figure A. 2 Dissolution rate of tablets made at different compaction loads

3. Selection of Binder:

Different binders, including PEG, corn starch, waxy corn starch, corn starch slurry and H_2SO_4 were tested as the binder for the urea granulation. The trails are listed in Table. A.1. The liquid/solid rate was set at 8% and the granulation rotation speed was set at 15 rpm with a 3-minute granulation time. After granulation, the samples were dried overnight. The performance of the granules was tested using isua observation dissolution and by measuring the mechanical strength.

Table A. 1 . Granulation trials

Trials	Binder
1	PEG (37%)
2	PEG (47%)
3	PEG (37%) + Normal Corn Starch
4	PEG (47%) + Normal Corn Starch
5	Normal Corn Starch + Water
6	Waxy Corn Starch + Water

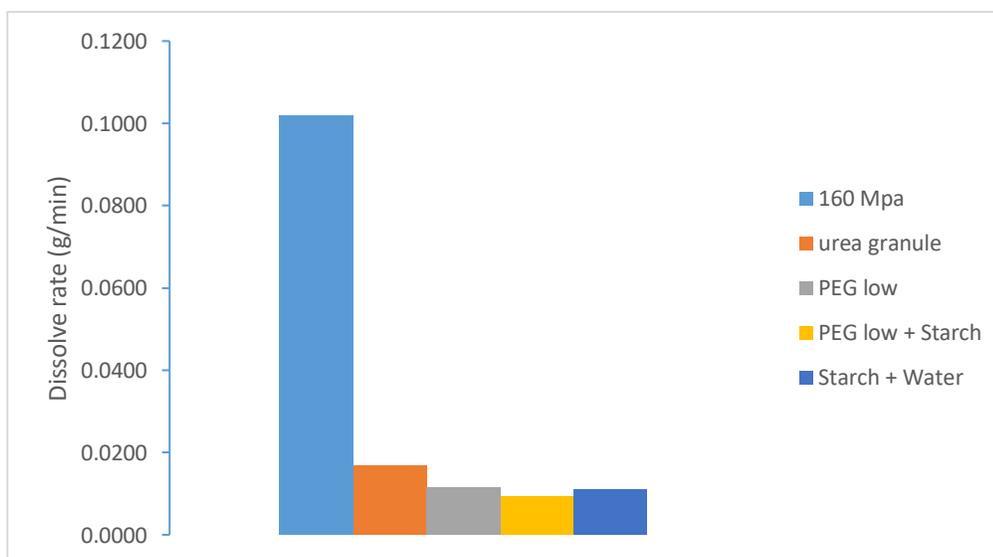


Figure A. 3 Dissolution rate of granules manufactured with different binders

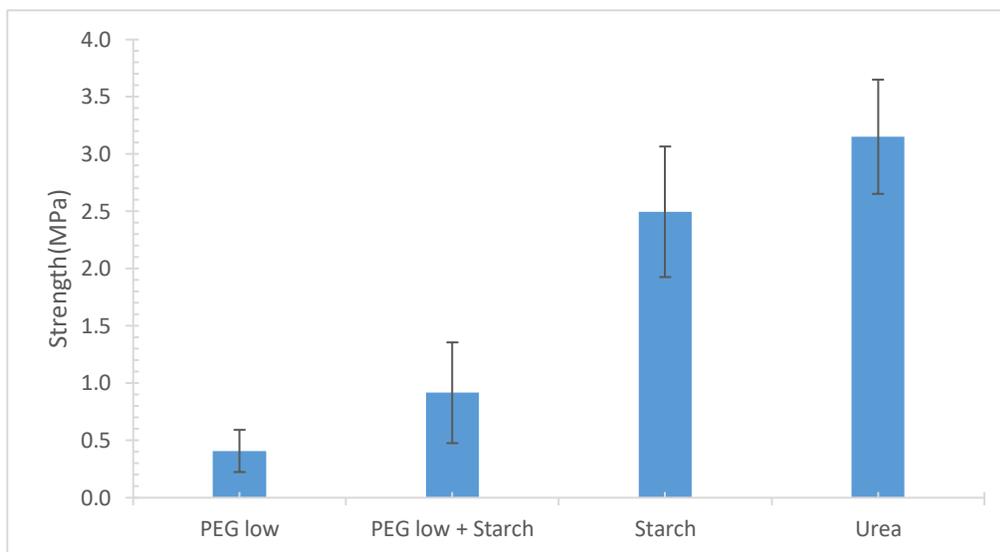


Figure A. 4 Fracture pressure of granules made with different binders

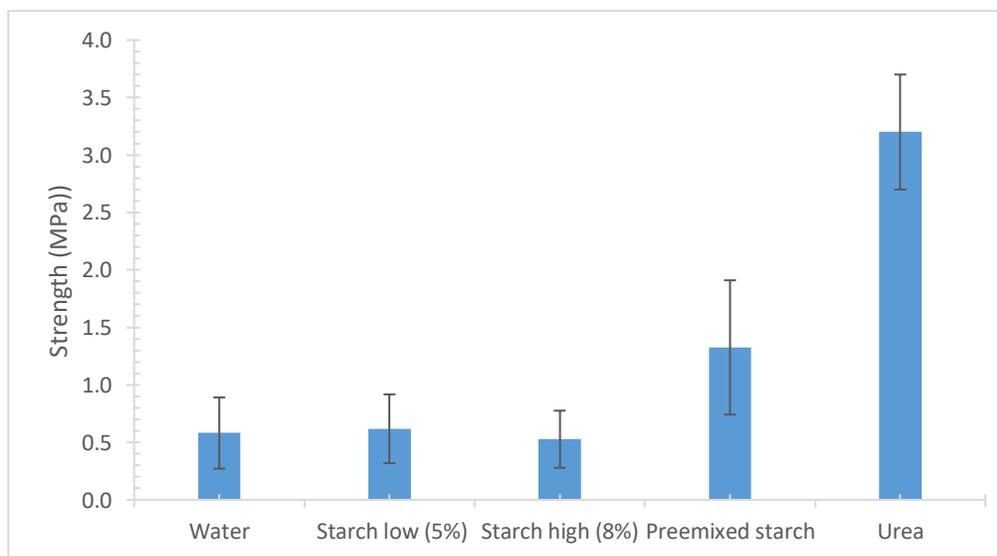


Figure A. 5 Fracture pressure of granules with different percentage of starch binders

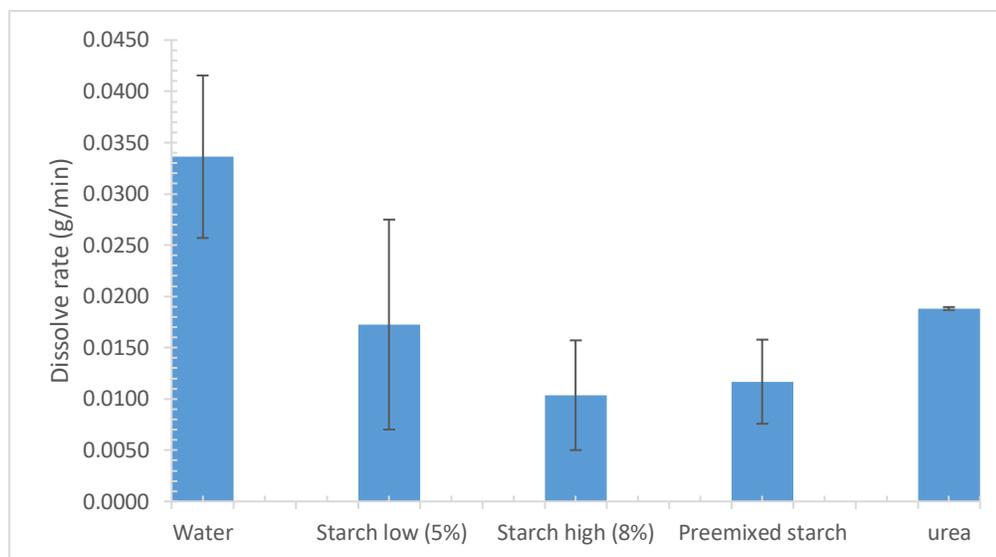


Figure A. 6 Dissolve rate of granules with different amount of starch binders

4. Size of Urea Powder:

In order to get a better granulation result, the market urea granules were ground using a ball mill and the urea powder less than $212\ \mu\text{m}$ was used in granulation. The liquid/solid rate was kept at 11%. Water, 5% corn starch and 8% corn starch were applied as the binder with a 20 rpm granulation speed under 11 and 15 minutes granulation time. The granules within a size range of 2—3.35 mm were used as core granules and some double layer granules were further made using cores. The visually checked dissolution rate and fracture pressure were measured using standard procedure.

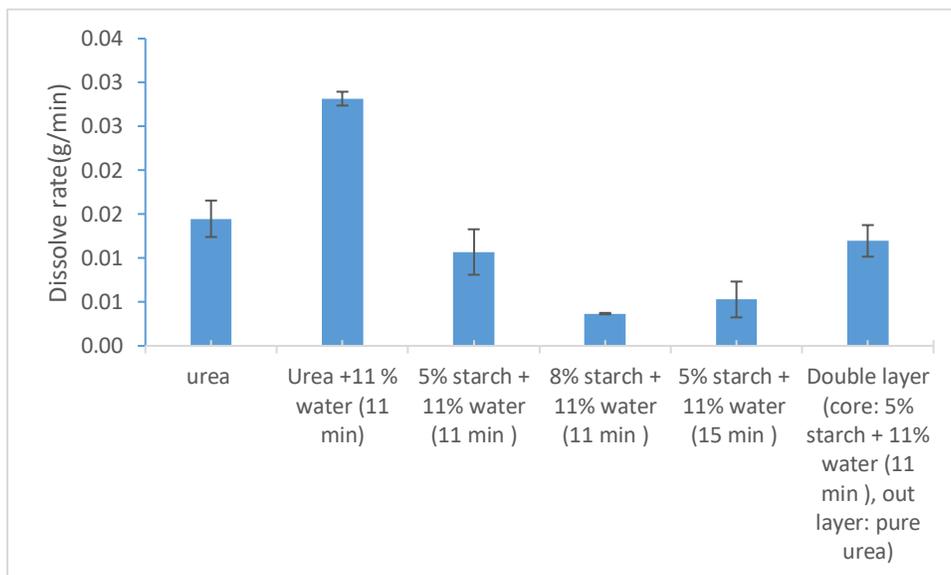


Figure A. 7 Dissolve rate of granules with different granulation times and binders

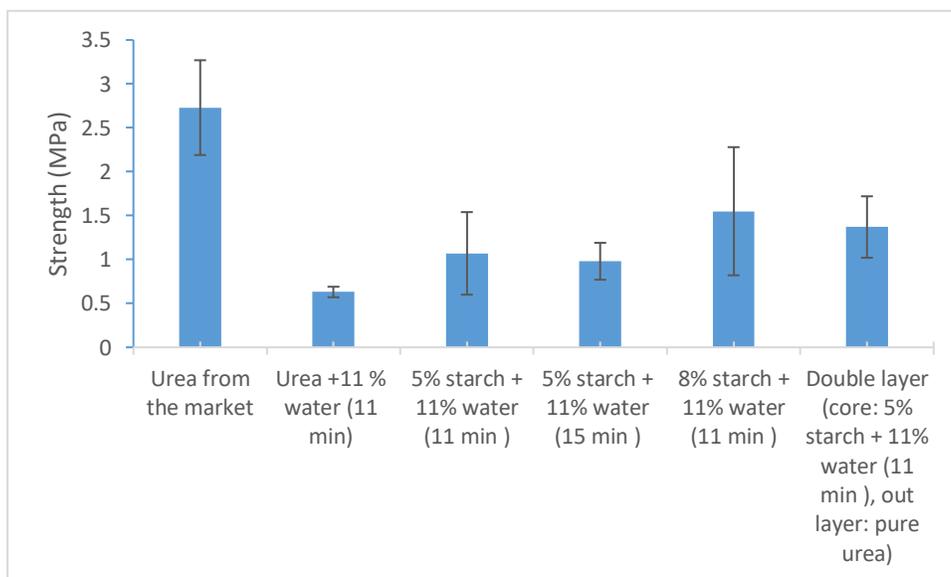


Figure A. 8 Fracture pressure of granules with different granulation times and binders