Study the Effect of Granular Urea Fertilizer Coated by Biodegradable Materials (Starch/ Polyvinyl Alcohol / Glycerol)

Salma Awad Nouh 1*, Dulail Nasir Hassan Algabary 2, Kuzialti Ku Shaari 3, Aisha O. M. Ahmed 4

1.3 Department of Chemical Engineering, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia.
2. Faculty of Applied Sciences, Department of Chemistry, Taif University, Turaba branch, KSA.
4. Faculty of Engineering, Chemical Engineering Department, Red Sea University, Port Sudan, Sudan

* salmanouh@gmail.com

Abstract
Several techniques has been developed to reduce the nitrogen loss of urea fertilizer and produce more capable nitrogen fertilizer, but most of these techniques have led to many environmental problems such as high concentration of toxic, nutrient waste, eutrophication and global warming. Thus the aim of this study is to investigate a new generation of environmentally friendly fertilizer using biodegradable binder and urea as the main nitrogen source. The starch/ Polyvinyl Alcohol (PVA)/glycerol in the composite films were prepared in different formula of chemical proportion. The influence of the blending ratio biodegradable starch/PVA/glycerol in coating urea has found that, coated urea dissolution rate in water decreased as the amounts of Starch, PVA, and Glycerol in the composite film increase. Therefore, the swell ability of the composite film is increased and the urea is released from the composite film in the wet environment. The soil burial biodegradation results indicated that the biodegradability of Starch, PVA, and Glycerol/ urea composite film strongly depended on the PVA.

Keywords: Biodegradable, Coating, PVA, Granular Urea.
Introduction

Within the wide variety of industries that utilize granulation to produce particles with defined properties, the fertilizer manufacture has an essential role in securing food supplies around the world. Currently, it accounts for approximately 51% of the world’s agricultural nitrogen consumers [1]. Urea is one of the most often used nitrogen-based fertilizers because of its high nitrogen content (45%), being marketed as prills or granules. The last form is the preferred route of production, since the particles are larger, harder, and more resistant to moisture than prills. As a result, urea in granular form has become a more suitable material for fertilizer blends [2]. However, about 20–70% of the applied urea fertilizer is lost to the environment, causing serious pollution and increasing costs. The losses are due to leaching, decomposition and ammonium volatilization in soil, handling and storage [3]. The Controlled-release fertilizers (CRFs) are now the most widely used fertilizers in the nursery industry for container-grown plants. A fundamental motivation for the development of CRFs has been the goal of delivering nutrients to plants at a rate that closely approximates plant nutrient demand over an extended period [4, 5]. Fertilizers with this ability can provide many benefits to agriculture, such as greater nutrient use efficiency, better plant growth and quality, lower labor costs, and reduced fertilizer runoff pollution [3, 4 and 5]. At present, CRF coating materials are composed of either sulfur or polymeric substances, or a combination of both. Polymer-coated fertilizers (PCFs) are now the most sophisticated and advanced means of controlling nutrient release and fertilizer longevity. Although polymer-coating technology is quite expensive compared to other CRF technologies [5], still there has been an increasing interest in the use of polymers combining with starch as coating material over the last years. Starch is one of the most abundant biopolymer and fully biodegradable,
renewable and environmentally friendly, therefore, research frontiers have been shifted towards the investigation of starch base coating biodegradable materials such as polymer polyvinyl alcohol (PVOH) which has been studied as a potential biodegradable polymer [1-11].

**Urea Coating Process**

Coating is a process to generate a thin layer or film on the surface of the granular. In most cases, the coating is introduced in a liquid form (often aqueous polymer dispersion) and the solvent is evaporated. Depending on the granular dimension and coating functionality, the film thickness varies between 5 µm and 100 µm [12]. Although coating systems are quite diverse, the underlying principle of most of the modern systems is the same (Figure 1) [13].

![Diagram of coating process](image)

**Figure 1:** General principle of a particle coating process. (Coating in the spray zone, transportation and drying, re-enter the spray) appears in most types of coating units. [14]

Several studies have been reported for the use of starch [15, 16], cellulose derivatives [17, 18] chitosan [19, 20]. Starch is abundantly available naturally occurring polysaccharide polymer which is cheap, biodegradable, renewable, and environmentally friendly [21]. Starch blends with polyvinyl alcohol (PVA) coating film, it is biocompatible [22], biodegradable and green polymer blend [23], Han
[23] studied biodegradability and controlled release characteristics of starch/polyvinyl alcohol blends (St-PVA) in the presence of formaldehyde as a crosslinker. Tudorachi [24] investigated biodegradation of St-PVA/glycerin/urea blends in the presence of microorganisms. Hence the objective of this work is to investigate a new generation of environmentally friendly urea fertilizer using biodegradable binder starch/PVA/glycerol.

**Equipment Used in the coating process**

In industries there are different coating equipment have so far been employed to produce CRFs including immersion technique, rotary pan/drum coating [25, 26], and film coating in fluidized/spouted beds [27, 28]. Amongst them, coating in fluidized beds “which are, top spray, side spray, bottom spray and Wurster systems (Figure 2)” is considered more appropriate due to its inherent advantages of superior heat and mass transfer characteristics, good mixing, coating uniformity, isothermicity, single unit operation, and reduced processing time [29]. The principle of coating process in a fluidized bed involves fluidization of the fertilizer granules by hot air introduced from the bottom, spraying of the polymer suspension, wetting of the granules by droplet spreading, evaporation of the solvent and coverage of the surface by the polymer film [30]. Several studies have been reported for the use of fluidized beds for the production of CRU [27, 28]. Another type of such coating equipment is the rotary fluidized bed coater (RFBC). It is equipped with a motor driven rotating disk at the base. The centrifugal force by the rotating disk pushes the granules outward towards the equipment wall.
Nevertheless, fluidized bed technology is a common step undertaken in the course of processes used in chemical, agricultural, pharmaceutical and food industries over fifty (50) years. Solid-containing liquids like solutions, suspensions or melts are transferred to the solid state by spraying into a fluidized bed of particles [31]. In most cases, this phase transition involves growth of the particles. Three different growth mechanisms can be distinguished. If the sprayed liquid acts as a binder, and clusters of initial particles are formed, the process is called spray fluidized bed agglomeration; fluid bed spray agglomeration is similar to the fluid bed granulation, use in food powders agglomeration [32] and laundry powder agglomeration [33]. The second mechanism when fluidized beds operate under drying conditions, evaporation capacity of the bed increases sufficiently drying the particle surface before collision thus terminating the formation of liquid bridges [34]. The researches by Smith and Nienow [35] and Maronga and Wnukowski [36, 37] have shown that particles are uniformly wet in a so-called wetting zone which is a small region in the vicinity of the spray nozzle. The repeated wetting – drying cycle of fluidized particles creates of a uniform, layered structure around individual particles; this type of particle growth is called
“layering” [35]. Layering represents the preferred growth mechanism in coating applications. Dry processing conditions are required to improve the layered growth mechanism. Under such conditions, however, considering the fact that the coating solution is sprayed counter currently with the fluidizing air, premature droplet evaporation is likely to take place before droplet can come in contact with particle surface [38], is called spray fluidized bed coating in case of a different material is sprayed onto carrier particles, forming a layer on the surface of the particles. This process is used, to produce pellets for a controlled release of pharmaceuticals [39], to ensure a controlled release rate of pharmaceutical ingredients [40] or for encapsulation of anti-oxidants [41] (Figure 3). However if the sprayed liquid contains the same material as the initial particles, the process is called spray fluidized layering. This mechanism can be used, to produce large fertilizer granules from small initial crystals [42].

**Figure 3:** Overview of fluidized bed coating operation. [43]
Methodology

The objectives of the experiments is to study the effect of starch, PVA, glycerol at different ration as adhesive in urea fertilizer on water dissolution and absorption behavior, soil burial degradation

A. Materials & Preparation of coating solution

The granular Urea (Sabic, Saudi Arabia) was sieved in sieve tray 2 mm of diameter. Starch, PVA, Glycerol, and Formaldehyde were of analytical purity. The coating solution were produced as follow. The calculated amounts of starch, PVA, glycerol and 0.5 gram formaldehyde were mixed at various ratios (starch content is from 0 – 2 wt%) and mixture was slowly added water of 10 mL at room temperature under continuous stirring until homogenous. Then, thus coating solution is ready for use (Table 1).

B. Apparatus

The fluidized bed was made from a flexi glass. A spraying nozzle of an air-atomized nozzle was centrally set above the fluidized bed. Urea particles of 100 g in weight were put in the fluidized bed, and the bed was fluidized at higher than their minimum fluidization. The coating solution of 30 mL, at room temperature and flowrate of 0.5 mL/min, under a pressure was atomized with compressed air, and sprayed onto the urea particles in the fluidized bed for coating. After spraying a set quantity of coating material, the particles were taken out for analysis.

C. Dissolution rate

5 g of urea particles in a beaker containing 30 ml of double distilled water maintained at room temperature. Magnetic stirrer was used at constant speed. The time required for complete dissolution of urea was noted down [10], then compared with the uncoated urea.

E. Water Absorption Test

5g coated urea granules (W1) were immersed in 30 ml distilled water for 30min. the water solution was then separated from the residue by filtration and the water on the residue surface was absorbed by a filter paper, then the residue maintained
in the air at room temperature for 10 min to get rid of the surface water and then weighted ($W_2$) accurately.

The water absorption capacity (WA) of coating films was calculated using following equation: [10].

\[
\text{Water Adsorption}\% = \frac{(W_2 - W_1)}{W_1} \times 100\%
\]

**G. Soil Burial Degradation Test**

5 g of each coated urea sample was weighed and placed in agriculture soil in beaker at different soil moisture 5, 10, 15 % then the sample were maintained at ambient condition for 30 days. Degradation rate in the soil burial test was indicated by the weight loss of the sample with time.

**Table 1: Composition of the coating films.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Urea (g)</th>
<th>Distilled water (ml)</th>
<th>Starch (g)</th>
<th>PVA (g)</th>
<th>Glycerol (g)</th>
<th>Formaldehyde (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>10</td>
<td>0.5</td>
<td>1</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>10</td>
<td>0.8</td>
<td>1</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>E</td>
<td>10</td>
<td>10</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>F</td>
<td>10</td>
<td>10</td>
<td>0.8</td>
<td>0.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Results & Discussion**

The results shown were obtained from the experiments, the manipulating parameters were different ration of starch, PVA, and glycerol inside the coating film. The responses evaluated were:

**Dissolution rate**

Figure 4 describes the influence of polymer concentration (PVA) to the dissolution rate. The dissolution rate decreases when the concentration of PVA increases. This is illustrated by the increase in dissolution time occurred from 25 to 10 min at not
coated urea. Where the A, C and D show a higher resistance to water. Where the polymer serves as a physical barrier urea release into the environment. So the more PVA the more physical barrier on the surface of the urea which resulted in the release of the longer time and dissolution rate (release rate) is getting smaller.

![Figure 4: The influence of weight of PVA in coating solution on dissolution rate](image)

**Water Absorption Test**

As shown in Figure 5 the water absorption capacity of the coated urea increased along with PVA content (sample A & B) due to the properties of itself whereby PVA is a synthetic hydrophilic water-soluble polymer. The presences of hydroxyl groups in PVA are responsible for the tendency for water absorption of the coating films [10]. As far as the starch proportion in the coating film are concerned, it is found that the water absorption capacity increased as the amount of starch in the coating sample increased (samples C & D). This is consistent with the findings of Lum et al. [10] and indicated that starch is sensitive to water and can absorb a quantity of water.
**Figure 5:** Water absorption capacity of the coated urea

**Soil Burial Degradation Test**

Biodegradability of the samples in soils was studied for different soil moisture by evaluating percentage weight loss of starch/PVA/glycerol coating films over time (Figures 6, 7 and 8). After 3 weeks of exposure in soil, the coating film appeared brittle and fragile in size indicating the natural biodegradation of these films in the soil environment. The coating film degraded rapidly in the initial 7 days followed by slow degradation until the end of the experiment, this results for the low soil moisture (Figure 6), but when we increased the soil moisture to 10% and 15% the coating films degraded rapidly and with a high rate starting from 20% up to 80% for sample F (Figures 7 & 8) even for the high PVA content films. All the analyzed samples show important weight losses between 20% and 80%. In contrast it has been observed that, the higher PVA concentration in the coating film the higher the resistance against soil burial biodegradability. Thus it is suggested that most of the starch/glycerol/urea component degraded extensively, leaving the PVA component as residual [10].
**Figure 6:** Weight loss of samples exposed to soil for 20 days (5% soil moisture)

**Figure 7:** Weight loss of samples exposed to soil for 20 days (10% soil moisture)
Conclusion
Controlled Release Urea has been successfully produced by coating urea with starch/PVA/Glycerol using a fluid bed spray coater. Variation of the blending ratio of starch, PVA and glycerol influence the swell ability and biodegradability. Dissolution rate of coated urea products will be lower with the higher concentration of starch. The water absorption capacity of starch/ PVA/ Glycerol coating film increased along with starch and PVA content. From the biodegradability test it is observed that as the PVA content increased the biodegradability decreased.
References


[14] www.pharmatutor.org


[18] Pérez-García, S., et al., 2007 Controlled release of ammonium nitrate from ethylcellulose coated formulations. Industrial & engineering chemistry research, 46 (10) 3304-3311.


based thermoplastic compounds used in protheses: identification of the degradation products in solution”. Biomaterials, 25(13) 2687-2693.


particles with different glass transition temperatures”. Powder Technol. 20, 445–452.


