Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(11):83-87
(http://derpharmachemica.com/archive.html)

Effect of Bioblend Polystyrene/Polycaprolactone and Polystyrene/Starch Utilization toward Coating Thickness and Release of Active Substance from Urea Granule

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ABSTRACT

The effect of utilization bioblend polystyrene/polycaprolactone [PS/PCL] (F1, F2, F3, F4, F5) and bioblend polystyrene/starch [PS/starch] (F6, F7, F8, F9, F10) coating toward the thickness of the film formation and release of active substances urea granules had been studied. In this study, urea granule coated with bioblend PS/PCL with different variations of the number of PS. Evaluation of the original urea granule and product includes granules size distribution, film thickness measurement, and the release rate of urea in distilled water testing media. Results showed that bioblend polystyrene has a slow release characteristics because the release rate is lower than the non-coating urea granules. Spray coating method can produce urea granules with size of 1.5 - 3 mm with the film thickness range from 0.125 - 0.196 mm. According to the release kinetics model of order 0 with r values for the formula 2, 3, 4 and 5 respectively are 0.9992; 0.9995; 0.9997; 0.9992. Release of urea following the zero-order kinetics model means the release of urea occurs constantly from beginning to end. As for the formula 1, 6, 7, 8, 9 and 10 following the release kinetics model of Langenbucher, with the value of r for formula 1, 6, 7, 8, 9 and 10 respectively are 0.9927; 0.9582; 0.9779; 0.9591; 0.9330; 0.8990. The release following the urea kinetics model of Langenbucher means diffusion and erosion process happened in solution fraction, where there is no lag time or slow release at the early stage.

Keywords: polystyrene, polycaprolactone, starch, urea. bioblend. slow-release fertilizer.

INTRODUCTION

In modern agriculture, fertilizer becomes important aspect. These days, utilization of slow-release fertilizer or controlled-release becomes effective method to solve some issues from application of conventional fertilizer [1]. Slow-release fertilizer aims to increasing the efficiency of nutrient use by the plants and minimalizing the nutrient loss, so it will lessen the environment pollution and some health issues often associated with fertilization management. Not all of the conventional fertilizer given can be absorbed by the plants, where fertilization efficiency for urea only about 30-50% and rest of the fertilizer will be degraded or washed away by the water [2,3]. Using slow-release fertilizer will give some advantages such as increasing the efficiency, lessen the possibility of fertilizer loss by rain or irrigation, give continuous discharge for longer period, save on fertilizer consumption and minimalized the pollution [4,5].

Fertilizer coating had done by using several materials and methods to produce slow-release fertilizer. Selection and usage of coating material became a kind of effective approach to make an inexpensive and high quality slow-release fertilizer. One of the important factor to be considered in coating selection is the polymer coating compatibility level with urea. Good compatibility will increase the polymer coating efficiency with urea and extend the time of nutrients release of urea granule. Besides, thickness and strength of coating film will highly influence release level and pattern [6]. When the nutrients were released from slow-release urea has long period it will be suitable with the nutrient uptake period by the plants and the fertilization efficiency will be achieved [7].

Process of nutrient release from the fertilizer that coated by polymer happened by several stages, i.e: first stage, water will permeate the polymer layer. Second stage, after water come through core of urea the dissolution of urea core will occur and caused an inner pressure at the core of urea. There will be a swelling at the coating layer and diffusion pore will increase. At third stage, nutrients released through diffusion because it pushed by concentration gradient at the layer, or through the mass flow pushed by pressure gradient, or combination of these two [7,8].

The purposes of this study are to study the effect of urea coating of fertilizer using bioblend polystyrene toward the coating film thickness and release level of urea granule active substance.

MATERIALS AND METHODS

Equipment's: Hotplate magnetic stirer (Thermo Scientific), spectrophotometer UV-Vis (UV-1700 PharmaSpec), analytical balance (Shimadzu AUX 220), *Fourier transform infrared spectroscopy* (Perkin Elmer), pH meter (Thermo Scientific),oven, *Spray gun*and pump , *coating pan*, digital micrometer (Mitutoyo), glasses and other tools.

Materials: Polystyrene, polycaprolactone (Aldrich Chemical), cassava starch (Amprotab™, Bratachem), urea granule (PT. Pupuk Sriwijaya, Indonesia), chloroform (Merck), ethyl alcohol (Merck), reagen Erlich, and aqua DM.

Methods

Urea granule preparation

Before coating, all of urea granule washed using chloroform and then dried inside the oven at 50-60 ^oC. After that, the urea sorted for 1-2 mm to obtain the similar size.

Preparation of the coating solution

Coating solution PS/PCL made by combining 2 polymer with the comparation of polystyrene : polycaprolactone 2:1, 3:1, 4:1, 5:1, 6:1. The formula with 2 : 1 comparation was made with mixing 1 gram polystyrene with 0.5 gram polycaprolactone and dissolved in 50 ml chloroform. These solution was stirred using magnetic stirrer with 380 rpm speed for 15 minutes. The preparation of bioblend polystyrene/starch coating solution has the same procedures with preparation of bioblend polystyrene/polycaprolactone coating solution.

The Coating

As much as 25 gram of urea granules was put into the coating pan, coating solution poured into a spray gun. Then, urea granule was sprayed by the coating solution, the rotary speed of coating pan was adjustable and the temperature set for 60-70 °C. After that, the urea granule was dried using oven at 70-80 ^oC temperature for 1 hour.

Granule size distribution measurement

Granule size measurement had done by digital technique using software imagej version1.48v. The photo shoot for measurement used macro photography technique by DSLR Canon 1100D camera with macro lens Canon EF-S 60mm f/2.8 Macro USM Fixed Lens. From the digital measurement with software imageJ, granule size datas was obtained and then processed using software OriginPro [9–11].

Film Thickness Measurement

Film thickness measurement was done by using digital micrometer. Coating film that released from urea granule was assembled on digital micrometer. The film thickness will be showed at micrometer screen.

Release test and determination of urea level

a. Release test in water media

In this evaluation, 1 gram of bioblend-coated urea was dissolved into 500 ml distilled water. The water sample then collected every 1, 3, 6, 12 and 24 hour, then analyzed using spectrophotometer [5, 12-14]. On slow-release preparation, release profile or release kinetics model can be known by dissolution test of release test. The result from release test will be put into a drug-release model equation, i.e orde-0, orde-1, Korsemeyer-Peppas and Higuchi, so the release mechanism for slow-release preparation can be known.

b. Urea level determination

Determination of urea using spectrophotometric methods and color-forming reagents para-amino benzaldehyde (DMAB). According to Erlich reaction (DMAB) can react with urea to form the color kelly lemon (yellow-green color) which will absorb visible light at 420 nm, the color formed should be stable after 10 minutes [13.15-17]. Reagent solution is prepared by dissolving 2 grams of DMAB in 95% ethyl alcohol (90 ml) and concentrated hydrochloric acid (10 ml). To determine the amount of urea, a calibration curve made with a standard solution with a concentration of 5, 10, 20, 40, 60, 100, 400, 600, 800, 1000 and 1200 ppm.

RESULTS AND DISCUSSION

Granule size distribution and film thickness

Film thickness and film strenght that produced by spray coating method will depends on polymer coating characteristic, tools operation that will affect the whole mechanism of coating film formation. Formation of coating film could be explained in 3 steps, those are (1) coating polymer drops reach the substrate, (2) coating polymer drops spreads on substrate, and (3) dewatering of coating polymer and formation of coating film layer. Those steps repeated over and over when spray coating process happened until the whole film formed (Figure 1).

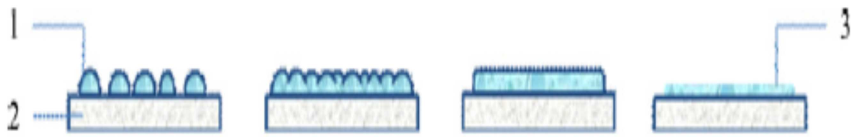

Figure1. Steps of spray-coating film formation, (1) polymer drops, (2). urea substrate, (3) film layer [1, 18]

The solvent from polymer which sprayed to urea substrate in certain interval will be evaporated and gone by the hot air flow. Dewatering capacity significantly affects spray coating process. When dewatering capacity suitable with the entry of solvent amount, then a good film layer will be produced. Otherwise, when dewatering capacity is not enough, then damping will happened and aggregate formed. But, too fast dewatering will caused the shortage of solvent for the drops, then it will formed bubbles inside the film because drops has high viscosity and the spreads will be weak and uneven. Uneven polymer spreading at urea substrate will create many small pores inside the coating film. The layer of coating film which formed will be weak and not compact due to the rough surface and not solid component [1, 18].

The result of coating film's thickness showed different thickness for each formula, ranged from 0.125 - 0.196 mm (Table 1). From the result of granule size distribution measurement, it had known that granule distributed with range size 1.5 - 3 mm (Figure 2). The greater mass of coating polymer, the more coating bound to the surface of the urea [19]. Besides, compatibility level between those two polymer also highly influenced, this can be seen in Table 1.

Table 1. Thickness of the coating film of urea granule produced from various formula of bioblend

No.	Formula code	Mean thickness of coating film (mm)
1	F1	0,150
2	F2	0,158
3	F3	0,193
4	F4	0,193
5	F5	0,196
6	F6	0,150
7	F7	0,152
8	F8	0,145
9	F9	0,125
10	F10	0,133

At formula 1, 2, 3, 4 and 5, the coating film thickness was increased together along with the increasing of coating polymer amount. This happened because the compatibility level between bioblend polystyrene and polycaprolactone is very good [20]. But, at formula 6-10, there was decrement of film thickness with the increasing of polymer polystyrene mass. Coating polymer used in formula 6-10 was bioblend PS/starch, and has poor compatibility level between the component. If combination compatibility from the two polymer was low, then the coating film formation level at urea granule surface will be low too.

Besides, the film formed will be fragile and weak. The case of mixing a polymer such as polystyrene bioblend, where polystyrene is easily lose solvent will produce dust (dustiness). The more number of polystyrene in the mixture formula will make the greater possibility of the dust, thereby decreasing the film thickness of the coating.

Dust or dustiness is very undesirable in the coating process, either in the process of coating urea and in other coating applications. Dustiness led to a number of material lost during the coating process, the storage or during use. Dust occurs because the polymer coating material can not bind strongly to the surface of the urea granules. Besides the dust can be formed because the operation of the tool is not appropriate, especially on the temperature setting, where the higher temperature of the bed will speed up the drying of coating process, quick drying process will caused the bond between coating surface of urea with a polymer coating on the wane (not formed) which will reduce the level of film formation on the surface of the granules. The research explained that the amount of dust formed with larger particles on dry coated urea particles than the wet coated urea particles. There will be a lot of dust formation when the dry coating particles presents, because the coating polymer material can not form a strong bond with urea surface.

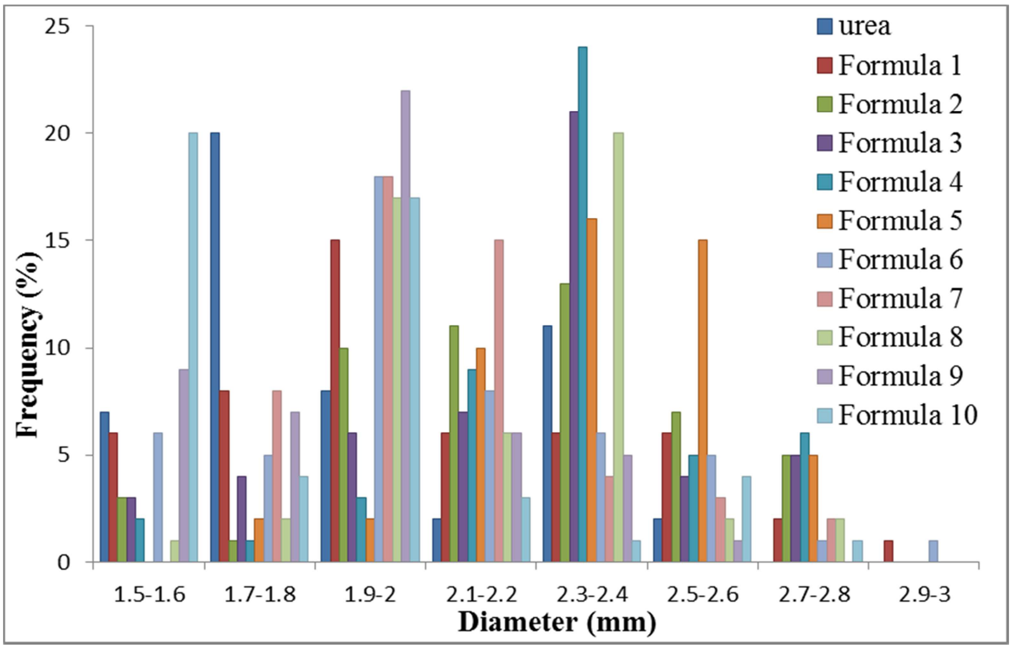

Figure 2. Profile of urea granules size distribution from various formula of bioblend

Amount of urea release in water media

The release testing of coated urea bioblend polystyrene at room temperature with distilled water media shows within 24 hours, released urea was more than 80%, only the formula 2 and 3 which has released less than 80% urea (Table 2). This is because the coating films formed is not too strong, which caused the film can not resist the pressure of the core urea granule and resulted in broken of coating film layer. To explain the mechanism from the release of coated urea bioblend polystyrene/polycaprolactone and biolend polystyrene/starch in distilled water at room temperature it can be divided into three stages. In the tolerate period (lag time) (i), water passes through the coating layer bioblend polystyrene, but urea is not released. The lag period is determined by the coating percentage by bioblend polystyrene and the similarity of coating layer. ii) Period/time of constant rate release: urea inside the core was started to dissolve and taken out by the coating layer. Urea concentration inside the core was really dense in this stage and will be occured until all of urea in the core completely dissolved. iii) Declining stage: Urea inside the core completely dissolved and urea concentration started to declined [7, 8, 21].

Table 2. Amount of urea release toward time for each formula in distilled water media

Sample formula	Amount of urea release for every hour (% w/w)					
	0	1	3	6	12	24
Formula 1	0	6	17	37.6	75.9	95
Formula 2	0	2.7	7.7	17.3	34.2	66
Formula 3	0	3.2	9.5	20.4	37.8	76
Formula 4	0	3.4	10	21.2	40.1	80
Formula 5	0	4	11	25.6	47.0	96
Formula 6	0	8,5	26,0	53,0	95,6	95,6
Formula 7	0	8,0	24,0	50,1	92,9	97,1
Formula 8	0	10,0	31,0	63,8	98,3	98,4
Formula 9	0	12,1	35,0	77,7	93,9	93,9
Formula 10	0	14,0	42,0	90,8	96,6	96,6

Kinetics release profile on water media for formula 2, 3, 4 and 5 is following the orde 0 kinetics model. In this model r value for formula 2, 3, 4 and 5 respectively were 0.9992; 0.9995; 0.9997; 0.9992. Release of urea following the zero-order kinetics model means the release of urea occurs constantly from beginning to end. If the formula following the Korsemeyer-peppas model, it means the urea release based on Fickian diffusion mechanism. As for the formula 1, 6, 7, 8, 9 and 10 following the release kinetics model of Langenbucher, with the value of r for formula 1, 6, 7, 8, 9 and 10 respectively are 0.9927; 0.9582; 0.9779; 0.9591; 0.9330; 0.8990. The release following the urea kinetics model of Langenbucher means diffusion and erosion process happened in solution fraction, where there is no lag time or slow release at the early stage.

CONCLUSSION

The used of the bioblend polystyrene as a coating for urea granules by spray-coating technique was suitable for the production of slow-release urea. Where in the polymer coating processes and materials greatly affects the film thickness, the size of the granules and release profile of the active substance. The thickness of the film formed depends on the nature of the compatibility between the surface of the polymer blends and granular urea. The film thickness will affect the strength of the film coating, which ultimately will affect the release rate and slow the rate of release of nutrients from the polymer-coated fertilizers.

Acknowledgements

Authors appreciate to Ministry of Research, Technology and Higher Education, Republic of Indonesia. Part of this work is supported by Penelitian Ipteks, Simlitabmas Research Grant, Ministry of Research, Technology and Higher Education, Republic of Indonesia, Fiscal Year 2016, Contract No.020/SP2H/LT/DPRM/II/2016, University of Andalas, Padang, Indonesia

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