

Slow-Release NPK Double-Coating Granules Using Bioblends Polystyrene–Polycaprolactone as a Coating Polymer

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Abstract: Formulation of coatings have been carried out to obtain slow-release NPK granules by double coating technique using cheap and environmentally friendly coating and solvent materials, polystyrene (PS) and biodegradable polymer polycaprolactone (PCL) using ethyl acetate solvent at a pilot scale production stage. PS, a non- biodegradable polymer was mixed with PCL biopolymers to obtain the suitable characteristics of biodegradable to form pores. PS - PCL bioblends have good compatibility with NPK granules that can reduce the release of nutrients from fertilizers. Results showed that the release rate of double-coating NPK granules obtained was slower than the non-coated NPK granules and single-coating NPK granules as well. The release of active substances in distilled water media after 48 hours from un-coated, single coated, and double coated NPK granules were 84.56, 25.02, and 21.05 %, respectively. The slow-release double-coating NPK granules using bioblends PS/PCL was fulfilled the criteria as a slow-release fertilizer product.

Keywords: NPK granules, fertilizer, bioblends, polystyrene, polycaprolactone.

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I. Introduction

Fertilizer is one of the most important products from the agrochemical industry. Fertilizers are treated to the soil to feed plants needed for plant growth (6). The main disadvantage of conventional fertilizers is the solubility of fertilizers in the soil that relatively faster than the absorption of fertilizers by plants. Rainwater could rinse fertilizer nutrients, reduced its availability and contaminated the surrounding environment (1). One possible way to improve nutrition and specifically the efficiency of nitrogen use while reducing environmental hazards is using the controlled-release fertilizers or slow-release fertilizers. The use of slow-release fertilizer can increase efficiency and yield, and reduce nutrient loss from washing due to heavy rainfall to soil or groundwater (7). The price of slow release fertilizer is more expensive compared to conventional fertilizer, but its application to plants is less compared to conventional fertilizers that usually used several times by farmers during the growing season (4). The higher price of slow release fertilizers caused by using of relatively expensive coating materials and organic solvents (3;8). One of the cheap polymer coating material that can be used as an alternative coating material is PS known as Styrofoam. It is widely used in various applications, including food packaging, electronic device packaging and insulators on building construction materials⁶. However, PS is an un-biodegradable polymer. Consequently, it is difficult to be decomposed by microbes and difficult to recycle, so it often causes problems in the environment (2). To overcome this problem, the coating material containing PS, that has un-biodegradable characteristic can be changed into biodegradable by mixing PS with a biodegradable polymer or other natural polymers. Mixing non-biodegradable polymers with at least one biodegradable polymer is called bioblends. To create the polymer mixture into bioblends, the two polymers mixed should be compatible (5). In this study, the coating of NPK granules was carried out slowly by a two-layer method using cheaper and environmentally friendly coating and solvent materials i.e PS and PCL, a biodegradable polymer, using ethyl acetate solvents continued to pilot scale production. The purposes of this study were to formulate NPK double coating fertilizers using PS-PCL bioblends coating in the first layer and PCL in the second layer using ethyl acetate organic solvent, to examine its physicochemical characteristics and to investigate the problems arising during fertilizer production on a pilot scale.

II. Materials and Methods

Materials

PS, PCL (Sigma Aldrich), NPK fertilizer granules (Pupuk Mahkota NPK 16-16-16 Origin of Russia - PT Wilmar Chemical Jakarta - Indonesia) diameter 2-3 mm, technical ethyl acetate, ammonium molybdate (Merck, Germany), potassium antimonyl tartrate (Merck, Germany), concentrate sulfuric acid (Merck, Germany), ascorbic acid (Merck, Germany), potassium dihydrogen phosphate (Merck, Germany), distilled water.

Preparation of NPK Granules

NPK Granules was sieved using a 2-3 mm sieve to obtain the uniform NPK sizes, washed with ethyl acetate and then dried in an oven at a temperature of 50-55^o C for 30 minutes. Coating formulations can be seen in Table 1.

Table 1. PS-PCL Bioblends Coating Formula

Coating Method	Materials	Pilot Scale Formula		
		F0	F1	F2
1 st Coating	NPK (g)	1.000	1.000	1.000
	PS (g)	-	80	80
	PCL (g)	-	20	20
	Ethyl Acetate (mL)	-	1.200	1.200
2 nd Coating	PCL (g)	-	-	20
	Ethyl Acetate (mL)	-	-	300

Preparation of Coating Solution

The first layer used was PS-PCL bioblends at a ratio of 4:1. 80 grams of PS was dissolved in 900 mL of ethyl acetate and 20 grams of PCL dissolved in 300 mL ethyl acetate. The mixtures were stirred using a magnetic stirrer at a rate of 70 rpm and at a temperature of 60 °C until all PS and PCL dissolved. Two solutions obtained were mixed and stirred using a magnetic stirrer at a rate of 1000 rpm for 10 minutes. The second layer coating solution was prepared as follows. 20 grams of PCL was dissolved in 300 mL of ethyl acetate, stirred using a magnetic stirrer at a rate of 70 rpm and at a temperature of 60 °C until the PCL dissolves appropriately.

Coating Process

The coating was carried out using a spray coating method. The un-coated NPK granules was sprayed with a prepared coating solution. 1000 grams of NPK granules was placed into a coating pan. The coating solution was pour into a solution container in the spray gun. NPK granules was sprayed with coating solution in the pan coating, rotated at a rotational speed of 70 rpm and at the temperature 50-55 °C. NPK granules obtained were dried using an oven at a temperature of 50-55 °C for 30 minutes to make sure the evaporation of solvent completely. Dried first coated NPK granules was coated with the second coating solution in the same way as at the first coating.

Characterization of Coated NPK Granules

Granules Topography

Characterization of granule surface morphology was carried out to evaluate the characteristics and compatibility between NPK coating polymers. This evaluation was carried out using a Scanning Electron Microscope (SEM).

Chemical Interaction

Possible interactions between components of coating materials and NPK granules were evaluated using a Fourier Transform Infrared Spectroscopy (FTIR).

Coating Efficiency

The coating efficiency of bioblends was determined as follows. A certain amount of double coated NPK granules, M_{total} (g), was dissolved into 100 mL of distilled water at room temperature of ± 24 °C. The polymer was crushed, dissolved in distilled water, and filtered using filter paper. The residue was washed with distilled water, dried at a temperature of 120°C for approximately 4-6 hours and weighed, M_{polymer} (g). The percentage of coatings was calculated by the equation:

$$\% \text{ Coating} = \frac{\text{M polymer residue (g)}}{\text{M total (g)}} \times 100\%$$

Where:

% coating is the percentage of polymer coated in NPK granules.

M polymer residue is mass of polymer residue (g) and M total is the total mass (NPK + polymer).

Release and Determination of NPK Levels Release in Aqueous Media

0.5 gram of double coated NPK granules was placed in a container containing 100 mL distilled water at a temperature of 25-30°C. Five mL of the liquid from the container was taken at 0.083; 0.25; 0.5; 1; 4; 12; 24; 48 hours. The fresh medium was added up to 100 mL after each sampling. Absorbance of each sample was measured using a spectrophotometer.

Determination of NPK Levels

NPK levels were determined using a spectrophotometer. Ammonium molybdate was used as a color maker. Orthophosphate compound was reacted with ammonium molybdate to form ammonium phosphomolybdate complex. The color was stable for 10 minutes. The substance obtained was blue in an acidic condition. It will absorb visible light at a wavelength of 714 nm. The coloring reagent solution was prepared by dissolving 1.2g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ with distilled water in a 100 mL volumetric flask. 0.0277g $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot 5\text{H}_2\text{O}$ was added into the solution. 14 mL of concentrated H_2SO_4 was added slowly. Then distilled water was added up to 100 mL. 0.106 g of ascorbic acid and 10 mL of concentrated reagent was mixed and added with distilled water up to 100 mL. A calibration curve was create using KH_2PO_4 standard solution at a concentration of 0.001, 0.002, 0.003, 0.004, 0.005, 0.006, and 0.007 ppm.



III. Results and Discussion

Morphology and Characterization of NPK Coatings

Morphological and cross sections examination using the Scanning Electron Microscope (SEM) of non-coating NPK granules and slow-release NPK granules at 300 dpi magnification can be seen in Figure 1 a and b. Figure 1 a Scanning electron micrograph of non-coated NPK granules showed core of granules without coating layer. Figure 1 b showed the first layer slow released NPK granules morphology. It can be observed that the boundary between NPK granules core and coating polymer. Figure 1c showed the morphology of double coating slow-release NPK granules. It showed the surface of the coating look like a fine thin film. The outer polymer layer has water retention characteristics. The first polymer layer acts as a physical barrier for mass transfer, thereby reducing the rate of water diffusion into the center and NPK diffusion of fertilizers out the nucleus and providing a slow-release effect.

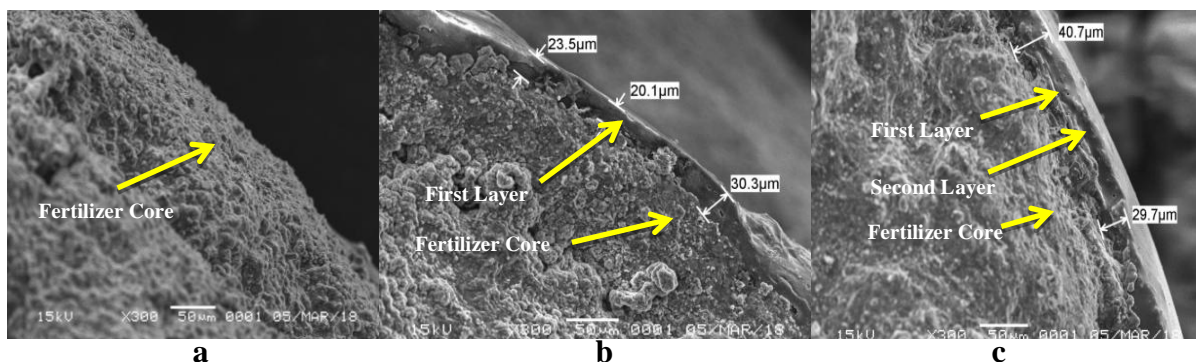


Figure 1: Micrograph SEM of the NPK granules with a magnification of 300 dpi, a) Non-coating NPK granules morphology, b) Single Coating NPK granules morphology, c) Double Coating NPK granules morphology.

FTIR Analysis

FTIR spectrum analysis bioblends PS/PCL double-coating NPK samples showed similarities with the non-coating NPK (Figure 2). The peak at 3029 cm^{-1} (NPK), 3020 cm^{-1} (slow-release single-coating NPK) and 3037 cm^{-1} (slow-release double-coating NPK) is a strain vibration of C-H. The peak at 2389 cm^{-1} (NPK), 2397 cm^{-1} (slow-release single-coating NPK) and 2366 cm^{-1} (slow-release double-coating NPK) is a strain vibration of the phosphorus compound. The peak at 1080 cm^{-1} (NPK), 1081 cm^{-1} (slow-release single-coating NPK) and 1074 cm^{-1} (slow-release double-coating NPK) is a bending vibration of C-O. The peak at 890 cm^{-1} (NPK), 897 cm^{-1} (slow-release single-coating NPK) and 887 cm^{-1} (slow-release double-coating NPK) is a bending vibration of C-H. This proves that the NPK and polymer coating materials used are compatible, there was no new functional groups. It can be stated that no chemical interaction occurred.

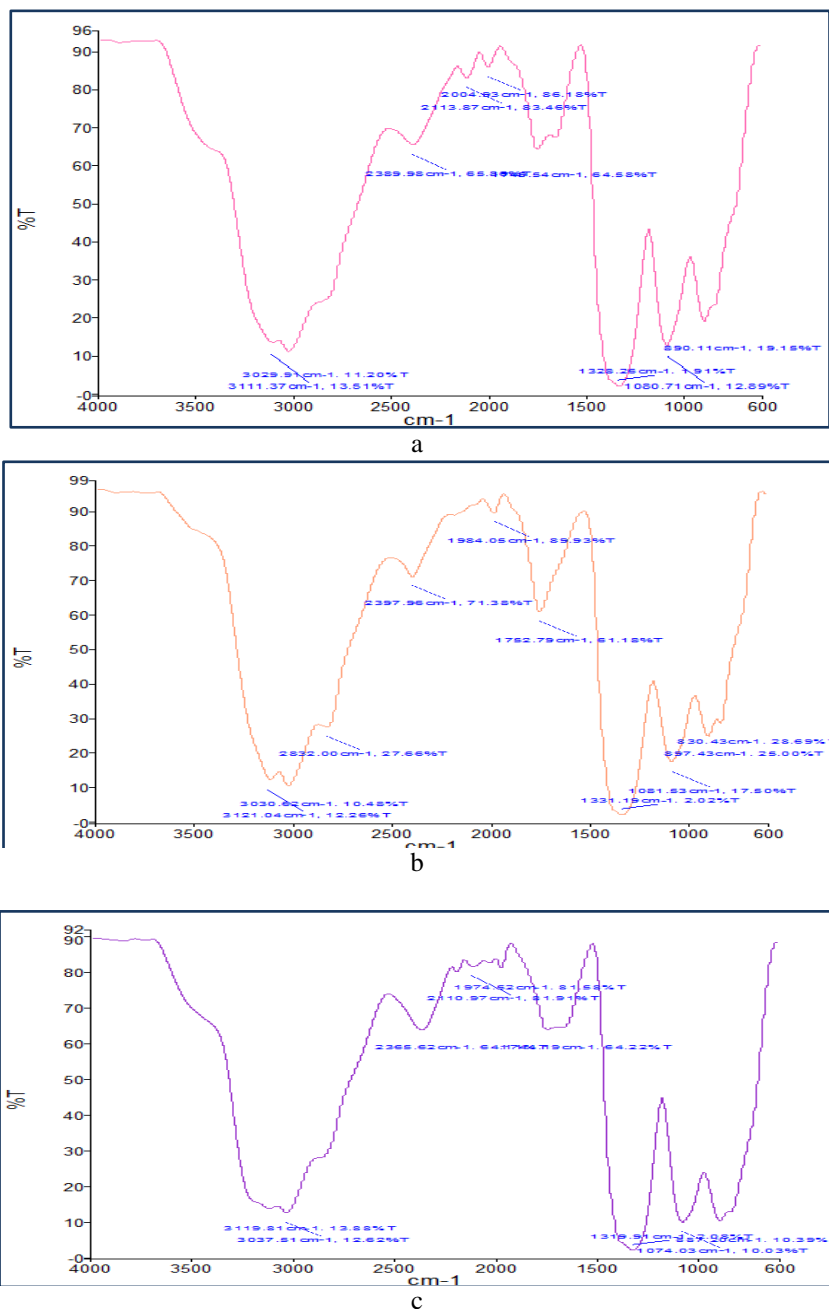


Figure 2. FTIR Spectrum of NPK granules: a) Non-coating, b) Single-Coating, and c) Double-Coating.

Coating Efficiency

Several factors that can influence the quality of film coating are the interaction between the core materials with the coating solution, the drying process especially the drying temperature, and uniformity of distribution of the coating. A faster drying rate will affect coating and increase dust formation. This condition will reduce the percentage of coating efficiency. The percentage of coating efficiency in the first layer of single coating was 92.98 ± 1.24 %, while in the second layer (two layers) was 93.79 ± 2.25 %. It can be seen that the percentage of coating efficiency in the double-coating NPK granules was greater than the percentage of single coating. It was due to an increase in the number of polymer ratios used. Results of the measurement of the percentage of coating efficiency in slow-release NPK granules provided a coating efficiency above 90%. It indicated the most perfect coating process when the polymer was sprayed onto the core of the granules.

Characteristics of Phosphate Release From Coatings

Characteristics of phosphate release from slow-release NPK samples in distilled water was evaluated at room temperature. The phosphate release profile generally occurs due to immersion and penetration of water vapor into NPK granules that can dissolve a small portion of solid fertilizer. It occurs because of the

diffusion resistance by the polymer layer. During at a period of constant release rate, the concentration of the solution in the granules becomes saturated and finally becomes constant. In this step the diffusion of nutrients from the inside out of the granules through the polymer layer also becomes constant. During the reducing stage of nutrient release, all nutrients were dissolved, the concentration gradient begins to decrease and the diffusion rate also decreases. It means the nutrient release stage start with the step of accelerating the nutrient release rate and ended with reducing the nutrient release rate.

Figure 3 showed the phosphate release profile of non-coating NPK granules and slow-release NPK granules in the medium of distilled water at room temperature. The percentage of phosphate release from uncoated, single coated, and double coated NPK granules within 48 hours were 84.56, 25.02, and 21.05 %, respectively. This showed that the release of phosphate from two-layer polymer granules was slower compared to phosphate release from one-layer polymer and non-coated NPK granules.

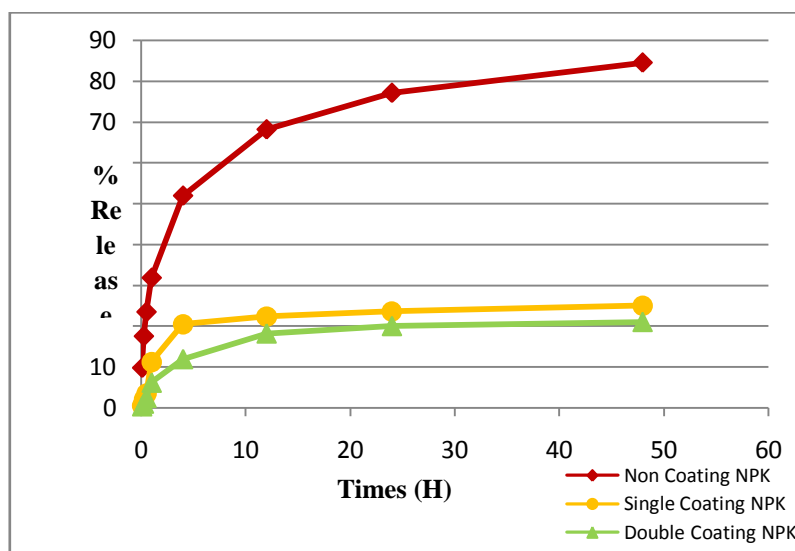


Figure 3. Profile of phosphate release from NPK versus time for each formula in distilled water media.

IV. Conclusions

Results showed that slow-release double-coating NPK granules obtained had a lower release rate than slow-release single-coating and non-coating NPK granules. The use of PS-PCL bioblends on NPK fertilizer granules as the first coating and biodegradable polymer in the second coating can affect the morphology and release profile of the active substance. The product obtained has been fulfilled as a dosage form of slow-release fertilizer.

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References

- [1]. Al-Shamaileh, E., Al-Rawajfeh, A. E. and Alrbaihat, M., 2018. 'Mechanochemical Synthesis of Slow-release Fertilizers: A Review', *The Open Agriculture Journal*, 12(1), pp. 11–19.
- [2]. BPOM, 2008. 'Info POM', *Kemasan Polistirena Foam (Styrofoam)*, 9(5), pp. 1–12. BPOM: Jakarta.
- [3]. Cong, Z., Yazhen, S., Changwen, D., Jianmin, Z., Huoyan, W. and Xiaoqin, C. (2010) 'Evaluation of waterborne coating for controlled-release fertilizer using Wurster fluidized bed', *Industrial and Engineering Chemistry Research*, 49(20), pp. 9644–9647.
- [4]. Godoy, A. and Cole, J., C., 2000. 'Phosphorus source affects phosphorus leaching and growth of containerized *Spirea*', *HortScience*, 35(7), pp. 1249–1252.
- [5]. Mohamed, A., Gordon, S. H. and Biresaw, G., 2007. 'PCL/PS bioblends characterized by thermogravimetry, modulated differential scanning calorimetry and infrared photoacoustic spectroscopy', *Polymer Degradation and Stability*, 92(7), pp. 1177–1185.
- [6]. Tomaszewska, M. and Jarosiewicz, A., 2002. 'Use of polysulfone in controlled -release NPK fertilizer formulations', *Journal of Agricultural and Food Chemistry*, 50(16), pp.
- [7]. Tomaszewska, M. and Jarosiewicz, A., 2004. 'Polysulfone coating with starch addition in CRF formulation', *Desalination*, 163(1–3), pp. 247–252.
- [8]. Yang, Y. C., Zhang, M., Li, Y., Fan, X. H. and Geng, Y. Q., 2012. 'Improving the quality of polymer-coated urea with recycled plastic, proper additives, and large tablets', *Journal of Agricultural and Food Chemistry*, 60(45), pp. 11229–11237.

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