Preparation and Properties of Polypropylene/Polycaprolactone Blends Coated NPK Compound Fertilizer With Controlled-Release And Water-Retention On Some Application Media

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ABSTRACT

Research has been carried out on coating conventional NPK fertilizers using Polypropylene + Polycaprolactone bioblend polymer by spray method with concentrations of 0.1%, 0.2%, 0.4%, 0.6%, 0.8% and 1%. The percentage of coating and coating efficiency are 10.65% and 91.02%, respectively; 11.76% and 91.30%; 13.89% and 92.72%; 15.58% and 93.51%, 17.96% and 94.62%; 9.36% and 87.75 %.

INTRODUCTION

Currently the use of Controlled-Release (CR) technology has become a trend and solution to answer the challenges of using fertilizers in the modern agricultural industry, especially in solving problems associated with conventional agrochemical applications (Akelah, A., 1996), the limitations of conventional fertilizers. make formulation scientists take advantage of opportunities to create innovations in agriculture, especially to make slow-release fertilizer innovations by modifying conventional fertilizers that have been circulating in the market into slow-release fertilizers by coating using natural, synthetic polymers or a mixture of natural polymers with synthetic polymers that can produce a polymer with new properties. Slow-release or controlled-release formulation technology is a technology that is often applied in the pharmaceutical field, the main purpose of which is to make the release of active ingredients on target at a controlled rate. The method that is often used in the manufacture of slow-release products is the coating method, especially the spray coating technique. In addition to the pharmaceutical sector, slow-release technology can also be used for applications in agriculture such as in the manufacture of pesticides and fertilizers, slow-release or controlled-release (Suharti, N., Salman, Muslim, S., Dwisari, D., Febriyenti, Idris, Akmal). , D, 2016; Costa, Cabral-Albuquerque, Alves, Pinto, & Fialho, 2013) .

In modern agriculture, fertilizer is one of the determinants of success and also has a role in increasing agricultural production and productivity, in agricultural practice it is often a problem, especially because the efficiency of absorption of fertilizer is very low. One type of fertilizer that is widely used is NPK fertilizer. Nitrogen (N), phosphorus (P), and potassium (K) are three essential elements for plants , which plants require in large amounts for adequate growth (Fageria, Baligar, & Clark, 2002) . The efficiency of fertilizers that can be absorbed by plants is only about 40-50% for nitrogen, 80-90% for phosphorus, and 50-70% potassium, the rest of the fertilizer used will be lost to the environment and cannot be absorbed by plants, this not only causes economic loss and resources but will result in very serious environmental pollution. One way to increase fertilizer efficiency is to make fertilizer slow-release or controlled-release so that fertilizer nutrients can be released according to the nutritional supply needs for plants. But in the manufacture of slow-release fertilizers, problems are often found, especially in terms of coating techniques, and coating materials, such as the coating materials used are not sufficient to provide a release profile as expected, in addition to the coating materials used also determine the selling price, the price of loose fertilizers. slowly circulating in the market sold at a price 5 to 8 times higher than the price of ordinary NPK fertilizer. (Akelah, 1996; Yang, Zhang, Li, Fan, & Geng, 2012 ; Wu, Liu, & Liang, 2008) .

Polymers with low prices are currently dominated by synthetic polymers such as polypropylene (PP) and polyethylene (PE). However, this synthetic polymer is not biodegradable, to make this polymer biodegradable, it can be done by mixing the synthetic polymer with other biopolymers or biodegradable polymers such as polycaprolactone. So that synthetic polymers that are not biodegradable can become biodegradable polymers. However, until now there has been no research report on the use of synthetic polypropylene polymers as a coating material for sustained-release NPK fertilizers, either single or pure use or the use of a mixture (*poly blend*) of this type of synthetic polymer as a coating material for slow-release NPK fertilizers. Therefore, in this study, researchers will be interested in examining the use of polypropylene and polypropylene/polycaprolactone blends . The use of polycaprolactone as a polymer mixture of polypropylene aims to produce biodegradable polypropylene, mixing non-degradable polymers with biodegradable polymers produces a biodegradable polymer. Polycaprolactone is a semi-crystalline biodegradable synthetic polymer that is often used in the medical world, has compatibility and is non-toxic in human tissues and also to the environment, has a low melting point, which is between 58 to 64 ^{o}C, glass transition temperature (Tg) - 60 ^{o}C and the mean molecular weight of polycaprolactone varies from 3000 to 80,000 g/mol (Hayashi, 1994; Douglas, Andrews, Jones, & Walker, 2010; Martínez-Abad et al., 2013).

EXPERIMENTAL SECTION

Equipment and Materials

Ingredients : The ingredients used are NPK Yaramila fertilizer granules with a diameter of 2-4 mm, Polypropylene (PP), Polycaprolactone (PCL), Technical Xylen, Ammonium sulfate (Merck), Sodium hydroxide (Merck), Salicylic acid (Merck), Disodium hydrogen phosphate (Merck), Disodium dihydrogen ethylene diamine tetra acetate dihydrate / EDTA (Merck), Sodium hypochlorite (Merck), Sodium nitroprusside (Merck), Aqua DM.
Tool : Hotplate magnetic stirrer (Thermo Scientific) , UV-Vis spectrophotometer (UV-1700 PharmaSpec), analytical balance (Shimadzu AUX 220), *F ourier transform infrared spectroscopy* (PerkinElmer) , pH meter (Thermo Scientific), *scanning electron microscopy* (SEM) JEOL-JSM-6510LV , *spray gun* and pump, *coating pan* , glassware and other equipment.

Methodds

Preparation of NPK granules
NPK raw materials (standard) and has also met the provisions of the Indonesian National Standard (SNI) 2803:2010 for NPK granules . The results of the examination can be seen in Appendix 3, Table IV.1 and Table IV.2 .
Preparation of coating solution
Polypropylene as much as 0.1, 0.2, 0.4, 0.6, 0.8 and 1 gram according to table III.1 was dissolved with 100 mL of technical xylene then heated on a hotplate *magnetic stirrer* at a speed of 380 rpm until the polypropylene polymer granules dissolved . After that, 10 grams of dissolved polycaprolactone were added to each, then the solution was stirred using a magnetic stirrer at a speed of 380 rpm.

NPK Coating
The coating is carried out using the spray-coated method, where NPK fertilizers are coated by spraying with a previously prepared coating solution. Twenty-five grams of NPK fertilizer was put into a coating pan, while the coating solution was put in a solution container in a *gun spray* . Then the NPK fertilizer is sprayed with a coating solution, the rotation speed of the *coating pan* is adjusted, at the time of spraying it is also directly dried using a *heat dryer* with a coating pan temperature of around 40-60 ^{o}C. After the coating is complete, the fertilizer is again dried in the oven at a temperature of 70-80 ^{o}C for 1 hour to ensure that the solvent has evaporated and the fertilizer is completely dry.
Product Characterization Test
a. Granule size distribution
b. The morphology and surface characterization of the granules using *scanning electron microscopy* (SEM),
   This evaluation was carried out using a *scanning electron microscopy* (SEM) JEOL-JSM-6510LV.
c. Fourier transform infrared spectroscopy (FTIR) analysis
   This analysis was carried out using the PerkinElmer brand FTIR Universal ATR . type

Release test and determination of NPK levels :
a. Release test on aqueous media
   In this evaluation 5 grams of polymer -coated NPK was dissolved in 500 ml of distilled water . Samples were taken at an interval of 1-14 days , to be analyzed for nitrogen content (Tomaszewska & Jarosiewicz, 2004) ; (Chen et al., 2008) ; (Vashishtha, Dongara, & Singh, 2010) .
b. Release test on slurry media
   In this evaluation 5 grams of polymer -coated NPK was dissolved in 500 ml of mud water . Samples were taken at an interval of 1-14 days , to be analyzed for nitrogen content (Tomaszewska & Jarosiewicz, 2004) ; (Chen et al., 2008) ; (Vashishtha, Dongara, & Singh, 2010) .
c. Release test on soil media
   In this evaluation, 100 grams of dry soil were weighed. Then the dry soil is placed into a glass funnel that has been given a filter paper base. Then 3 grams of coated NPK samples were weighed. The weighed formula samples were then planted in dry soil on a glass funnel . The funnel is then placed in a glass bottle with a height of 27 cm. The soil in a glass funnel was moistened with 20 mL of distilled water, the wetting was carried out at a constant speed, namely at a water flow rate (flux) of 5 mL/minute. Where the highest rainfall in West Sumatra reaches 4000 mm / year, equal to 11.1 L per day / meter ^{2}, equivalent to 11100 mL per day / meter ^{2} or 7.71 mL per minute / meter ^{2} (BMKG, 2014).
d. Determination of NPK levels
   Determination of total nitrogen content with this method is carried out based on the principle of the Berthelot reaction.

Reagent manufacture
a) Preparation of N stock solution with a concentration of 2500 mg/L.
   dissolved 11.793 grams of ammonium sulfate($(NH_4)_2SO_4$), with distilled water in a 1000 mL volumetric flask to the mark.

b) Preparation of 10 mol/L . sodium hydroxide solution
Dissolved 200 grams of sodium hydroxide (NaOH), with 400 mL of distilled water and let it cool and then add distilled water to make it 500 mL.

c) Preparation of salicylate solution
Dissolve 110 grams of samsalicylate (C7H6O3) , in 105mL sodium hydroxide solution and add distilled water to make 250ml . (preferably made before use).

d) Preparation of buffer solution pH 12.3
dissolved 26.70 grams of disodium hydrogen phosphate dihydrate ($Na_2HPO\ 4.2H_2O$), in a 2 liter volumetric flask, water. 10 mL of sodium hydroxide solution was added and diluted with the addition of distilled water to the limit mark , pH was measured and adjustments were made if necessary.

e) Preparation of EDTA solution
Dissolve 4 grams of disodium dihydrogen ethylene diamine tetraacetate dihydrate ($Na_2EDTA.2H_2O$) in 100mL of distilled water .

f) Preparation of hypochlorite solution
hypochlorite solution containing approximately 1 M sodium hypochlorite in 0.1 M NaOH, (must be purchased commercially) diluted 20 ml of this stock solution with distilled water to 100 ml (made fresh / *fresh* every day).

g) Preparation of nitroprusside solution
Dissolved 50 mg sodium nitroprusside dihydrate , $Na_2[Fe(CN)5NO].2H_2O$, in 100m distilled water , prepared prior to use .

h) Mixed reagent I / *Mixed Reagent* I
50 mL of salicylate solution (solution c) was mixed with 100 mL of nitroprusside solution (solution g) and added 5 mL of EDTA solution (solution e).

i) Mixed reagent II / *Mixed Reagent* II
200 mL of buffer solution (solution d) is mixed with 50 mL of hypochlorite solution (solution f).

Percent Coating

Coating efficiency can be determined by dissolving a known mass of product, M_{total} (g) in 100 mL of distilled water at room temperature (±24 ° C, it must be ensured that the mass of NPK is below the saturation limit. To accelerate the dissolution of NPK polymer-coated granules) first crushed and then dissolved in distilled water.After the fertilizer is completely dissolved, then filtered using filter paper, it will obtain a residue (coating polymer) that is released from NPK.The residue is then washed with distilled water and then dried at a temperature of 120oC for less over 4-6 hours, then weighed, $M_{polymer}$ (g).
Coating efficiency is calculated by the equation:

$$\%\ penyalutan = \frac{M\ residu\ polimer\ (g)}{M\ total\ (g)} \text{x } 100 \qquad (2)$$

Where: % coating is the percentage of polymer coated on NPK granules, $M_{polymer}$ is the mass of polymer residue and M is the total mass (NPK + polymer) (Salman, 1988 ; Costa et al., 2013) .

Table 1Coating polymer formula

Code Formula	Coating _	Coating polymer composition
		PP + PCL
F1	PP + PCL 0.1%	0.1
F2	PP + PCL 0.2%	0.2
F3	PP+PCL 0.4%	0.4
F4	PP + PCL0.6 %	0.6
F5	PP + PCL 0.8%	0.8
F6	PP+PCL 1%	1

RESULTS AND DISCUSSION

Granule size distribution analysis

The results of the measurement of the size distribution of granules, it is known that the granules are distributed with sizes ranging from 2 mm to 4 mm. The complete results can be seen in Table II.

Table I I . Data on the measurement results of the size distribution of NPK granules.

Size range(mm)	**Granule size distribution frequency (%)**						
	NPK	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**
2.0-2.2	5	3	2	1	2	1	0
2.3-2.5	12	6	7	9	9	10	9
2.6-2.8	10	8	9	10	9	12	11
2.9-3,1	6	10	9	11	11	14	10
3,2-3.4	8	10	11	6	9	6	9
3,5-3,7	3	10	9	8	7	5	8
3,8-4,0	6	2	3	5	3	2	3
Total	50	50	50	50	50	50	50

Morphology and characteristics of the coated NPK fertilizers

The results of the morphological examination using a *Scaning Electron Microscopy* (SEM) for NPK granules coated with a *bioblend polymer* Polypropylene + Polycaprolactone showed the morphology of NPK granules with a magnification of 100 0 times, the surface of the coating skin looked smooth, compact, and uniform, also appeared in some parts of the small granules. such as not fused , there are also pores in the NPK granules which are coated with a polymer solution . For more details can be seen in Figure I.

NPK Core

Coating polymer

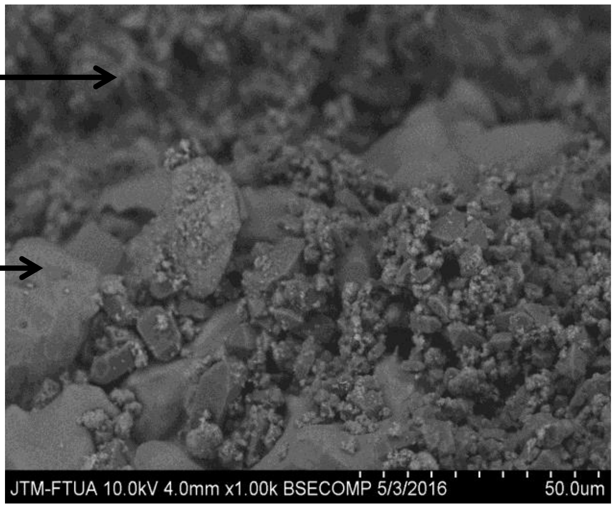

Figure I . SEM micrograph cross section of NPK granules coated with polypropylene + polycaprolactone , magnification 100 0 times.

FTIR Analysis of Coating Shells

The spectrum of the FTIR test results from the NPK sample, polypropylene + polycaprolactone (*bioblend coated NPK)* , can be seen in Figure II.

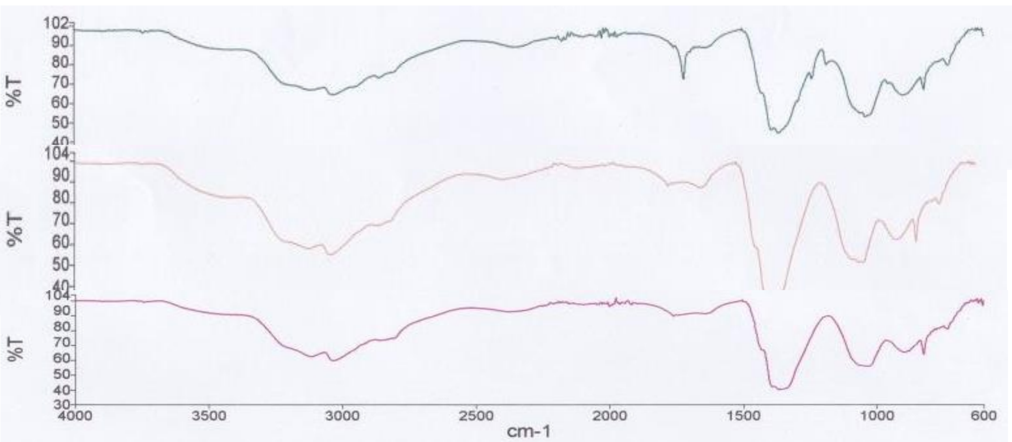

Figure 2 . FTIR spectrum *overlay* of pure NPK polypropylene, pure polycaprolactone, pure NPK and NPK coated with polypropylene + polycaprolactone.

Percent coating and coating efficiency

At a concentration of 0.1% + 10%, the coating efficiency is 10.65%, the coating efficiency is 91.02%, the concentration is 0.2% + 10%, the coating efficiency is 11.76%, the coating efficiency is 91.30%, the concentration is 0, 4 % + 10 % obtained coating percentage 13.89% coating efficiency of 92.72%, concentration 0.6% + 10% obtained coating percentage of 15.58 % coating efficiency of 93.51 %, concentration 0.8% + 10 % obtained coating percentage of 17.96 % coating efficiency of 94.62 % while at a concentration of 1% + 10 % obtained coating percentage of 9.36% coating efficiency of 87.75 %. Details of the calculation of the percent coating measurement and the percent coating efficiency can be seen in Table III.

Table III . Measurement data of coating percent and coating efficiency

No.	Formula	Coating polymer weight (g)	Heavy NPK (g)	Percent Theoretical coating (%)	Initial weight of sample (g)	Weight of polymer residue (g)	Percent coating (%)	Coating efficiency (%)
1	PP+PCL 0.1 %	0.1 + 10	100	11.70	10	1.065	10.65	91.02
2	PP+PCL 0,2 %	0,2 + 10	100	12,88	10	1,176	11,76	91,30
3	PP+PCL 0,4 %	0,4 + 10	100	14,98	10	1,389	13,89	92,72
4	PP+PCL 0,6 %	0,6 + 10	100	16,66	10	1,558	15,58	93,51
5	PP+PCL 0,8 %	0,8 + 10	100	18,98	10	1,796	17,96	94,62
6	PP+PCL 1 %	1 + 10	100	10,70	10	0,939	9,39	87,75

CONCLUSION

From the results of the research that has been carried out, it can be concluded that : The results obtained from measuring the percentage of coating and coating efficiency are Polypropylene (PP) + Polycaprolactone (PCL) 0.1% concentration + 10% coating percentage 10.65 % coating efficiency 91 0.02%, 0.2% concentration + 10% coating percentage 11.76% coating efficiency 91.30%, concentration 0.4% + 10% coating percentage 13.89% coating efficiency 92.72%, concentration 0.6 % + 10% coating percentage 15.58 % coating efficiency 93.51%, concentration 0.8% + 10% coating percentage 17.96 % coating efficiency 94.62 %, concentration 1% + 10% coating percentage 9.36% the coating efficiency is 87.75%.

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