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UREA CORE COATING WITH CROSSLINKED HYDROPHILIC POLYMERS FOR CONTROLLED RELEASE FERTILIZER APPLICATION

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Abstract.

Controlled release fertilizer (CRF) can be made by coating the fertilizer core with a polymer layer. The simultaneous coating reaction of the polymerization needs to be controlled in the reactor. A controlled reactor system was developed for the polymerization of granular fertilizer coating using integrated electronic control of the 8-bit ATTiny 2313 AVR microcontroller chip. Urea granule fertilizer is coated with hydrophilic polymer polyacrylamide and crosslinked polyacrylate with N,N'-methylene-bis acrylamide (MBA). The reaction was initiated by benzoyl peroxide (BPO) at 61 ^oC. The coating was successfully formed in 45 minutes reaction. The coating process in the control reactor was more effective than without control, thereby reducing the deposition of polymer deposits that did not coat the fertilizer. The characterization of the fertilizer coating layer based on infrared spectroscopy (FTIR) showed that polymerization synthesis had occurred based on the presence of C=C bonds. The IR spectrum showed a reduced absorption of the C=C stretching vibration medium in the acrylamide monomer compared with the polymer (crosslinked polyacrylamide), namely the wave numbers of 1614 cm^{-1} in acrylamide and 1601 cm^{-1} in polyacrylamide spectrum. Similarly, the loss of C=C absorption in the crosslinked polyacrylate spectrum but appeared in the acrylic monomer spectrum at 1636 cm^{-1} wave. This group is reduced or lost after polymerization due to an addition reaction.

Keywords: urea; polymers; fertilizer

1. INTRODUCTION

Controlled release fertilizer (CRF) is a fertilizer that can be controlled for its release rate to the soil environment and its pattern through the manufacturing process **[1].** CRF can be obtained through coating treatment or encapsulation of fertilizers. Research on coated fertilizers has been carried out for a long time by Abraham **[2]** regarding urea granules coated with hydrophobic and hydrophilic polymers and also Subbarao et al. **[3]** regarding hydrophilic polymer-coated potassium oxide fertilizer.

The coating materials used are mainly polymers, one of which is a hydrophilic polymer. Hydrophilic polymers which widely applied in agriculture are polyacrylamide and polyacrylate, mainly as superabsorbents made by graft and cross-link copolymerization. Research on the application of superabsorbents to soils was reported by Hua et al. **[4]** used polyacrylate composites and Mas'ud et al. **[5]** used polyacrylamide composites. Polymers are suitable as fertilizer coating materials because they are not significantly affected by soil conditions, namely pH, texture, salinity, microbiological activity, ionic strength of groundwater, redox potential, but are more dependent on temperature and permeability. Fertilizer application is usually at normal temperature or room temperature, while permeability can be controlled through the parameters of the amount or composition of the coating **[6].**

There are several techniques to produce slow-release fertilizers namely spouted bed, rotating drum, fluidized bed technique, and polymerization coating simultaneously. Research related to slow-release fertilizers has been carried out by Tzika et al. **[7]** that is coating fertilizer granules through the fluidized bed technique and Hoeung et al. **[8]** regarding a mixture of fertilizer and zeolite which is processed using an inclined pan granulator. Abraham **[2]** reported using a fertilizer coating technique simultaneously with the formation of the coating layer through radical polymerization so that the polymer formed was directly deposited on the surface of the fertilizer. Radical polymerization takes place randomly or uncontrollably so that there can be significant differences in the repeatability of the polymer produced. Therefore, it is necessary to make a reaction control system in the reactor. This study aims to create a urea granule as core to be coated with hydrophilic polymer through an controlled reactor electronically. The hydrophilic polymers used were polyacrylamide and polyacrylate, each cross-linked with N,N'-methylene-bis acrylamide (MBA). The electronic system is controlled by a microcontroller chip that has been programmed and can be connected to the Internet of Think (IOT). This system controls the polymerization reaction in the reactor consistently and automatically and responds to the challenges of the industrial era 4.0 which requires electronic loading, digitization, automation, and wireless control.

2. RESEARCH METHODS

This research used granulated urea fertilizer, acrylamide, acrylic acid, N,N-methylene-bis acrylamide (MBA) p.a (Merck), benzoyl peroxide/BPO p.a (Merck), chloroform/$CHCl_3$ p.a (Merck). The tools used in this research are polymerization reactor designed consist of automatic control system, water bath, magnetic stirrer, condenser, chiller, 8-bit AVR ATtiny2313 microcontroller, Emko ESM-4410 temperature indicator-controller, type K thermocouple sensor, spectroscopic instrument Fourier Transform Infrared (FTIR) IRPrestige-21 Shimadzu, and other glassware.

2.1. Coating

Coating of Granular Urea Fertilizer with Polymer. The polymerization method applied is a modification of Abraham's **[2]** method with the use of azo-bis isobutironitrile (AIBN) as an initiator replaced with benzoyl peroxide (BPO) and the reaction process is carried out in a controlled system. The polymerization was carried in chloroform ($CHCl_3$) solvent. Preliminary observations were made for determination of polymerization temperature, coating-polymerization time, etc. Manual synthesis was started by mixing 1.06 g of monomer (acrylamide or acrylic acid), 0.1 g of MBA (crosslinker), 0.05 g of BPO (initiator), and 15 g of granulated urea fertilizer into a reactor flask containing 56 mL $CHCl_3$. The reactor is fitted with a condenser, then heated in a water bath at a temperature of 40 °C, 50 °C, until the maximum temperature until the solution mixture boil, i.e., 61 oC. After finding the polymerization temperature, the urea granules were precoated at that temperature. Taking several samples of urea granules was carried out at several point place in the reactor every 15-minute interval, then the samples were immersed in water to observe the solubility and the coating layer. Furthermore, the reactor was set, programmed, and equipped to control the polymerization process and fertilizer coating. The main system is a polymer injection pump, temperature control of the heating component (water bath) and stirring. Other supporting components prepared are computers for programming and control, condensers for reflux, chemical resistant teflon tubing, and other related components. The polymerization and coating reaction process is carried out on lab scale starting with the preparation of two separate solutions, the first solution is a mixture of 1.06 g monomer (acrylamide or acrylic acid) and 0.1 g MBA in 8 mL $CHCl_3$ and the second solution is 0.05 g of BPO in 8 mL of $CHCl_3$. The two solutions were put into the reactor reagent input bottle. A total of 15 g of urea granules and 40 mL of $CHCl_3$ were put into the control reactor. The reactor is operated in an optimized setting especially automated cycle control of polymer feeding/injection. The results were observed and further characterized by FTIR.

2.2. Characterization

Characterization by Infrared Spectroscopy. The characterization of the synthesis results in the reactor was carried out using a Fourier Transform Infrared (FTIR) infrared spectroscopy instrument. Polymerization reagents and fertilizer coating polymers were analyzed for the chemical functional groups. Samples of coating polymer were obtained by crushing the coated fertilizer, then put into 100 mesh stainless steel gauze and soaked in distilled water until the fertilizer was dissolved, then rinsed with distilled water and dried in an oven at 60 °C. The IR spectroscopy analysis method used is Diffuse Reflectance Spectroscopy. A total of 100 mg of KBr and 2 mg of the sample were mixed until homogeneous. Then the mixture was put into a sample container and given a little pressure until solid, then put into the instrument and scanned in the range of 400-4000 cm^{-1} with Happ-Genzel apodization.

3. RESULTS AND DISCUSSION

The parameters of the coating polymerization were determined by preliminary tests. The monomers used were acrylamide and acrylic acid, while the cross-linker was N,N-methylene-bis acrylamide (MBA). The solvent used is chloroform because it can dissolve the reagent but does not dissolve urea. Polymerization using benzoyl peroxide (BPO) initiator. ODS decomposes at a temperature of 38 – 80 °C **[9].** In the initial observations, the polymer did not form at a temperature of 40 °C. Therefore, polymerization with BPO was carried out at a higher temperature. A polymer deposits were formed at 61 °C when the mixed solution was boiling (Figure 1). Therefore, the design of the reactor system was designed to support reflux process to return the chloroform solvent. The resulting polymer tends to be deposited because it is insoluble in chloroform and water solvents, different from the monomers and reagents which are soluble in chloroform and water.

The crosslinked modified polymers will form interconnected chains (Figure 2). Modification of the polymer by crosslinking serves to make the polymer more stable and form a net-like structure that is useful for coating purposes **[2].** The type of polymerization that occured was radical polymerization. The radical polymerization process occurs randomly or uncontrollably so it can cause significant differences in the repeatability of the resulting polymer. Synthesis of this polymer occured simultaneously with polymer deposition to get effective and perfect coating. The main controls were on the transfer of reagents and stirring.

Figure 1. Crosslinked polymer deposits

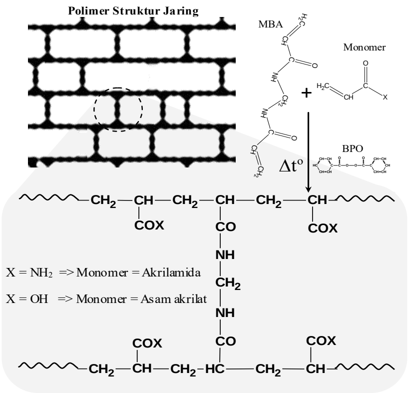

Figure 2. Structure of the crosslinked polymer

Sampling of urea granules from the reaction flask was carried out at 15, 30, 45, and 60 minutes to observe the deposit or coating layer formed. Samples of fertilizer granules are immersed in water so the fertilizer will dissolve and leave a coating deposit. Observations showed that there were empty coating envelope and deposits formed, which indicated that crosslinked polymer coatings could occur both on polyacrylamide and polyacrylate based. The results of the synthesis observation at 15 minutes showed that the polymer deposit had not yet formed a perfect coating envelope of urea granules. The results of observations at minute 45, a perfect coating was formed, both based on acrylamide monomer and acrylic acid (Figure 3). The coating looks transparent and empty when the fertilizer is completely released. Acrylamide-based coatings appear to swell more in water than acrylamide based. The reaction process for the coating reaction was set for 60 minutes to complete the reaction.

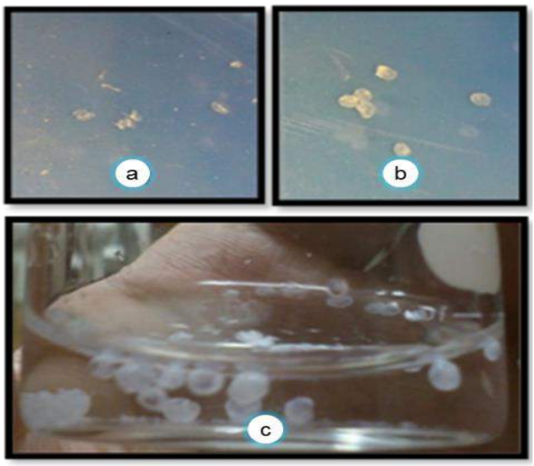

Figure 3. Deposits of urea granules coating on reaction time: (a) 15 minutes, (b) 45 minutes, (c) 60 minutes

The coating process was carried out simultaneously and controlled using the reactor designed for the automation of polymer synthesis. Control was carried out by an electronic controller system which controls the reagent distribution component, stirrer, temperature in the water bath, and reaction time (Figure 4). The electronic controller system consisted of an 8-bit ATTiny 2313 AVR microcontroller and a temperature controller with a K type thermocouple. The temperature was controlled separately from the microcontroller to focus on constant temperature control.

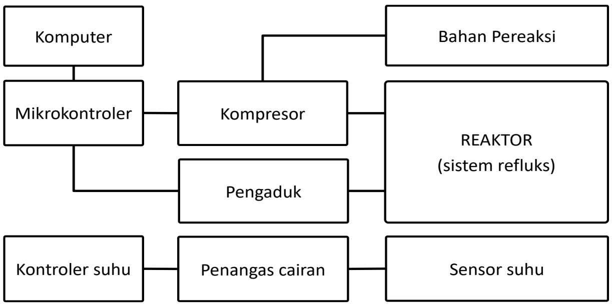

Figure 4. Components of polymerization coating reactor

The design of the reaction apparatus for coating-polymerization reactor was prepared to support the planned program as needed (Figure 5). The reactor was assembled from components that were resistant to organic solvents, especially for the transfer reagent component a teflon tube was used. The temperature of the reactor was conditioned with a water bath so that the consistency and uniformity of temperature is better maintained than direct element contact heaters. The temperature control of the water bath was carried out with a K type thermocouple temperature sensor and a controller that connected to the heating element. The fluid convection in water bath was assisted by magnetic stirrer and pump to ensure temperature uniformity. Magnetic induction stirrer was used to stir the materials in the reactor. The reactor stirrer was not only rotating but also circulating around the edges of reaction mixture. Another related component used was also a condenser that is connected to the chiller machine. The reaction trigger switch and the computer are alerted to control the program or change the program if there is a reaction error in the microcontroller system.

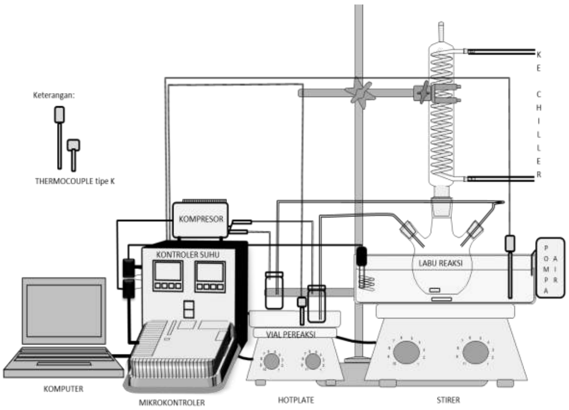

Figure 5. Coating-polymerization reactor system

The control and reaction steps follow the program algorithm which is a function of time (Figure 6). The program starts from the sequential ignition of all components that are integrated with the microcontroller. Then the process continues with the activation of the pump to push the reagents mixture of monomers, crosslinkers, and initiators. A total of 3 execution cycles of the reagent injection stages are uploaded to the microcontroller. One cycle was added which without injection to complete the reaction and rinse the reagent line. Each cycle was set for 15 minutes so the total reaction time was 60 minutes. Stirring reactor was pulse controlled, turned on-off every 2 seconds interval. The time interval setting provides sufficient time for polymer deposition on the urea granules but not to cause the solvent to become viscous or the polymer to be deposited on the reactor surface.

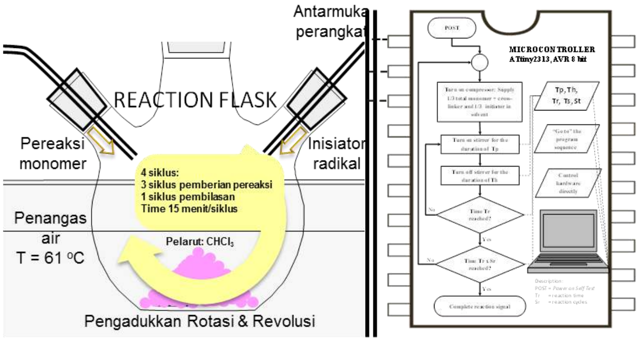

Figure 6. The coating-polymerization reaction program

The uncontrolled reaction process caused most of the polymer not to be completely deposited on the surface of the urea granules, but rather to settle on the surface of the reactor vessel wall (Figure 7). In addition, it also causes the solvent to become viscous and form a large deposit that inhibit stirring. Therefore, the transfer of reagents must need to be controlled gradually. Therefore, reagent injection and stirring need to be controlled to effectively coat the urea granules. In addition, it is difficult to maintains the condition of the reaction manually (without automatic control), especially to prevent the oxygen which interferes with the radical polymerization and the release of chloroform solvent that occurs when opening the lid of the system when transfer the reagents. The results of the urea coating were dried for later characterization (Figure 8). Urea CRF needs to be developed and given further treatment in other studies to optimize the coating and its permeability so that the appropriate release rate is obtained.

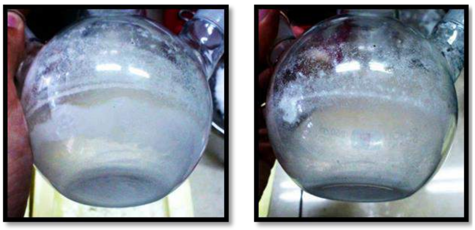
a b

Figure 7. Polymer deposit in reaction flask: (a) uncontrolled reaction, (b) controlled reaction

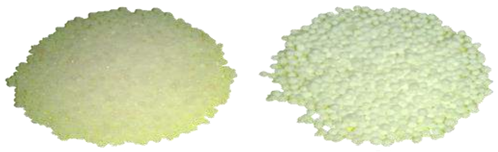
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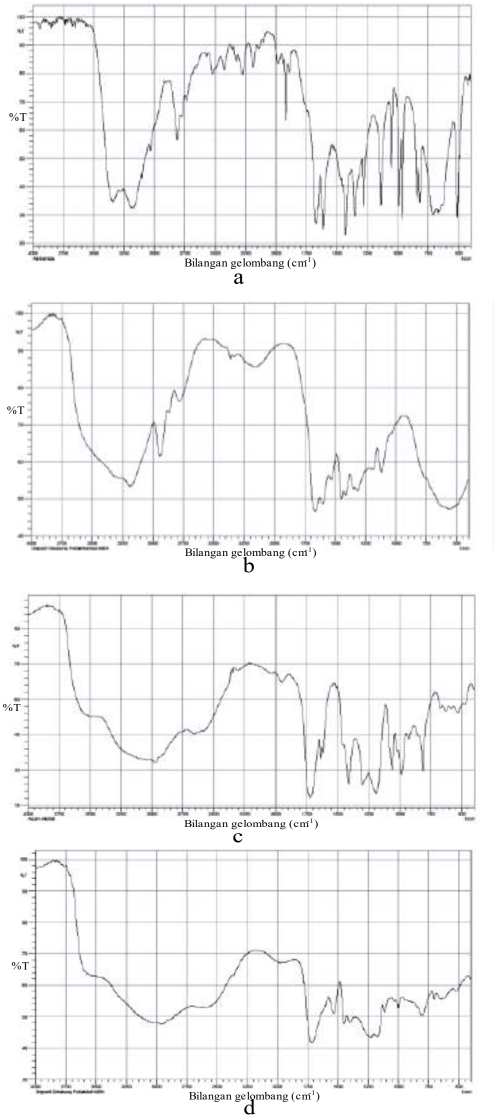
Figure 8. urea granules: (a) no coat, (b) coated

Analysis of infrared spectroscopy was carried out to characterize the material and deposit of urea granules after polymerization. The infrared spectrum (IR) in Figure 9 shows the difference in absorption between the monomer and after the polymerization reaction. These are shown a functional group change due to chemical structure change.



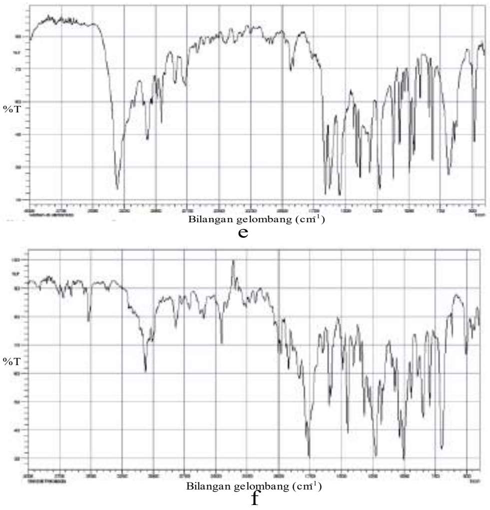


Figure 9. IR Spectrums: (a) acrylamide, (b) crosslinked polyacrylamide, (c) acrylic acid, (d) crosslinked polyacrylate, (e) MBA crosslinker, (f) BPO initiator

The spectrum between the two coating materials, namely crosslinked polyacrylamide and polyacrylate, were compared in Figure 10. The difference between crosslinked polyacrylamide and polyacrylate is mainly in the functional group that is bound to the carbon atom of carbonyl, carbon atom of acrylic acid binds -OH, while acrylamide binds -H_2. The -OH stretching vibration was observed between 3400-2400 cm^{-1} for polyacrylamide, while -NH_2 stretching vibration was found at 3500-3100 cm^{-1} for polyacrylate. From the spectrum, C=O stretching vibration of amide was observed at 1662 cm^{-1} for polyacrylamide, while C=O stretching vibration of carboxylic at 1708 cm^{-1} for polyacrylate. Polyacrylate spectrum showed strong stretching vibration of carboxylic at 1227 cm^{-1} which was not found on the polyacrylamide spectrum. Polyacrylamide spectrum showed C-N stretching vibration of primary amide at 1416 cm^{-1}. Polyacrylate spectrum also showed C-N absorption at 1400 cm^{-1} which can come from urea residue as Pavia found **[10].**

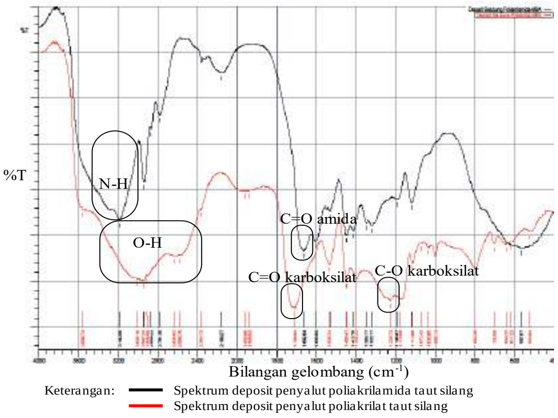
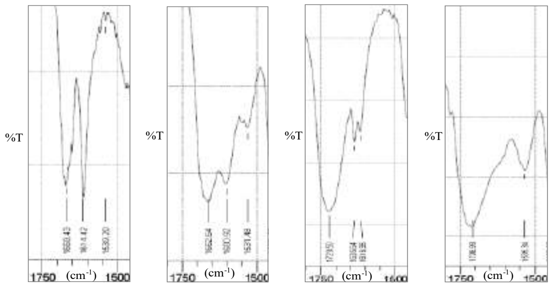


Figure 10. Stacked IR spectrum between the two coating polymers

The characterization of the synthesis was carried out by comparing the IR spectrum of monomer reagents and the synthesized polymer. The acrylamide monomer spectrum showed the decreasing C=C absorption at 1601 cm^{-1} compared with polyacrylamide spectrum. Similarly, the loss of C=C absorption in the polyacrylate spectrum but appeared in the acrylic monomer spectrum at 1636 cm^{-1}. The C=C functional group is reduced or lost after polymerization due to an addition reaction. Both of these indicate that polymerization was occured. This spectrum also showed the presence of absorption at wave number 1532 cm^{-1} in the polyacrylamide spectrum and polyacrylate spectrum. The absorption correspond to bending vibration of the primary and secondary N-H amides that indicates crosslinking has occurred based on the entry of N,N-methylene-bis acrylamide (MBA) into the polymer chain. MBA has a secondary N-H amide functional group. The observation showed that the crosslinked polymers were successfully synthesized.



a b c d

Figure 11. IR spectrums in the range 1500-1750 cm-1: (a) acrylamide, (b) crosslinked polyacrylamide, (c) acrylate, (d) crosslinked polyacrylamide

4. CONCLUSION

Urea granule fertilizer was coated with hydrophilic polymer, namely polyacrylamide and polyacrylate each crosslinked with N,N'-methylene-bis acrylamide (MBA). The initiator used is benzoyl peroxide (BPO). The coating on urea granules was carried out in an electronically controlled reactor using an 8-bit ATTiny 2313 AVR microcontroller chip. The polymerization and coating reaction process begins with two separate solutions, the first solution is a mixture of 1.06 g monomer (acrylamide or acrylic acid) and 0.1 g MBA in 8 mL $CHCl_3$ and the second solution is 0.05 g BPO in 8 mL $CHCl_3$. The two solutions were put into the reactor reagent input bottle. A total of 15 g of urea granules and 40 mL of $CHCl_3$ were put into the controlled reactor. The reactor was operated with a reflux system at temperature of 61 oC with the main control is the feeding/injection of the polymer in an automated cycle. The method algorithm was uploaded to the microcontroller for 3 injection cycles and 1 rinse cycle. Each cycle was set for 15 minutes so the total reaction time was 60 minutes. Stirring reactor was pulse controlled, turned on-off every 2 seconds interval. The time interval setting provides sufficient time for polymer deposition on the urea granules but not to cause the solvent to become viscous or the polymer to be deposited on the reactor surface.

The coating process in a controlled reactor is more effective than without control. The uncontrolled reaction causes most of the polymeric aggregate polymer deposition not to be completely deposited on the surface of the urea granules but rather to settle on the surface of the reactor wall. In addition, it is difficult to maintains the condition of the reaction manually (without automatic control), especially to prevent the oxygen which interferes with the radical polymerization. It was observed that a deposit and an empty coating envelope were appeared on the observations which indicated that cross-linked polymer coating could formed, both on coating of polyacrylamide and polyacrylate. A perfect coating was formed in 45 minutes of reaction.

The characterization of the fertilizer coating layer based on infrared spectroscopy (FTIR) showed a reduced absorption of the C=C stretching vibration medium from the acrylamide monomer spectrum compared with the polymer, at 1614 cm^{-1} for acrylamide and 1601 cm^{-1} for crosslinked polyacrylamide. Similarly, the loss of C=C absorption in the crosslinked polyacrylate spectrum but appeared in the acrylic monomer spectrum at 1636 cm^{-1}. Both indicate that polymerization has occurred based on the presence of the C=C functional group. This group is reduced or lost after polymerization due to an addition reaction. The N-H bending vibrations of the amides was found at 1532 cm^{-1} in the polyacrylamide and polyacrylate spectrum. The N-H bending indicates crosslinking has occurred based on the crosslinker that is N,N-methylene-bis acrylamide (MBA) which has a secondary N-H amide. The observation showed that the crosslinked polymers as coating were successfully synthesized.

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