Characterization of Irradiation Chitosan Coated on NPK as A Corn Growth Stimulant

Gatot T Rekso[1*]

[1] *Radiation Process Technology Research Center– National Innovation Research Agency (BRIN), Jl. Lebak Bulus Raya No. 49, Jakarta 12440, Indonesia*
[*]*Corresponding author. Email:* gatot2811@yahoo.com

ABSTRACT
Due to the long molecular chain and high molecularweight of chitosan, the application is very limited. The radiation process can reduce molecular weight and shorten the molecular chain. This study aims to determine the characterization of irradiated chitosan coated on NPK as a growth stimulant for maize and to know the influence of NPK fertilizer coating with chitosan (R-1) and irradiated chitosan (R-2) on the growth and yield of corn. Chitosan before and after irradiation was characterized, including free radical analysis, changes in functional groups, thermal properties, viscosity, and molecular weight. The results showed that the form of the free radical spectrum of chitosan was peroxide radical. For functional group analysis using FTIR equipment between chitosan without irradiation and chitosan irradiated at a dose of 50 kGy showed no change in the functional group. Thermal analysis with DSC shows exothermic at a temperature of 250^0C to 350^0C. To determine the application of NPK fertilizer coated with chitosan (R-1) and irradiated chitosan (R-2) on the growth of corn plants. Growth parameters included the number of plants starting to flower from 50 plants, the weight of corn fruit, and the average weight of corn cobs after 60 days of planting. From the results that have been achieved, the treatment of NPK fertilizer coated with irradiated chitosan increased the weight of the corn cobs. The administration of NPK + chitosan (R1) and NPK + chitosan radiation (R-2) showed that on the 47th day after planting, almost all of the maize trees flowered at 84% and 96%, while only NPK was 54%. Corn fruit has given NPK + chitosan radiation (R-2) aged 60 days can be harvested and only with NPK 84 days old.

Keywords: *Chitosan, Irradiation, Coating, NPK, Corn*

1. INTRODUCTION

Chitosan is a natural biopolymer with the second-largest abundance after cellulose, is a product of chitin deacetylation either through chemical reactions or enzymatic reactions. These compounds can be found in the shells of shrimp, crabs, insects, annelids, and some fungal and algal cell walls. The modified chitosan produces specific properties and benefits. The rapid interest in exploring chitosan further proves that the prospect of chitosan is up- and-coming. Chitosan and Chito oligosaccharides have attracted considerable interest due to their biological activities. Numerous investigations of the antimicrobial activity of chitosan, its derivatives, and chitosan against many bacteria, filamentous fungi, and yeasts have been published so far, and nowadays it is commonly accepted that the activity depends on molecular weight (MW), degree of deacetylation (DD), target microorganism, and experimental conditions [1].

Fertilizer is one factor that significantly affects plant production because fertilizer is a source of nutrition for plants, given the limited soil in meeting the nutrient needs of cultivated plants. Besides that, with proper fertilization, the fertilizer given is more efficient and follows the plant's needs, thereby saving fertilization costs and being more effective [2]. It is just that currently, the types of fertilizers circulating in the market are more general, and have not led to multi-functional fertilizers; modification of NPK fertilizer with chitosan is expected to have NPK in addition to functioning as nutrient fulfillment, plus its function as a growth stimulant [3].

Oligo-chitosan in agriculture is known as a growth-inducing and anti-bacterial agent. It can control the rate of release of easily lost nutrient fertilizer elements.

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Modification of NPK fertilizer with oligo chitosan is expected that NPK in addition to function as a nutrient fulfillment plus its function as a growth stimulant [4].

The main problem with the use of chemical fertilizers such as NPK on agricultural land is its low efficiency due to its high solubility and loss due to water-soluble, evaporation, and the denitrification process of the fertilizer itself [3]. Therefore, a modification of NPK will be carried out with a natural polymer of chitosan which has a function as a plant growth inducer. The purpose of this study was to determine the characterization of irradiated chitosan coated on NPK as a growth stimulant for corn plants.

2. EXPERIMENT

2.1. Materials

Preparation Of Chitosan Raw Materials: This research takes about 200 kg of dry shrimp shells to produce 25 kilograms of chitosan, the chemical used are NaOH, HCl, and Lactic Acid (98%): all technical grades.

2.2. Preparation of chitin

Chitin was extracted from a prawn shell (*Penaeus monodon*), it was got from MuaraKarang, North Jakarta. To deproteination, the shell, an aqueous of 1 N sodium hydroxide was used to remove protein from a known weight of a particular fraction. The deproteinated shell was then demineralized using 1,0 N hydrochloric acids to remove inorganic salt.

2.3. Preparation of chitosan

Chitosan can be obtained by treating chitin with 50%(w/w) sodium hydroxide with the liquid-solid ratio of 20: 1, at 100^0C for 120 minutes.

2.4. Radiation Source

Gamma radiation source of Co-60, IRKA batch irradiator, with irradiation dose rate about 8,5 kGy/hr was employed in these experiments. This radiation source is located at Pasar Jumat, BRIN.

2.5. Free radical analysis

Free radicals were measured using an electron spin resonance (ESR) instrument. The ESR cuvette tube is checked with an ESR tool to ensure that there is no contamination. Each sample that has been irradiated with gamma rays is weighed 0.0500 grams in an ESR cuvette, then assigned a sample number code. The sample measured is the dose; of 0 kGy; 25kGy; 50 kGy; and 75 kGy, in the following conditions: Centerfield 335.7 mT, sweep width 25 mT, field modulation 0.5 x 1 mT, and receiver gain 500 x.

2.6. Viscosity analysis

Chitosan viscosity was measured using a Brookfield viscometer model DV-II, the sample weighed was 2.5 grams of chitosan from each dose of 0; 25; 50; and 75 kGy, then dissolved in 100 ml of 1% acetic acid and allowed to stand for 24 hours, then measured with a viscometer [1].

2.7. FTIR Analysis

The samples were pressed into KBr pellets and analyzed using transmission mode. For hydrogel samples, the samples were shaped into films and characterized using the Attenuated Total Reflectance (ATR) technique, with 64 scans at a resolution of 4 cm^{-1}[3]

2.8. Thermal Analysis

Thermal Gravimetric Analyzer (TGA/SDTA851) from Mettler Toledo was used to characterize the thermal properties of the samples. All experiments were done under nitrogen purge, with a flow rate of 60 ml min^{-1}. A heating rate of 10 ^{o}C min^{-1} was used for TGA experiments [3]

2.9. Chitosan formula as NPK coating and fertilizer for corn plants

In this experiment, two formulas were used, namely chitosan without irradiation (R-1) and irradiated chitosan (R2). Chitosan without irradiation and which has been irradiated made a solution with a concentration of 2 g/L with acetic acid (2 %v/v). The chitosan solution was then coated with NPK fertilizer using a sprayer and dried at room temperature. NPK fertilizer that has been coated with chitosan is then spread on corn plants according to the usual procedure for fertilizing with NPK. The evaluation included the development of plant growth and fruit growth of treated maize compared with no treatment. Observations included the number of trees that flower every week after 32 days of planting and the weight of corn fruit after fruiting once every 15 days until harvest time [5].

3. RESULTS AND DISCUSSION

3.1. Free radical spectrum

Gamma-ray radiation on the polymer will cause the formation of cross-links or termination of the polymer chain (degradation), for cellulose or chitosan polymers will generally experience degradation [5].

The radiation process in chitosan is indicated by the formation of free radicals which in turn free radicals in chitosan will auto-oxidize and cause degradation in chitosan [6].

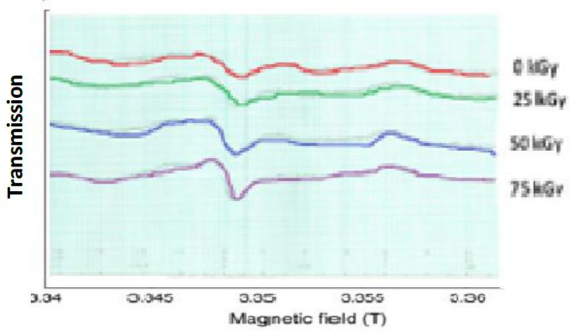

Figure 1 ESR spectrum of chitosan irradiated by gamma rays

Figure 1. shows the spectrum of chitosan irradiated at doses of 0 kG, 25 kGy, 50 kGy, and 75 kGy in the presence of air. The results showed that the free radical spectrum of irradiated chitosan at a dose of 25 kGy to 75 kGy did not change the shape of the spectrum.

3.2. Viscosity

One of the indicators of chitosan, if irradiated with gamma rays, degradation will occur, which can be measured by the viscosity value because viscosity is correlated with molecular weight, the higher the viscosity value, the longer the polymer molecular weight [7]. The results are shown in Figure 2.

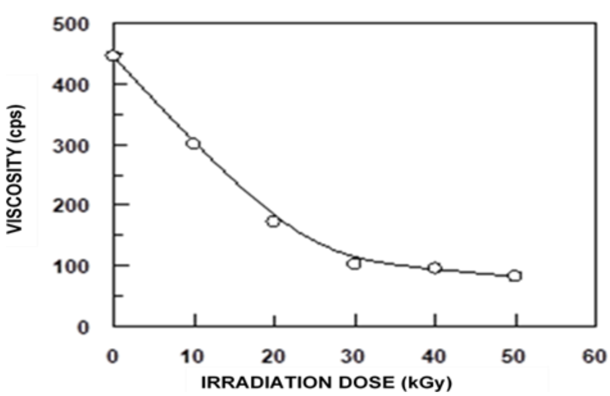

Figure 2 Viscosity value of chitosan irradiated by gamma rays

In Figure 2, it is shown that the viscosity value of chitosan decreases exponentially with the irradiation dose, the non-irradiated viscosity value is 460 cps and at a dose of 50 kGy is 90 cps. This shows that the chitosan molecular chain is cut due to the interaction between gamma rays and chitosan molecules. This interaction causes the degradation of the chitosan molecule [8].

3.3. Functional Group Analysis with FTIR

The wavelength spectrum of the FTIR indicates the presence of functional groups in the sample being measured. In Figure 3. The FTIR spectra of non-irradiated chitosan and 50 kGy irradiated chitosan are shown. There is no significant difference in the shape of the spectrum or the addition of a new spectrum. This shows that gamma- ray irradiation at a dose of 50 kGy did not form new functional groups in chitosan [9].

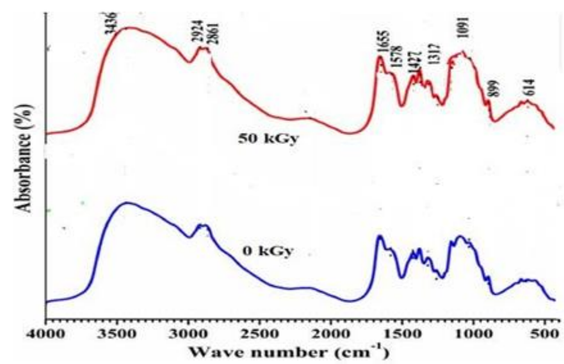

Figure 3 The spectrum of FTIR irradiated chitosan at 0 and 50 kGy

3.4. Thermal analyzer

Thermal properties indicate the resistance of polymers given heat energy, crystalline polymers will show a melting point at a certain temperature, while amorphous polymers will start to degrade. Thermograms of non-irradiated chitosan and 50 kGy chitosan are shown in Figures 4 and 5. At temperatures of 250ºC to 350ºC, the reactions that occur between exothermal and chitosan begin to undergo decomposition and degradation. This means that although chitosan has degraded, heat energy does not decrease in decomposition temperature. Exothermic peaks are shown from the results of TG Figure 4 and Figure 5 analysis between 250ºC to 500ºC decomposition curves of polymers beginning at 250ºC.

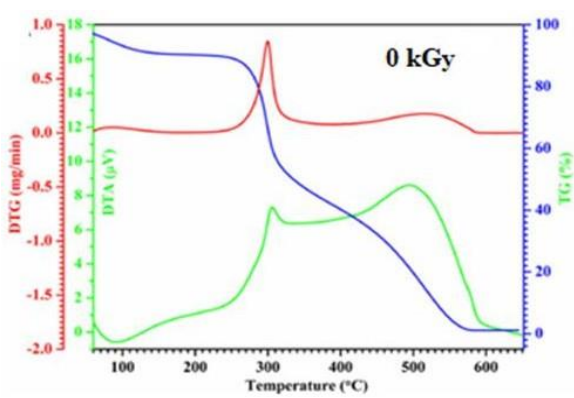

Figure 4 DSC chitosan thermogram non radiation

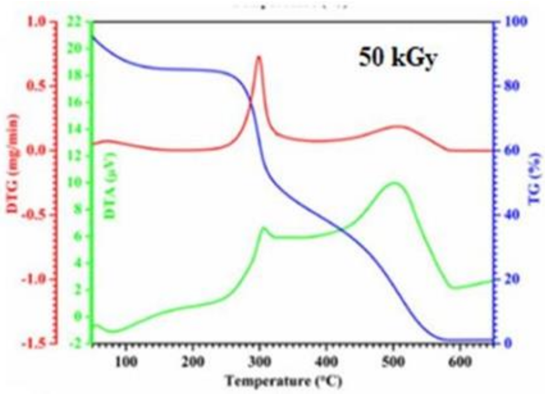

Figure 5 DSC chitosan thermogram radiation at 50kGy

Figure 4 and Figure 5 show a ratio of non-irradiated chitosan and 50 kGy chitosan. This image shows the loss of non-irradiated chitosan and 50 kGy chitosan to temperature function there is no difference even for 50 kGy irradiated chitosan has been degraded but cannot be detected with TGA. Thermogravimetric results analysis of chitosan split the two-weight loss of the TGA curve. The first phase of weight loss between 30^{0}C and 250^{0}C showed a 5% weight loss, this was due to evaporation from the water. On the second curve weight loss starting at 150^{0}C to 600^{0}C is 47%, which begins decomposition and degradation of the chitosan.

The results show that the thermograms of 50 kGy chitosan and non-irradiated chitosan are almost similar, with no peaks indicating other transitions or other substances [8].

3.5. The formulation and physical appearance of chitosan as a coating material

In the experiment, two formulations were used, namely the formula R-1 chitosan which was used without irradiation, and R-2 chitosan which was used irradiated at a dose of 50 kGy. The composition and characterization of chitosan as an NPK coating material are shown in Table 1.

Table 1 Composition and physical appearance of chitosan as NPK coating material.

	Physical composition and appearance	
Component	**R-1**	**R-2**
Chitosan (%)	2	2
Acetic acid 2 %(v/v) (%)	98	98
Radiation (kGy)	0	50
Viskocity (cPs)	465	320
pH	5.5	5.2
Tensile strength (kg/cm^2)	1.22 x 10^2	0.78 x 10^2

3.6. Corn plant growth development

The first observed growth development of corn plants was the number of flowering trees from each block (50 trees) and the second was the development of fruit weight (cob + corn husks) and cobs after 2 months of planting.

Table 2 Growth of flowering trees observed from 50 trees

No	Days to	Number of flowering trees out of 50 trees		
		NPK	**NPK-Chitosan (R-1)**	**NPK-Chitosan (R-2)**
1	0	0	0	0
2	32	4	15	23
3	40	18	21	36
4	47	27	42	48

From the observations of 1-month-old plants starting to flower as maize fruit, NPK + chitosan (R- 2) the number of plants that flowered the most, namely 23 trees out of 50 trees, then NPK-Chitosan R-1 as many as 15 trees and the control (NPK) was 4 trees. On the 47th day after planting, almost all of the maize trees that used NPK-Chitosan (R-1= 84%, R-2= 96%) had grown, while those that only used NPK were only 54%.

In the experiments carried out, the weight of the corn fruit was observed at a certain time after the corn had fruited. For each observation, 10 corn kernels were taken from each block and weighed (cobs + cobhuks) and the weight of the cobs alone without the cob husks. The results are shown in Figures 6, 7, and 8.

The results showed that maize plants that only used NPK when the plants were about 60 days old had very small fruit, while plants that were given NPK-R1 had larger fruits, and plants that used NPK- R2 had 2 times higher yields compared to NPK and NPK-R- 1. After 70 days of weight gain, the increase was relatively low and after 77 days there was a decrease in weight because the cornhusker dried up. The best yield for harvesting corn using NPK-R-2 is after 70 days. This shows that the addition of chitosan radiation can accelerate growth and harvest time [10].

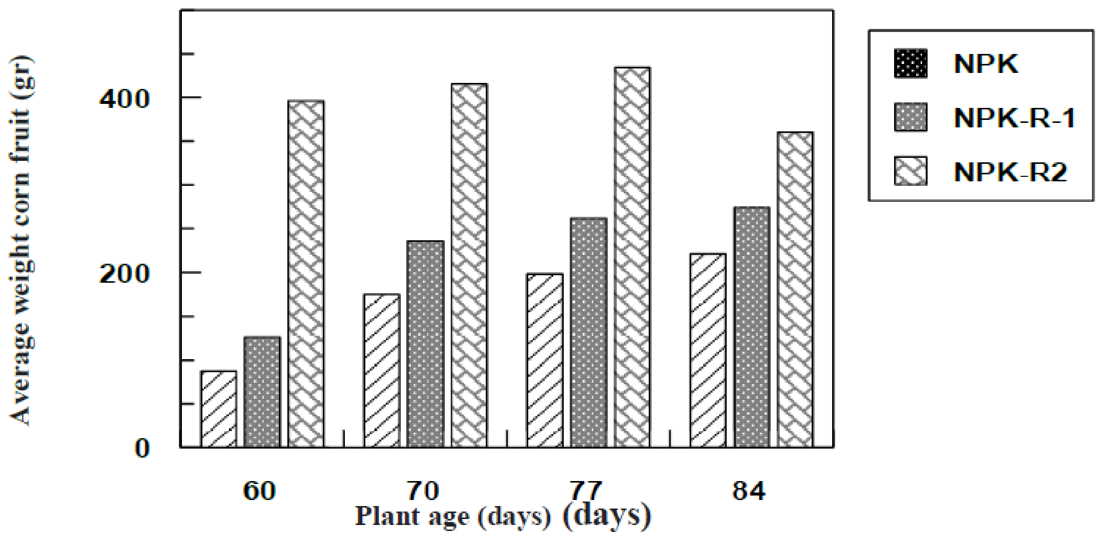

Figure 6 The development of the average weight of corn fruit (cob + cornhusk) after 84 days of planting

Figure 7 The visual image of corn fruit after 60 days

Figure 8 Visual description of corn (cob) fruit after 77 days

4. CONCLUSION

From the experimental results it can be concluded: The type of free radicals irradiated by gamma rays in the air is peroxide radicals. The results of the DSC thermogram analysis showed that there was no difference between chitosan irradiated with 50 kGy and non-irradiated, spectrum thermogram at a temperature of 50°C to 120°C. Coating of irradiated chitosan on NPK accelerated the harvesting age of corn plants and corn plants that were given NPK fertilizer coated with irradiated chitosan with, harvesting age of 70 days from growing. The average weight of corn fruit using NPK fertilizer coated with irradiated chitosan resulted in a higher weigh.

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