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Submission date: 11-Apr-2020 07:19AM (UTC+0700)
Submission ID: 1294819322
File name: ARTIKEL_BNCT_sesuai_Template.docx (128.95K)
Word count: 1938
Character count: 10515

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Abstract. Chitosan is a potential natural blood lead chelating agent. In order to improve its chelating capability, the solubility of chitosan must be enhanced. It is an essential property which is also closely related to molecular weight and viscosity. One of the most renowned and effective methods to reduce the molecular weight and viscosity of a certain particle is irradiation. This research aims to examine the effect of Gamma ^{60}Co irradiation upon molecular weight and viscosity of chitosan. 80 mesh chitosan was irradiated using Gamma ^{60}Co with different doses (0, 50, 100, and 150 kGy). This process was carried out using gamma irradiator in the Centre of Isotopes and Radiation Application at BATAN (National Nuclear Energy Agency). Viscosity and molecular weight measurements were conducted using the viscosimetric method in the chemistry laboratory of FMIPA UNNES, while molecular weight was calculated using the Mark-Houwink equation. Results showed that the specific viscosity of chitosan decreased after the irradiation process from the initial specific viscosity of 4.98 η (0 kGy dose) to 3.28 η (50 kGy), 2.87 η (100 kGy), and 2.09 η (150 kGy). A similar trend was also found in the molecular weight of chitosan from the initial molecular weight of 2.10×10^5 kDa (0 kGy dose) to 1.25×10^5 kDa (50 kGy), 1.04×10^5 kDa (100 kGy), and 5.72×10^4 kDa (150 kGy). It was concluded that Gamma Co^{60} irradiation decreases the viscosity and molecular weight of chitosan by the effective dose of 150 kGy.

1. Introduction

Heavy metal exposures take place in many working environments. Although several cases are proven for being nontoxic, many heavy metal exposure cases are also held accountable for being toxic and yielding detrimental impacts for the workers. Several xenobiotic heavy metals are known for harbouring negative effects on human health, such as lead, mercury, cadmium, and etc.[1].

Most of industrial workers, particularly in industries that use Pb as raw material, are highly susceptible for being exposed to Pb pollutant. Pb is difficult to eliminate from human body that it tends to be accumulated inside. Chronic Pb accumulation will cause functional disruption in nervous, hematopoetic, and reproductive system; kidneys; and also bones.

Chitosan, a natural compound, is known for being nontoxic and possessing chelating properties. Chitosan is made of chitin deacetylations and has six free arms that are capable of binding to free radicals from heavy metal ions. This compound is a natural polysaccharide that has 1-4 glycosidic bond that is bound to N-acetyl-2-amino-2-deoxy-D-glucopyranose (glucosamine) and 2-amino-2-deoxy-D-glucopyranose (N-acetyl-glutamine)[2]. Chitosan is also capable of scavenging free radicals[3].

As reported by research, chelating activity of chitosan towards Pb^{2+} ions in blood is lower than NaEDTA[4]. Such condition is allegedly caused by its large molecule size with molecular weight of 1 MDa. By having large molecule size, chitosan is not easily dissolved in solutions.

Therapeutic effects of chitosan may deplete due to its low solubility. Therefore, an effort to decrease molecular size of chitosan, especially to improve its bioavailability and therapeutic effects, is required. Several *in vitro* and *in vivo* researches prove that molecular weight affects the antioxidant activity of chitosan. Lower molecular weight displays higher antioxidant activity[5][6]. Viscosity rate of chitosan is also affected by the molecular weight. As the molecular weight gets lower, so does the viscosity rate. Low viscosity rate will yield more effective results in delivering and releasing solutes to tissues[7]. In nano size (10^{-9}), chitosan nanoparticles (CNP) shows more prominent activities compared to chitosan. Beside that, nanoparticles possess stronger curvature. This condition will provide higher pressure to improve its solubility[8].

One of the most effective and proven methods to decrease chitosan size and viscosity is irradiation. Gamma Cobalt 60 (^{60}Co)-irradiated chitosan, in the dose of 50 kGy, is proven to have significant decrease in molecular weight. Such condition occurs due to the scission of glycosidic chain in deacetylation rate of (72e75%)[6]. Irradiated chitosan also has improved bioactivity rate, proven by its significant antimicrobial activity, either in Gram positive (*Staphylococcus aureus*) or Gram negative (*Escerichia coli*) bacteria[9]. Nano-sized chitosan particles are expected to enhance its chelation capability towards Pb in blood. The purpose of this research is to examine the effect of Gamma ^{60}Co irradiation towards chitosan viscosity and molecular weight.

2. Materials and Methods

2.1. Chitosan

Chitosan was obtained from crab shells having 94% DD, viscosity 20-100 mPas, particle size Mesh 100-300 powder, purity 98%, moisture max 8% and residue of ignition max 0,75%.

2.2 Chitosan degradation using Gamma ^{60}Cobalt

Chitosan powder was irradiated using gamma irradiator at the activity of irradiation source on 300 kCi (^{60}Co) in Centre of Isotopes and Radiation Application of BATAN (National Nuclear Energy Agency), in the dose of 0 kGy, 50 kGy, 100 kGy, dan 150 kGy at doses rate of 1,02 kGy/h respectively.

2.3 Viscosity measurement of irradiated chitosan[10]

Chitosan was made onto various concentration (1%, 2%, and 3%). Viscosity was measured using Ostwald viscometer, using 10 mL of each sample. Time required for samples to flow inside the viscometer was recorded. As blank solutions, 0,1 M aqueous acetic acid and 0,25 sodium acetate. Based on the flow duration of solution, specific viscosity was calculated with this equation:

$$\eta sp = \frac{t - to}{to}$$

ηsp= specific viscosity (sec)
t = time required for samples to flow (sec)
to = time required for solvent to flow (sec)

Through this method, unit-less specific viscosity was obtained. Kinematic viscosity is related to specific viscosity through kinematic coefficient, which unit depends on used capillary viscometer. Kinematic viscosity was calculated based on this equation:

$$\eta_{kin} = t \times k_{kin}$$

η_{kin} = kinematic viscosity (centistokes= cSt)
t = time required for samples to flow (sec)

k_{kin} = kinematic coefficient of Ubbelohde viscometer type 1B M 132 = 0,009671 cSt/sec.

Flow rate data was analysed using least square method to determine the intrinsic viscosity.

2.4 Molecular weight measurement of irradiated chitosan [6]

Chitosan molecular weight was measured using intrinsic viscosity (η). Based on obtained data, viscosity was mapped onto a graph of ηnsp/C vs C. Intrinsic viscosity is a point in the graph that shows C=0. Molecular weight was determined based on Mark-Houwink equation:

$$[\eta] = kM^{\alpha}$$

[ŋ] = intrinsic viscosity
k = solvent constant
α = constant
M = molecular weight
C = chitin and chitosan concentration (mL)

2.5 Data Analysis

Data was descriptively analysed based on the laboratory test results of chitosan.

3. Result and Discussion

Chitosan, which was irradiated using Gamma ^{60}Co on various doses, shows gradual reduction in viscosity and molecular weight, following the increasing dose. As the irradiation dose gets higher, the viscosity and molecular weight get lower (Figure 3.1 and 3.2). This result is in align with many researches[10][6] [11][12]. Moreover, irradiation of solid chitosan may cause the chain scission, leading to the side reactions such as oxidation and deamination, which increase with the irradiation dose[14].

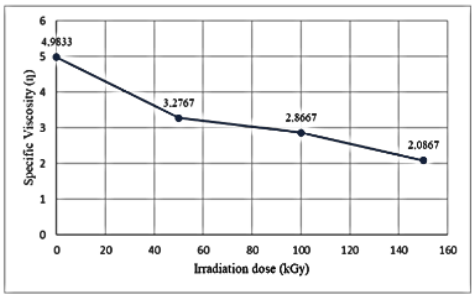

Figure 1. Specific viscosity of chitosan with different irradiation dose of Gamma ^{60}Co

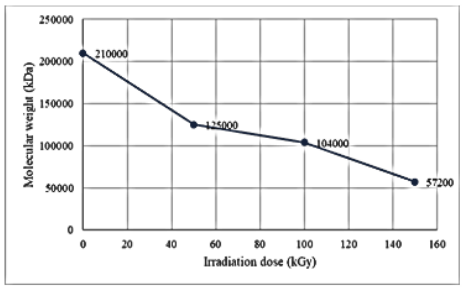

Figure 2. Molecular weight of chitosan with different irradiation dose of Gamma ^{60}Co

Gamma irradiation is commonly used to modify biodegradable polymeric material by inducing degradation, crosslinking, and the grafting process [6]. Gamma irradiation is a powerful tool to reduce chitosan molecular weight through the chain scission reaction without a loss of their main backbone structure, which affects the unique characteristics of chitosan [11].

In this research, chitosan irradiation at the dose of 150 kGy yielded lowest viscosity and molecular weight, compared to the other doses (0, 50, and 100 kGy). Reduction of intrinsic viscosity is commenced by polymer degradation on amorphic solid, upon low-dose irradiation exposure, continued by the same process on crystal solids and upon exposure of high-dose irradiation (above 100 kGy). Degradation process takes less time on amorphic solids, compared to crystal solids [10]. Higher

intrinsic viscosity refers to higher crosslinking activity. Increasing the dose in gamma irradiation can decrease the crosslinking degree of the chitosan chain.

Direct correlation between the escalation irradiation dose and reduction of molecular weight occurs due to the depolymerisation reaction during irradiation process that causes the scission mechanism, making the chitosan chain shorter [12].

$R\text{-}H \sim R\ (C_4\text{-}C_6) + H$

$R\text{-}H + H \longrightarrow R\ (C_1\text{-}C_6) + H_2$

$R\ (C_1, C_4) \longrightarrow F_1 + F_2$ (scission)

$R\text{-}NH_2 + H \longrightarrow R\ (C_2) + NH_3$

Where R-H and R-NH2 are macromolecules of chitosan, R (C_2) is a macro-radical of chitosan located in the carbon atom Cn. F1 and F2 are chain fragments after the scission. Scission of chitosan chain occurs randomly as in gamma-irradiated cellulose acetate [13]. The exposure duration has considerable influence on the amount of scission and, consequently, on the intrinsic properties and their parameters. The intrinsic properties play a major role in the kinetics of chitosan degradation.

The increasing rate of chitosan chain depolymerisation is also affected by the gradual pH change from acidic to the alkaline environment subsequent to the irradiation process [12]. The alkaline environment is held accountable for degrading the amino and hydroxyl group on the side chain of chitosan that reduces chitosan viscosity and molecular weight.

Chitosan viscosity and molecular weight alteration to a nanoparticle size, due to gamma irradiation, is expected to enhance its solubility rate inside the blood. Escalation of solubility rate is proven to enhance the antioxidant activity of chitosan [9][14][3][12]. By enhancing the antioxidant activity, chitosan may diminish the detrimental effects of free radicals (Pb^{2+} ions) for people who are chronically exposed to Pb from surrounding environments.

4. Conclusion

Gamma ^{60}Co irradiation reduces chitosan viscosity and molecular weight in a dose-dependent manner. The reduction is caused by depolymerisation of chitosan chain by scission mechanism. The effective irradiation dose in this research is 150 kGy.

5. Acknowledgement

We thank Dr. Widhi Mahatmanti, M.Si., lecturer in the Chemistry Department of FMIPA UNNES, for sparing her valuable time to discuss and support the viscosity and molecular weight measurement processes in the Laboratory of Chemistry, FMIPA UNNES.

6. Funding

This research is funded by UNNES through DIPA UNNES No. SP DIPA-042.01.2.400899/2019 on 05 December 2018

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