Synthesis of bio-polymer based chitosan and starch with methyl orange dyes as a material potential for low dose gamma film dosimeter

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Abstract. Low dose gamma film dosimeter based on chitosan and starch bio-polymer with methyl orange dyes has been synthesized and characterized. The aim of this research was to synthesis radiochromic film dosimeter used biopolymer material such as chitosan and starch with methyl orange dyes as the color indicator and also to investigate the effect of gamma irradiation on film dosimeter response. The film dosimeter was prepared by mixing chitosan and starch at gelatinization temperature then added with methyl orange dyes. Biopolymer solution then casting on the flat glass to produce a thin film with uniform thickness, after that film dosimeter was irradiated at 1, 3, 5, and 9 kGy. To analyze the quantitative response of irradiation, the film dosimeter was characterized by UV-Visible. The result shows that the film dosimeter has changed its color as a response to the irradiation. The higher the dose of gamma irradiation, the higher the net absorbance of it. This research showed that bio-polymer based chitosan and starch is material that has the potential for low dose gamma dosimeter.

1. Introduction
Dosimetry is the science of dose measurement which represents the main function of the radiation process. To observe the dose during the irradiation process, color film polymers are considered the most commonly used as dosimeters. Many color films have been developed and investigated for absorption dose measurements in nuclear reactors, X-rays, gamma rays and electron beams [1], [2], [3].

Methyl Orange or Sodium 4 - [(4-dimethylamino) phenyldiazenyl] benzenesulfonate is an azo dye and an acid indicator in aqueous solution conditions. Azo dyes are not easily degraded under normal conditions but can be degraded well under gamma irradiation. Irradiation will cause the radiolysis process which has alternative opportunities for degradation. Methyl orange is one of the azo dyes that has been investigated in the radiolysis process [4], [5], [6]. One indication of the success of degradation is from natural color changes that are quite easily observed and can be measured spectrophotometrically to determine the absorption dose.

Dosimeters in liquid form are usually for high dose applications and in gels for low dose applications between 1 to 200 Gy [7], [8], [9]. Various gel systems can be used as substrates for gel dosimeters, including agar and gelatin which are popular but have limitations when preparation. In addition, resulting in irradiated-dose distribution diffuses over time, the evaluation technique is time-limited due to the resulting blurred dose distribution [10]. An alternative of the dosimeter gel that has been developed is a polymerization-based dosimeter of an irradiated polymer. One study mentioned
that a 1 mm thick PVA film is very useful as a gamma-ray dosimeter in the range 1-30 kGy and the film response is more stable [11], [12]. Thin-film dosimeters have the advantage of a system that more reliable, more stable, simpler and cheaper for routine dosimeters [13], [14].

Film dosimeters can be derived from natural polymers such as starch, rubber, chitosan, cellulose, protein and lignin. The natural polymer is considered as an alternative to simplify the recycling procedure and is designed to be returned to nature after use. Starch is cheaper, renewable, biodegradable and not damage the product. Natural starch is hydrophilic and its mechanical properties decrease when interacting with water or hydrophilic. Starch will be mixed with other polymers such as chitosan for reducing the hydrophilicity. Chitosan is also known as a material that has strong properties and is difficult to tear [15].

The purpose of this paper is to produce a dosimeter film from bio-polymer. The operation of the dosimeter is also expected to be easier, cheaper, has high selectivity and sensitivity, and can be applied to low doses such as sterilization of medical devices, food irradiation, polymer crosslinking, and degradation.

2. Materials and method

2.1. Film Preparation
Chitosan 1% w/v is divided into two solutions A and solution B each 25 mL. Sample A added by 7.5 mL of 1% w/v tapioca starch solution and 5 mL of 0.01% v/v methylene orange (MO), while sample B was added by 10 mL of 1% w/v tapioca starch solution and 5 mL of 0.01% MO. Samples A and B are stirred at a gelatinization temperature of around 52 to 64 °C until homogeneous. Each sample A and B is poured on a flat glass plate and dried at 70°C. Each film was cut to a size of 1 x 4 cm.

2.2. Gamma irradiation
Irradiation was performed by 60Co with an activity of 24 kCi and a dose rate of 4 kGy/hour (at STTN-BATAN Yogyakarta). Each sample A and B were irradiated at a dose of 1, 3, 5, 9 kGy and a dose of 0 kGy as blank, respectively.

2.3. Measurement of Film Dosimeter

2.3.1. Qualitative Measurement. The irradiated film investigated by color changes before irradiation and after irradiation.

2.3.2. Quantitative Measurement. Dosimeter film before irradiated was determined by the wavelength between 400 nm and 800 nm with UV-Vis STTN-BATAN. The highest absorbance was obtained at the optimum wavelength of 433 nm. All absorbance films A and B after irradiation were measured then get the relation between absorbance over absorbed dose.

3. Results and Discussion

3.1. Absorption Spectra
Figure 1 shows the absorption spectra of the dosimeter film before being irradiated. The maximum absorption band at 433 nm shows the yellow characteristics of methyl orange. The maximum wavelength that appears is used to measure the absorbance of dosimeter films in this research.
3.2. Response Curves

Figure 2 shows the relationship of optical density change per unit thickness ($\Delta A \text{ mm}^{-1}$) at wavelength 433 nm compared to the absorption dose of starch/chitosan/MO dosimeter film with different starch volume contents. $[\Delta A = A_o - A_i]$, where $A_o$ and $A_i$ are optical densities of film dosimeters before and after irradiated [16]. From the graph shown in Figure 1 the value ($\Delta A \text{ mm}^{-1}$) increases with increasing gamma irradiation dose from 0 kGy to 9 kGy.
After irradiated from 0 kGy to 9 kGy, a linear regression equation is formed $y = kx + b$ and the linearity depends on the coefficient ($R^2$). From the equation, $k$ is the slope of the line which means sensitivity while $R^2$ shows the ability of the dose-response [17]. Sample A has a linear regression equation $y = 0.0884x + 0.1756$, $R^2 = 0.9808$ while sample B has a linear regression equation $y = 0.0414x + 0.0186$, $R^2 = 0.9832$. From the slope can be seen that the sensitivity of the dosimeter film sample A is greater than sample B, however the dose response-ability of sample B is better than sample A.

3.3. Radiation Effect on Dosimeter Film

The $-N=\equiv N-$ group of azo dyes in methyl orange is very sensitive to radiation and resolved immediately when exposed to low doses of gamma irradiation [18], [19]. When the film is irradiated with gamma radiation, a radiolysis process will occur which produces $H_2$, $H_2O_2$, $H^+$, $OH^-$ and electron hydrates ($e_{aq}$), hydroxyl radicals ($\cdot OH$) and hydrogen atoms ($\cdot H$) as intermediate species in various amount depending on linear energy transfer value of radiation (Eq. 1).

$$H_2O \leftrightarrow \cdot OH, \cdot H, e_{aq}^-$$  

From the results of radiolysis, which plays a significant role in decolorization and degradation are $e_{aq}^-$ and hydroxyl radicals ($\cdot OH$). Electron hydrate ($e_{aq}$) is very effective for decolorization but less active for the degradation. Electron hydrates ($e_{aq}$) and $\cdot H$ atoms will be converted to $O_2\cdot$ and $\cdot HO_2$ respectively, but these compounds are quite less reactive to aromatic groups so they are not effective for degradation. However, the addition of $e_{aq}^-$ to $-N=\equiv N-$ groups from the azo of methyl orange can still destroy its double bonds (Eq. 2).

$$-N=\equiv N- + e_{aq}^- \rightarrow -N-N^- \rightarrow (+H_2O) \rightarrow -N\cdot-\cdot NH^- + OH^-$$  

Hydroxyl radicals ($\cdot OH$) can destroy color chromophores more efficiently than hydrated electrons. The main color of methyl orange is caused by the azo group conjugated with other parts of the molecule, the double bonds of these groups will break when first exposed to radiation. Among oxidative species, $\cdot OH$ is the main oxidative transient reacting to benzene and azo moieties ($-N=\equiv N-$) with a high rate coefficient. The addition of $\cdot OH$ to the $N=\equiv N$ bond will attack the aromatic ring of methyl orange. This reaction might cause intensive color destruction [20].

In Figure 3, the benzene aromatic ring will be degraded to a hydroxycloloexehenyl radical. This radical will react with dissolved oxygen to produce hydroxide hydroperoxide that is not stable. The next reaction is the removal of a water molecule and the formation of an aromatic ring from hydroxide hydroperoxide to mucodialdehyde. Mucodialdehyde then oxidized to mukanot acid. In the oxidation process, glyoxal will be formed which is then oxidized to carboxylic acid [21].

Carboxylic acid is a weak acid and methyl orange is an indicator of acid that sensitive to acids with a color change for pH less than 3.1 will be red, pH greater than 4.4 will be yellow and a pH between 3.1 and 4.4 will be orange. Figure 4 shows the change color after exposure of gamma radiation from 0 kGy to 9 kGy. The results show the color of the film dosimeter changes from yellow to murky yellow which tends to approach orange after irradiation. This change in yellow to murky yellow indicates a carboxylic content with a pH close to 4.4.
Figure 3. Mechanism reaction of azo methyl orange degradation

Figure 4. Starch/chitosan/MO dosimeter film before and after irradiation
The higher the dose causes the higher the turbidity of the dosimeter film and the absorbance. High doses will further increase the results of radiolysis in the form of H₂, H₂O₂, H⁺, OH⁻, electron hydrates (e⁻aq⁻), hydroxyl radicals (•OH) to break the double bond –N=–N– from the azo methyl orange. Carboxylic acids are formed even more and will increasingly clarify the change in the color of methyl orange. This color change from yellow to murky yellow indicates the increased color concentration cause increasing irradiation dose and followed by increasing absorbance. It indicates that film dosimeters from bio-polymer can be created. For the next project, the operation of the dosimeter is also expected to be easier, cheaper, has high selectivity and sensitivity, and can be applied to low doses such as sterilization of medical devices, food irradiation, polymer crosslinking, and degradation.

To indicate that the degradation process has occurred, it can be analyzed through HPLC or FT-IR analysis because if only indicate from decolorization it will be hard to observe.

4. Conclusion
Dosimeter film from chitosan and starch biopolymer has been created. polymer dosimeter film has high potential to measure low radiation doses in the range of 0 kGy to 9 kGy. These dosimeter applications include sterilization of medical devices, food irradiation, crosslinking polymers and degradation. The dosimeter polymer film can be produced in various forms for various applications, easy to control and cheaper. The change in color from the dosimeter film from yellow to murky yellow after irradiation indicates carboxylic acid. The higher radiation dose causes more murky yellow which tends to approach orange of the dosimeter film followed by an increase of absorbance. From the linear regression equation, the sensitivity of sample A dosimeter film is greater than the sensitivity of sample B, but the dose response-ability of sample B is better than sample A.

5. Suggestion
Need an analysis of the maximum absorbance of each sample from various doses. The stability test is needed to determine the stability of the film before being irradiated and after irradiation to know the proper storage conditions of the dosimeter film. Added the additive substances like chloral hydrate which can accelerate the reaction of degradation of the dye film color. FT-IR or HLPC analysis is needed to determine the success of the degradation of the functional group's changes.

Acknowledgment
Authors wishing to acknowledge assistance and encouragement from the Chemical Engineering Department, Polytechnic Institute of Nuclear Technology and financial support from the National Nuclear Energy Agency.

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