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Electron Beam Crosslinking of Glycerol-Plasticized Tilapia Gelatin for Enhanced Biopolymer Film Performance

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Polymer films derived from fish gelatin were evaluated for their moderate absorbency and moisture protection properties. To improve mechanical strength and hydrophilicity, irradiation-induced crosslinking was applied. Tilapia skin gelatin, plasticized with glycerol, served as the base material for assessing the effects of varying electron beam irradiation dose on the biopolymer's performance. The formulations were optimized and analyzed for changes in gel content, swelling capacity, and mechanical properties following irradiation. Water vapor transmission rate (WVTR) measurements were used to confirm the effective integration of the crosslinker and glycerol into the gelatin matrix, providing insights into the permeability of the films. This study supports the development of fish gelatin-based biopolymers with improved functionality for use in environmentally friendly and biodegradable products, potentially enhancing shelf life and product quality. Gel content is improved up to 15 kGy only, and swelling capacity is reduced due to irradiation doses. WVTR is decreased by an increase in irradiation doses due to less permeable films produced after being irradiated. The irradiated plasticized fish gelatin films can be a promising, biodegradable film with improved moisture resistance for packaging applications.

1. Introduction

Biopolymers such as polysaccharides, proteins, and lipids can be broken down into methane (CH_4), carbon dioxide (CO_2), water (H_2O), and inorganic compounds primarily through microbial activity. Each year, a significant quantity of agricultural by-products is generated, offering potential for use in food packaging as biodegradable, renewable, and cost-effective raw materials (Abdullah et al., 2021). Biodegradable polymers typically contain ester and amide bonds within their molecular structure, owing to the presence of biodegradable functional groups. Through aqueous and enzymatic hydrolysis, these biopolymers degrade into shorter, water-soluble fragments, ultimately decomposing fully without releasing toxic or harmful substances (Abdullah et al., 2022).

Fish gelatin, such as tilapia, is a type of protein that contains lower levels of imino acids, specifically proline and hydroxyproline; the amino groups act as a gelling agent, compared to mammalian gelatin, which is essential for the formation of a stable triple helix structure. As a result, fish gelatin exhibits inferior thermal stability and rheological properties relative to its mammalian counterpart (Ahmad et al., 2024). However, the extraction of fish gelatin from fish processing by-products has supported more sustainable food production practices, generating growing interest in its use as a potential substitute for mammalian gelatin (Kalita et al., 2025).

Plasticizers are additives with low volatility added to biopolymer materials, modifying the functional properties of films by improving their extensibility, dispensability, flexibility, elasticity, rigidity, and mechanical properties (Suderman et al., 2018). Some studies have shown that hydrophilic plasticizers, used in various concentrations, have enhanced the mechanical properties of gelatin. Among the hydrophilic plasticizers studied in plasticizing biodegradable films are glycerol in chicken skin gelatin (Nor et al., 2017), sorbitol in sago starch (Abdorreza et

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al., 2011), glycerol, sorbitol and xylitol in pullulan-alginate-carboxymethyl cellulose (CMC) (Tong et al., 2013), lignin, glycerol, and sorbitol as plasticizers in fish gelatin (Núñez-Flores et al., 2013), etc.
Among the various physical crosslinking techniques, ionizing irradiation—using either gamma rays (γ-rays) or electron beam (e-beam) radiation—is particularly advantageous due to its rapid processing and the absence of required additives or harsh conditions that might otherwise compromise the material's structure (Benbettaïeb et al., 2015). The high energy associated with irradiation can induce both crosslinking and degradation, modifying the material's physical and chemical properties through main chain scission and crosslink formation. Upon exposure to irradiation, polymers become excited, forming reactive intermediates such as ions and free radicals. These species initiate new chemical bonds and modify the material's properties through reactions along the polymer chains. Crosslinking occurs when two radiation-induced radicals combine to form a covalent bond, thereby increasing the polymer's molecular weight. Conversely, degradation results when the energy surpasses the binding forces between atoms, breaking chemical bonds and reducing molecular weight. These competing reactions ultimately determine the durability and functional lifespan of irradiated materials (Lee et al., 2017). This approach not only enhances the performance of irradiated glycerol-plasticized tilapia gelatin films but is also parallel with sustainable manufacturing practices due to the production of crosslinked biopolymers based on fish gelatin. Some of the previous studies have shown the improvement in tensile strength by using electron beam irradiation (EB irradiation) (Benbettaïeb et al., 2016) and gamma irradiation (Perkasa et al., 2013). These two previous studies have shown that the mechanical properties are increased after being irradiated. Novelty in this study would focus on the irradiated plasticized fish gelatin films because there are no reports using irradiation as a crosslinker on fish gelatin and glycerol as a plasticizer.

2. Preparation and characterization

Tilapia fish gelatin powder (8 g) with a 250-Bloom rating was mixed with 100 mL of distilled water using a mechanical stirrer at room temperature. The gelatin powder was purchased from Nichz Ingredient Shop in Shah Alam, Selangor, Malaysia. Subsequently, 30 wt% glycerol was added to the gelatin mixture. Glycerol was purchased from Biotek Abadi Sdn. Bhd., Malaysia. The mixtures were then heated to 50 °C and stirred continuously for 10 min to ensure a homogeneous consistency. For the irradiated fish gelatin films, the gelatin solutions were irradiated using an electron beam accelerator, Model EPS 3000 (Cockroft Walton), in liquid form, after 25 mL was poured into a clean Petri dish, with doses ranging from 0 to 25 kGy. The accelerator administered these doses at a rate of 5 kGy per pass and an energy of 2.2 MeV. The drying was carried out in an oven at 45 °C for 48 h. After drying, the films were carefully peeled from the dishes for further analysis.

2.1 Determination of swelling ratio and gel content

This method was proposed by Bigi et al. (2004) with little modification, where the crosslinked gelatin films were weighed at room temperature (approximately 0.5 g). They were then immersed in reverse osmosis (RO) water for 24 h. Wet samples were wiped to remove excess liquid and weighed. The amount of adsorbed water was calculated as Eq(1) (Bigi et al., 2004);

$$Swelling\ Ratio\ (\%) = \frac{W_w - W_i}{W_i} x100 \quad (1)$$

where Ww and Wi are the weights of the wet and the initial weight before being immersed in RO water. To determine the gel content of the crosslinked films, the swelled samples for the irradiated samples were dried in an oven at 30 °C for 24 h. The dried sample was calculated as Eq(2) (Ibrahim et al., 2019);

$$Gel\ Content\ (\%) = \frac{W_d}{W_i} x100 \quad (2)$$

where Wd and Wi are the weights of the dried sample and the initial weight before being immersed in RO water.

2.2 Determination of water vapor transmission rate (WVTR)

The water vapor transmission rate (WVTR) was measured by modifying the ASTM E96 described by Ibrahim et al. (2019). The sample films were cut into circular shapes with a diameter of ~17 mm and fixed on a glass vial containing 20 mL of reverse osmosis water (RO water). The glass vials were placed inside a desiccator containing silica gel for 24 h at 25 °C. The analysis was carried out in triplicate for each formulation to get the average weight. The WVTR (g m^{-2} day^{-1}) was calculated as Eq(3) (Ibrahim et al., 2019);

$$WVTR\ (g\ m^{-2} day^{-1}) = \frac{W_i - W_f}{A} \quad (3)$$

where Wi is the initial weight of vials, Wf is the final weight of vials, and A is the area of the vial opening.

2.3 Determination of tensile properties

Tensile strength (Ts) and elongation at break (EAB) values were measured using a Universal Tensile Machine (Shimadzu AG-Xplus, 20 kilonewton capacity) from Kyoto, Japan, according to the ASTM D882 method as suggested by Suderman et al. 2018 with a few modifications in the aspect of measurement of film strip, gauge length, and speed. Film strips measuring 60 mm x 15 mm were prepared using a cutting blade. The gauge length was set at 40 mm, and the film strips were stretched at a rate of 10 mm per min until they fractured. The Ts and EAB values were recorded from the average of five samples.

2.4 Morphology analysis

The surface morphology and film samples' cross-section were observed using a field emission scanning electron microscope (FESEM). The machine conducted this FESEM analysis (Brand: Carl Zeiss, Model: GeminiSEM 500). The samples were cut $2\ cm \times 2\ cm$ before observing the cross-section of the films. The images from Figure 5 were captured at an acceleration voltage of 10 kV with magnification ranging from 200 to 1,500.

3. Results and discussion

3.1 Determination of swelling ratio and gel content

Figure 1 shows the effects of gel content and swelling ratio on various irradiation doses. The figure shows the effects of irradiation dose (5 to 25 kGy) on gel content and swelling ratio. In the irradiation treatment, plasticized gelatin films must be irradiated in liquid (after gelatin powder is dissolved in water) to induce a crosslinking reaction in a gelatin solution (Haema et al., 2014). The gel content increased rapidly from 5 kGy to 15 kGy, up to 70 % for the gelatin content. After 15 kGy of irradiation dose, the gel content dropped drastically due to the degradation of plasticized gelatin films by irradiation modification. Marianti et al. (2020) reported that the viscosities of films decrease in response to an irradiation dose. This might correlate to the degradation stage at this higher dosage of irradiation. In contrast, Haema et al. (2014) and Kimura et al. (2021) reported that gelatin's crosslinking percentage can only achieve around 90 % above 100 kGy irradiation dose. Figure 1 also shows the swelling ratio of irradiated plasticized fish gelatin films. The swelling ratio is a measurement of the tendency of the polymer matrix to build up a three-dimensional (3D) structure after being cross-linked (Haema et al., 2014). Furthermore, this 3D network also recognized the capability to sustain water, where the low irradiation dose absorbs more water than the higher dose because the crosslinking density is lower. The results show that the swelling ratio decreased rapidly from 5 kGy to 25 kGy. As confirmed, the plasticized gelatin films were successfully irradiated in the liquid state at room temperature. The appropriate crosslinking method for gelatin, particularly focusing on water retention, must be selected. Irradiation is revealed to be a superior option, capable of achieving high moisture content and effectively inducing crosslinking at lower doses while maintaining a high swelling ratio. This method is considered more sustainable and environmentally friendly as it avoids using chemical additives, thereby enhancing the sustainability of the production process.

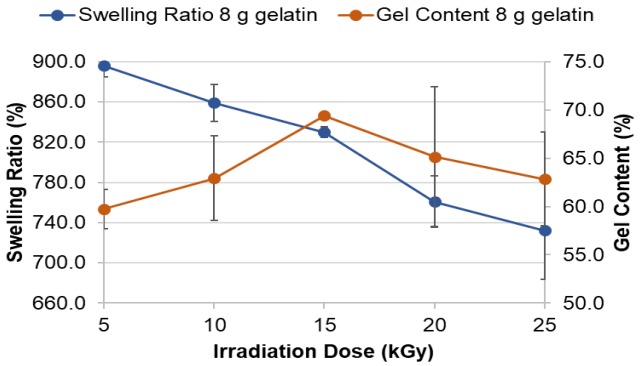

Figure 1: Effect of crosslinking modification on gel content and swelling ratio percentages of the irradiated plasticized 8 g of gelatin films

3.2 Determination of water vapor transmission rate (WVTR)

Figure 2 shows the effect of irradiation dose on WVTR on the optimized Ts and EAB formulations of plasticized gelatin films. Figure 2 shows a decreasing trend in WVTR upon irradiation dose (kGy). In contrast, Jo et al. (2005) reported that pectin and gelatin successfully crosslinked at 10 kGy, where their mechanical properties and water vapor permeability (WVP) increased and decreased, respectively. Section 3.1 has discussed the

effect of gel content on irradiated plasticized fish gelatin films. The increase of gel content from 5 kGy to 15 kGy was not significant, and the gel content only dropped to 60 to 65 % after 15 kGy. This can be evidence that irradiation modification has successfully obtained more than half the crosslinking percentage in the biopolymer matrix. With this amount of crosslinking percentage, the permeability of the films has decreased. The crosslinking percentage has helped in WVTR to decrease as the irradiation dose increases.
Hence, the irradiation-induced crosslinking produced less permeable films, and this is probably caused by the 3D network that has formed in the biopolymer matrix.

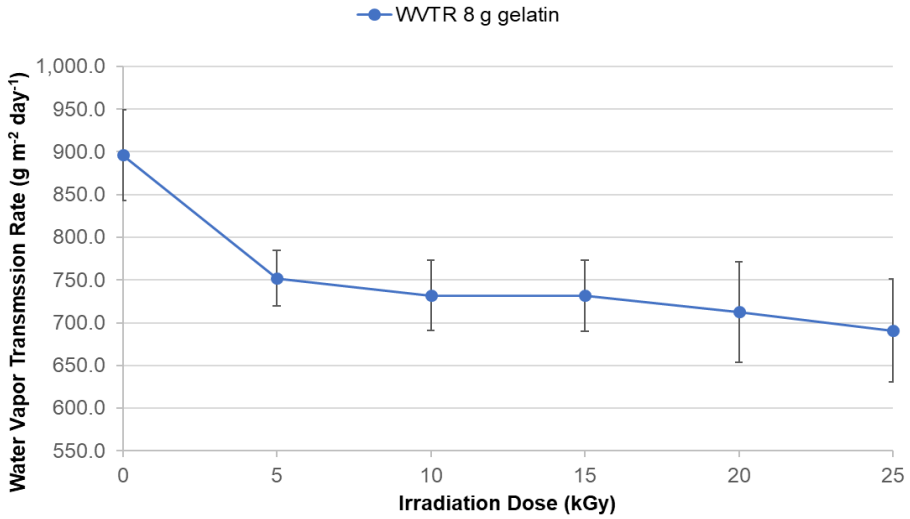

Figure 2: Effect of crosslinking modification on WVTR of the irradiated plasticized 8 g of gelatin films

3.3 Tensile properties

Figures 3 and 4 show he changes in tensile strength (Ts) and elongation at break (EAB) of gelatin films crosslinked at various irradiation doses. A decline in both Ts and EAB was observed due to the irradiation process. Nasreen et al. (2016) noted that exposure to gamma radiation can lead to cross-linking and chain scission in polymers. Specifically, gamma radiation tends to break down polysaccharides or other organic polymers by cleaving glycosidic linkages, particularly in polysaccharide compounds. Gelatin, a protein-based natural biopolymer, is also susceptible to degradation under gamma radiation (Nasreen et al., 2016). Lee et al. 2017 also mentioned that irradiation can cause degradation results when the energy surpasses the binding forces between atoms, breaking chemical bonds, and reducing molecular weight. Although irradiation-induced crosslinking can somewhat enhance the mechanical strength of plasticized gelatin films, it typically degrades the structure of natural polymers such as polysaccharides and gelatin.

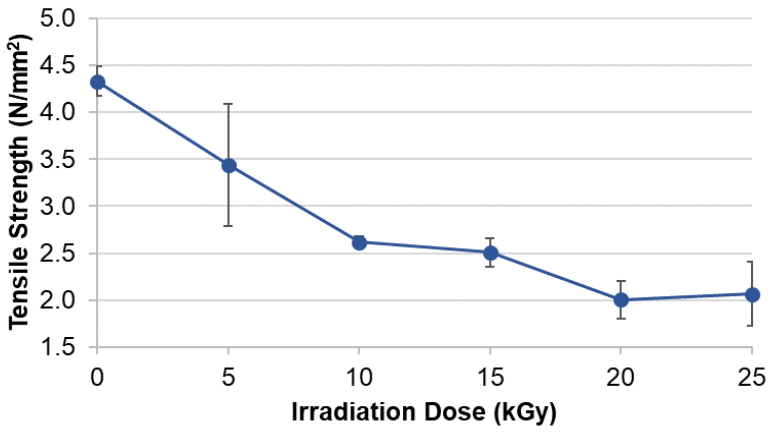

Figure 3: Effect of crosslinking modification on tensile strength (Ts) of the irradiated plasticized 8 g of gelatin films

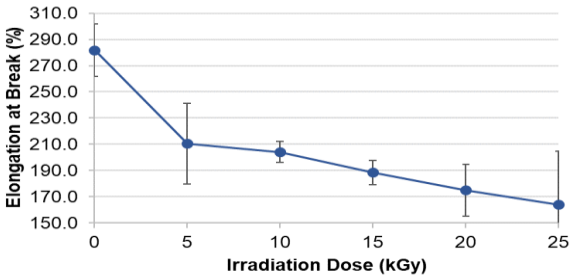

Figure 4: Effect of crosslinking modification on elongation at break (EAB) of the irradiated plasticized 8 g of gelatin films

3.4 Morphology analysis

Figure 5 depicts the microstructural changes from FESEM images of the optimized plasticized fish gelatin contents: 8 g gelatin and its irradiation modification. Based on Figure 5 (a), the uncrosslinked samples for 8 g of gelatin are displayed. The morphology of the unirradiated 8 g gelatin exhibited a smooth morphology without any voids, indicating the development of a regular, continuous network structure during preparation using this casting technique. This was also reported by Andreuccetti et al. (2012), Park et al. (2008), and Chuaynukul et al. (2018). The FESEM images of irradiated plasticized fish gelatin revealed that the films became smoother and more compact than the unirradiated films, as shown in Figures 5(b) and (c). Benbettaïeb et al. (2016) and Benbettaïeb et al. (2015) also reported the same results; this might be due to the discontinuous gaps decreasing, and there was an observed alignment of the gelatin strand. This behavior could result from forming new bonds that stabilize the protein network. These two studies clearly show that the mechanical properties have decreased due to the insufficient incorporation of plasticizers in the biopolymer matrix. However, Dey et al. (2014) contended that mechanical characteristics have dropped by gamma irradiation modification into a gelatin matrix with polyvinyl alcohol (PVA) that also acts as a plasticizer. This study claimed the same morphology, which is smooth due to the interaction that happened between gelatin and PVA during gamma irradiation.

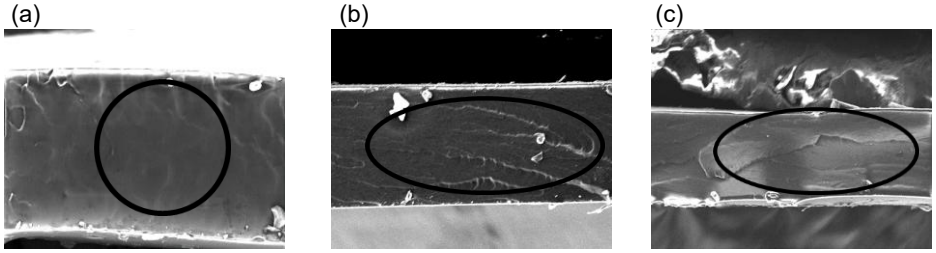

Figure 5: FESEM images of unirradiated and irradiated plasticized fish gelatin samples; (a) 8 g gelatin/0 kGy, (b) 8 g gelatin/15 kGy, (c) 8 g gelatin/25 kGy

4. Conclusions

Electron beam irradiation effectively enhanced the crosslinking of glycerol-plasticized tilapia gelatin films, improving their gel content and reducing the swelling ratio and water vapor transmission rate. Optimal crosslinking was observed at 15 kGy with the gel content of 70 % and beyond which degradation reduced performance. Although mechanical properties slightly declined (decreased 53 % for Ts and 39 % for EAB) due to chain scission, morphological analysis confirmed improved film compactness and structural alignment post-irradiation. These findings demonstrate the potential of irradiation-induced crosslinking as a sustainable method for developing biodegradable films with moderate absorbency and moisture barrier properties suitable for eco-friendly packaging applications. The electron beam irradiation is a promising, sustainable crosslinking method for producing biodegradable fish gelatin films with improved moisture resistance and moderate absorbency, making them suitable for eco-friendly packaging applications.

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