An eco-friendly bioplastic film obtained from water hyacinth

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Abstract. Water hyacinth is an invasive aquatic plant that causes adverse effects on the global environment. Due to high cellulose contents of water hyacinth, in this project aimed to covert water hyacinth to valuable raw materials for CMC-based bioplastic. Not only does the excess amount of water hyacinth reduces from natural water resources, but biodegradable CMC-bioplastic can also decrease the amount of plastic waste. Cellulose was extracted from water hyacinth followed by synthesis of carboxymethylcellulose (CMC) and preparation of bioplastic films, respectively. Gamma irradiation (1-10 kGy) was used to induce the crosslinking of CMC chains to improve the CMC bioplastic properties. The synthesized CMC from water hyacinth has comparable properties to the commercial CMC in that similar thermal stabilities, elemental components, and degradation mechanisms under controllable artificial weathering process. Further research regarding the role of CMC bioplastic derived from water hyacinth for food packaging would be promising applications.

1. Introduction

Many rivers in Thailand have been confronting with an environmental problem from water hyacinth, invasive aquatic plants. Due to the massive proliferation of water hyacinth, it covers river surface, blocking oxygen dissolution and transportation. However, water hyacinth has high cellulose contents (about 25%); thus, it can use as a raw material for carboxymethylcellulose (CMC), being an essential precursor for bioplastic production [1]. It could replace the use of non-degradable plastic. Nevertheless, the chemical processes are needed to transform non-water-soluble cellulososes to water-soluble CMC. Besides, bioplastic derived from water hyacinth would be compatible with food, pharmaceuticals, detergents, textile, and cosmetic applications. Also, CMC hydrogel can be applied in various applications, including tissue engineering, drug delivery, wound dressing, and plant breeding [2-6]. CMC can be synthesized by the carboxymethylation process substituted hydroxyl groups of cellulose with carboxymethyl groups [7,8]. However, water hyacinth has a large amount of hemicellulose and lignin, preventing the carboxymethylation [7,8]. Therefore, they are needed to be removed by NaOH and NaClO₂ treatment, respectively [9]. In general, only isolated cellulose would be used for CMC production by two main reactions, including alkalinization and carboxymethylation [1,8]. However, it was reported that CMC-based bioplastic films are brittle, which make them difficult to use. To solve this obstacle, adding plasticizers is considered as the best solution. Polyethylene glycol (PEG) is a favored plasticizer because it is a water-soluble compound, biodegradable and non-toxic, approved by the U.S. Food and Drug Administration (FDA) [2]. From previous studies, it was suggested that gamma irradiation could improve the properties of the polymer by induced crosslinking between polymer chains
making the polymer get tougher [1,10]. Also, the irradiation process can occur without radical initiators and toxic chemical. Moreover, not only crosslinking reaction can exist but also sterilization at the same time [11]. Therefore, this finding aims to produce the CMC-based bioplastic from water hyacinth as well as improve their physical and mechanical properties by gamma irradiation process.

2. Materials and methods

2.1. Materials and instrumentations

Sodium hydroxide (Univar), sodium chlorite (Alfa Aesar), acetic acid (RCI Labscan), monochloroacetic acid (Sigma-Aldrich), polyethylene glycol (Mw = 400 g/mol) (Sigma-Aldrich), Ethanol (Merck) and Methanol(Merck) are analytical grade. The instruments used to characterize the CMC films are FTIR spectrometer (PerkinElmer), SDTA 851e thermogravimetric analyzer (Mettler Toledo), 34SC-2 universal testing machine (Instron), JEM-ARM200F transmission electron microscope (JOEL), JSM-7610F scanning electron microscope (JOEL) and SML-21 environmental chamber (ESPEC).

![Figure 1. Scheme of bioplastic production from water hyacinth.](image)

2.2. Synthesis of carboxymethylcellulose (CMC)

The stems of water hyacinth were cleaned with tap water and chopped into small pieces, as shown in figure 1. Then they were dried at 90°C for 24 hours, following by blending and sieving to obtain a fine powder. The seventy grams of dried powder was mixed with 700 ml of 10% (w/v) NaOH and stirred continuously at 80°C for 2 hours to remove hemicellulose. After that, the product was filtrated and washed with distilled water, and then it was dried in the oven at 80°C for 12 hours. The 25 g of as-received powder was mixed with 750 ml of 1%(w/v) NaClO₂ and adjusted the pH to 4 with acetic acid and stirred continuously at 80°C for 2 hours to remove lignin. After that, the product was filtrated and washed with distilled water before drying at 80°C for 12 hours. The obtained powder already had abundant cellulose. The sixteen grams of the obtained cellulose was mixed with 20 ml of 55%(w/v) NaOH and 320 ml of 95% (v/v) ethanol, stirred at room temperature for 30 mins before adding 16 g of monochloroaetic acid. Then the mixture was kept stirring at 60°C for 6 hours. After that, the product was neutralized with acetic acid (pH 7). Then, it was
filtrated and washed by 70%(v/v) methanol as well as 70%(v/v) ethanol, respectively. The obtained powder was dried in the oven at 80°C for 12 hours, named as-synthesized CMC.

2.3. Preparation of CMC-PEG films
The 2.88 g of synthesized CMC was dissolved in 120 ml of distilled water following by stirring at room temperature until it was completely dissolved. Then the 0.72 g of polyethylene glycol (PEG) was added and homogenized for 20 mins. After that, 90 ml of the mixture was poured into an acrylic mold (size = 15x15 cm²) and dried in the oven at 60°C for 24 hours. In order to investigate an effect of gamma irradiation on CMC based bioplastic, the CMC-PEG film samples were irradiated at the dose of 1 kGy, 3 kGy, 5 kGy, and 10 kGy ($^{60}$Co γ-source under air atmosphere).

2.4. Characterization of CMC-PEG films
Fourier transform infrared spectroscopy (FTIR) was performed to study the functional groups in the range of 4000-400 cm⁻¹. The sample thermal stability was investigated by Thermogravimetric analysis (TGA) in the temperature range of 50-550°C. Their morphology was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Also, the elemental composition was investigated by energy-dispersive x-ray spectroscopy (EDS). For mechanical property, tensile testing was performed with dog-bone shape samples to determine the tensile strength and Young’s modulus of the samples. Weathering analysis was performed in the environmental chamber at 60°C RH = 60% for 18 days and the mass of the samples was measured before and after the process.

![Figure 2](image1.png)

**Figure 2.** SEM images of commercial (a) and synthesized (b) CMC-PEG films, TEM images of commercial (c) and synthesized (d) CMC-PEG films.

![Figure 3](image2.png)

**Figure 3.** EDS mapping of the location of Ca in the commercial (a) and synthesized (b) CMC-PEG films.

3. Results and discussion

3.1. Morphology of CMC-PEG films
The CMC powder derived from water hyacinth exhibited a pale yellow-brown color, as shown in figure 1. Similarly, their films also showed the same colour. Additionally, smoother surfaces were noticed from the film derived from the commercial CMC (figure 2a). It would be an effect of the residue fibers and their arrangement. Figure 2b shows the SEM images of CMC-PEG films derived from water hyacinths, the bright contrast represents the residue fibers in the films. Notably, the large sizes of residue fibers were observed spreading over the film (figure 2d); however; fine fibers were well distributed in the commercial CMC-PEG film (figure 2c). It can imply that the carboxymethylation process did not
complete; therefore, cellulosics remain in the CMC derived from water hyacinth. Interestingly, according to EDS results, both commercial CMC-PEG film and synthesized CMC-PEG film had the same elemental components (including C, O, N and Ca), but the Ca distributions were different in that massive accumulation of Ca only found in the synthesized CMC-PEG film as shown in figure 3b. It would influence the film properties, which will be discussed later.

3.2. Thermogravimetric analysis (TGA)

Figure 4a provides the TGA profiles of the film made from the pure CMC compared with the irradiated commercial CMC-PEG at 0, 1, 3, 5 and 10 kGy. For the pure CMC film, the mass rapidly decomposed at 275°C (41% of mass loss). On the other hand, the commercial CMC-PEG and irradiated samples exhibited a similar broad peak in the range of 100-320°C due to the decomposition of polyethylene glycol and CMC. Figure 4b shows the TGA plots of the film made from the pure CMC compared with the irradiated synthesized CMC-PEG films at 0, 1, 3, 5 and 10 kGy. Notably, the commercial CMC and synthesized CMC films exhibit similar characteristics of thermal stability.

3.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the synthesized and irradiated CMC-PEG films are shown in figure 5. The broad peak at 3400 cm\(^{-1}\) can be observed in FTIR spectra assigned as -OH group [2,8,9]. The sharp band at 2950 cm\(^{-1}\) is attributed to C-H stretching. The peak at 1600 cm\(^{-1}\) and 1100 cm\(^{-1}\) are indicated as C=O-O bonding of CMC and C-O-C bonding of PEG, respectively [2,8,9]. Notably, no significant difference in surface functional group can be observed in the CMC-PEG films after irradiation; however, the intensity of oxygen functional group was found to decrease with increasing the gamma irradiation dose. The surface functional group of CMC-PEG films fabricated from water hyacinth is also in a good agreement with V.S. Ghorpade et al. which reported the functional group of CMC-PEG films from commercial CMC [3].

![Figure 4. TGA profiles of commercial (a) and synthesized (b) CMC-PEG films.](image)

![Figure 5. FTIR spectra of CMC-PEG films with different doses of gamma irradiation.](image)
3.4. Tensile testing

The mechanical properties of irradiated CMC-PEG films derived from water hyacinth were investigated by tensile testing as shown in figure 6. What is interesting in this result is that the tensile stress increased after irradiated at the gamma dose of 3 kGy (approximately 40% higher than the unirradiated film), whereas dramatically dropped as the dose increased (figure 6a). It is therefore likely that at 5 and 10 kGy, the absorbed energy was high enough to break CMC chains, whereas at 3 kGy the crosslinking of the CMC chains was induced resulting in resultant higher tensile stress [11]. In the same way, as shown in figure 6b, Young’s modulus of the irradiated films at 3 kGy was higher, indicating that at the suitable gamma irradiation has a positive effect on their mechanical properties.

![Figure 6](image-url)

**Figure 6.** Tensile strength (a) and stress-strain curve (b) of irradiated CMC-PEG films at different gamma irradiation doses.

3.5. Artificial weathering

The mass difference of films was measured after 18 days in the environmental chamber at 60°C, and humidity RH = 60%. Table 1 shows the comparison of the percentages of sample mass loss between the commercial CMC-PEG films and the synthesized films at the different gamma irradiation doses (0, 1, 3, 5 and 10 kGy). The decomposition characteristics of both films are similar in that the higher irradiation doses used the more degradation had. The mass loss reached to the maximum at 10 kGy, which may be explained by the fact that at 10 kGy the CMC chains are shortening via radiation degradation [11]. Consequently, the films were easily decomposed. This result indicated that the synthesized CMC-PEG films derived from water hyacinths have high potential to replace the commercial synthesized. Also, the suitable irradiation dose can be used to adjust the degradation ability and sterile the film. Moreover, it is compatible with food and medical applications.

| Samples                | Gamma dose | % mass loss at day 18 |
|------------------------|------------|-----------------------|
| Commercial CMC-PEG films | 0          | 54.4                  |
|                        | 1          | 63.1                  |
|                        | 3          | 54.7                  |
|                        | 5          | 57.2                  |
|                        | 10         | 60.0                  |
| Synthesized CMC-PEG films | 0          | 56.8                  |
|                        | 1          | 58.7                  |
|                        | 3          | 59.7                  |
|                        | 5          | 59.7                  |
|                        | 10         | 61.0                  |

**Table 1.** The percentages of sample mass loss were measured after 18 days of artificial weathering test. Note that the mass at the starting of the test was 100 %.
4. Conclusion
The eco-friendly CMC-based bioplastic from water hyacinth was successfully fabricated. The tensile strength and Young’s modulus of CMC-PEG films can be improved by the gamma irradiation at the dose of 3 kGy. Commercial CMC-PEG films and synthesized CMC-PEG films have similar characteristics of thermal stability, elemental components and have close percentages of mass loss after artificial weathering process. Therefore, the synthesized CMC from water hyacinth has comparable properties to the commercial CMC. Thus, the fabrication of bioplastic from water hyacinth could potentially replace the non-biodegradable plastic in food packaging application.

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