



## CHAPTER III

# POLYETHYLENE FILM SURFACE FUNCTIONALIED WITH CHITOSAN VIA $\gamma$ -RAY IRRADIATION IN AQUEOUS SYSTEM: A SIMPLE APPROACH TO INDUCE COPPER (II) ION ADSORPTIVITY ON PE

### 3.1 Abstract

Functionalization of the surface of polyethylene (PE) film with chitosan via  $\gamma$ -ray irradiation technique followed by copper ion immobilization on this surface is proposed. The solubilization of chitosan in water by forming an organic salt with hydroxybenzyl triazole is a key factor in accomplishing the surface functionalization of PE with chitosan by  $\gamma$ -ray irradiation. The chitosan induces the metal ion adsorptivity on PE film surface resulting in the successful copper ion immobilization. The work demonstrates a practical way to convert a commodity polymer, such as PE, to a functional polymer.

Keywords: Chitosan; Polyethylene; Gamma-ray irradiation; Surface functionalization; Copper ion

### 3.2 Introduction

Chitin-chitosan is the second-most naturally abundant aminopolysaccharide, obtained from the shells of crustacean such as shrimp, crabs and squids. The copolymer consists of  $\beta(1-4)$ -2-acetamide-2-deoxy- $\beta$ -D-glucan and  $\beta(1-4)$ -2-amino-2-deoxy- $\beta$ -D-glucan and shows not only biodegradability [1] and biocompatibility[2], but also bioactivity [3], especially antimicrobial activity. The uniqueness of this aminopolysaccharide also includes the complexation with various metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  [4],  $\text{Co}^{2+}$  [5],  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  [6], and  $\text{Hg}^{2+}$ ,  $\text{UO}_2^{2+}$  [7] based on the nitrogen electron donor belonging to acetamido and amino groups, which is appropriated for environmental purposes. Chitosan in forms of powders and membranes are proposed as chelating agents [8], ion-exchange, and waste water treatment resins, etc [9, 10].

Considering the materialization of chitin-chitosan, one needs to accept two major limitations, i.e. the low solubility in most solvents and the non-thermal plasticity. As a result, conventionally, chitin is deacetylated to chitosan for the purpose of good solubility in acids and subsequent product preparation, such as casting to film [11], crosslinking to gel [12], wet spinning to fiber [13], etc. The structural modification of chitosan to be, especially, a water soluble chitosan [14] and an organosoluble chitosan [15-17], is proposed as ways to change the solubility of chitosan and prepare more types of chitosan-based materials.

Based on the specific properties of chitosan, the grafting or functionalizing of chitosan onto other polymer surfaces, especially the commodity ones, is a good way to develop a functional polymer. Polyethylene (PE) is a cheap commodity polymer with significant gas and moisture barrier properties, which is appropriate for the short lifetime products such as films, bags, tubes, bottles, etc. The modification of PE with other functional groups possibly gives new value-added products. In the past, the introduction of monomers, such as acrylic acid [18, 19], vinyl acetate and maleic anhydride [20], acrylamide [21], and methyl methacrylate [22, 23] onto the PE surface via radical pathways using  $\gamma$ -ray or electron beam irradiation followed by in-situ polymerization were reported. Polyacrylamide grafted onto PE has been demonstrated as a metal adsorption film for heavy metal ions, such as mercury [24].

The PE film functionalized with amidoxime groups has proven its high copper adsorption capacity [25].

It is important to note that metal ions, e.g. copper (Cu), cadmium (Cd) etc, shows acute toxicity to slug and snails on cellular metabolism. In previous, the uses of metals in the forms of chloride salts (i.e., CuCl<sub>2</sub>, CdCl<sub>2</sub>) and copper ammonium carbonate for pesticide or insecticide were proposed [26,27]. However, by simply mixing those metals with soil initiates the environmental issue related to the soil and water contamination. In order to avoid those problems, it is an ideal to embed those metals onto polymer film. As mentioned above, the inert surface of PE can be activated by modifying with specific polymer. Here, we focus on the approach to functionalize PE film surface with chitosan so as to effectively induce copper ion adsorption on the surface. The film obtained may be a practical insecticide or pesticide material as well as a toxic heavy metal adsorptive material.

On the view point of polymeric chemistry, the functionalization of PE film with chitosan needs an effective surface reaction. In the past, Mao et al. [28] modified chitosan with 4-azidobenzoic acid group and proposed the grafting of the derivative onto the PE surface using UV irradiation. The grafting of chitosan on PE via  $\gamma$ -ray irradiation is also practical when we use appropriate chitosan solution. Recently, we found that chitosan dissolves well in water with an equimolar of benzyltriazole [29]. This chitosan aqueous solution is useful and important since it provides us not only water-based chitosan to carry out the homogeneous reaction system but also provides an alternative way to avoid the acetic acid solvent, especially when we need the functionalization of chitosan in water.

The present article proposes a simple but effective and efficient process to functionalize PE surface with chitosan in water system via  $\gamma$ -ray irradiation. The metal ion adsorption, using copper ion as a model case, is also investigated to confirm the metal ion adsorptivity induced by the chitosan chains on PE.

### **3.3 Experimental**

#### **3.3.1 Materials**

Chitosan with 95 percent deacetylation (%DD) and  $M_v$  for  $9.5 \times 10^5$  Dalton, was provided by Seafresh Chitosan (Lab) Company Limited, Thailand. 1-Hydroxy-benzyltriazole (HOBt) and copper (II) sulphate were purchased from Aldrich Chemical Company, Germany. Acetic acid, isopropanol, and methanol were purchased from Lab Scan, Co., Ltd, Thailand. The food packaging PE film used was a product of Thai Polyethylene Public Co., Ltd. All chemicals were used without further purification.

### 3.3.2 Instruments and equipments

The  $\gamma$ -ray irradiation was carried out using a  $^{60}\text{Co}$  source via a  $\gamma$ -cell 220 Excel MDS Nodion G.C.200E at the dose rate of 15 kGy/h under a courtesy of the Office of Atomic Energy, the Ministry of Science and Technology, Thailand. Surface characterization was carried out by using a Thermo Nicolet Nexus 670 Fourier transform infrared spectrophotometer equipped with an attenuated total reflection (ATR) accessory. The scanning was 32 times at a resolution of  $2 \text{ cm}^{-1}$  in a frequency range of  $4000\text{-}400 \text{ cm}^{-1}$ . Elemental analysis (EA) was carried out using a Perkin Elmer 2400 CHN. The film contact angle was measured after dropping a water droplet on PE films for 60 seconds at five different positions by using a Kruss DSA10-Mk2 at  $25^\circ\text{C}$ . Surface morphology was observed by a JEOL JSM-6400 scanning electron microscope. X-ray fluorescence was measured by using a GUL0055P XRF equipped with a DSA2000 germanium (Ge) detector, and the spectra obtained were analyzed by the GENIES2000 WinQxas program. Atomic adsorption spectroscopy (AAS) was carried out by using a Varian, SpectrAA300.

### 3.3.3. Chitosan solutions

Photo-crosslinking agent, 4-azidobenzoic acid was prepared according to Hayashi et al. [30]. Chitosan (CS, 1 g, 0.0062 mole) was reacted with 4-azidobenzoic acid (Azide, 0.8288 g, 1 mole equivalent to CS) and 1-Ethyl-3-(3'-dimethylaminopropyl) carbodiimide (EDC, 1.1770 g, 1 mole equivalent to CS) in methanol. The reaction was carried out at room temperature in heterogeneous system for 8 h. The product was washed with methanol several times and dried to obtain

chitosan conjugated with 4-azidobenzoic acid (CS-Azide). CS-Azide (3 wt.-%) was dissolved in an aqueous solution of 2 vol.-% acetic acid to give **1** (Fig. 1(a)).

Chitosan acetic acid solution, **2**, was prepared at the concentration of 3 wt% (Fig. 1(b)). Chitosan with an equimolar of HOBt (Fig. 1(c)) was dissolved in distilled water at the concentration of 1 wt% and used as **3**.

### 3.3.4 $\gamma$ -Ray irradiation of PE film

PE films were cut into 5 × 8 cm strips. The strips were washed thoroughly with isopropanol at 70°C for 12 h, sonicated for 6 h, and dried in a vacuum oven at 50°C for 3 h before immersing in an excess amount of the solutions (10 ml), **1-3**, for overnight in glass tubes. The glass tubes with samples were evacuated followed by irradiating at various doses from 0 to 100 kGy in aerobic condition at room temperature. After irradiation, the samples were washed thoroughly with 1 vol.-% aqueous acetic acid, and water, followed by drying in a vacuum at 40°C for 3 h to obtain the films of **1F**, **2F**, and **3F**.

PE film (C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>; Calcd.: C 15.71, H 14.28, N 0.00; Found: C 86.09, H 13.84, N 0.09. Ideal formula structure of PE film functionalized with chitosan [(C<sub>8</sub>H<sub>13</sub>O<sub>5</sub>N)(C<sub>8</sub>H<sub>13</sub>O<sub>4</sub>N) (C<sub>2</sub>H<sub>4</sub>)]<sub>0.05</sub>[(C<sub>6</sub>H<sub>11</sub>O<sub>4</sub>N)(C<sub>8</sub>H<sub>13</sub>O<sub>4</sub>N)(C<sub>2</sub>H<sub>4</sub>)]<sub>0.95</sub>; Calcd.: C 42.05, H 7.04, N 7.41; For **1F** Found: C 86.09, H 13.91, N 0.04; For **2F** Found: C 86.10, H 13.87, N 0.07; For **3F** (20 kGy) Found: C 86.22, H 13.92, N 0.21; For **3F** (40 kGy) Found: C 86.01, H 13.92, N 0.26; For **3F** (60 kGy) Found: C 86.37, H 14.31, N 0.27; For **3F** (80 kGy) Found: C 85.67, H 14.01, N 0.42; For **3F** (100 kGy) Found : C 84.51, H 13.57, N 0.38.

ATR-FTIR for 3 F (100 kGy): 3 440 (OH), 897cm<sup>-1</sup> (pyranose ring), 1 463 (C-H)

### 3.3.5 Copper ion adsorption

The films, **1F**, **2F**, and **3F**, were immersed in a copper sulfate aqueous solution (2 wt.-%) for 48 h at room temperature to obtain **1FC**, **2FC**, and **3FC**. The films were then thoroughly washed with water several times and dried at 40°C in vacuum for 3 h.

### 3.3.6 Quantitative analysis of copper ion

The amount of copper ion adsorbed on **1FC**, **2FC**, and **3FC** was quantitatively analyzed by using the atomic adsorption technique. The films were treated in nitric acid: water (1:1 v/v) aqueous solution and heated at 60°C for 15 min before determining the copper ion amount in the treated solution.

### 3.3.7 Stability of copper ion immobilized on the films

The films, (**1FC**, **2FC**, and **3FC**) were immersed in aqueous solutions under different temperatures and pHs to study the stability of the copper ion on the films. For temperature, the films were immersed in deionized water at 30, 40, 50, and 60°C. For pH, buffers with a pH of 3.72, 4.01, 5.02, 7.00, 10.01, and 12.63 at 30°C were used. Both studies were done by treating the films in a shaker at 60 rpm for 2, 7, and 14 days. The amount of copper ion on the films was quantitatively analyzed by using the atomic adsorption technique (see *Quantitative Analysis of Copper Ion*).

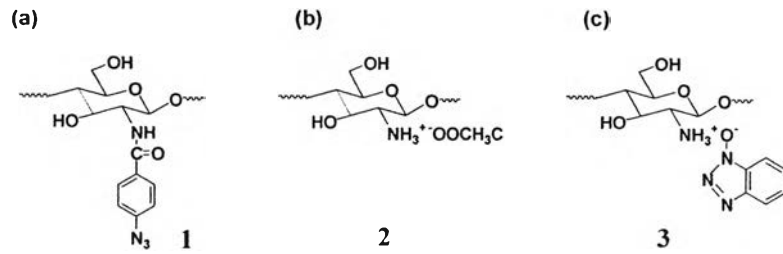
## 3.4 Results and Discussion

### 3.4.1 Functionalization of chitosan onto PE film

In this work, the functionalization of chitosan on PE film was carried out in water-based system as it is a convenient procedure. The films were simply immersed in each of the chitosan solution prepared.

In the past, Mao et al. [28] reported a reactive chitosan-azidobenzoic acid derivative (Fig. 1(a)) and the successful grafting on PE film using UV irradiation.

As chitosan is well-dissolved in acetic acid aqueous solution, the use of this solution, as shown in **2F**, is considered to be the simplest condition for this work. Previously, we reported that the chitosan in acetic acid solution maintained its structure, even when the  $\gamma$ -ray irradiation dose was up to 160 kGy [31]. It can be expected that the  $\gamma$ -ray irradiation in this dose range may not damage the chitosan structure and give us the good functionalization.



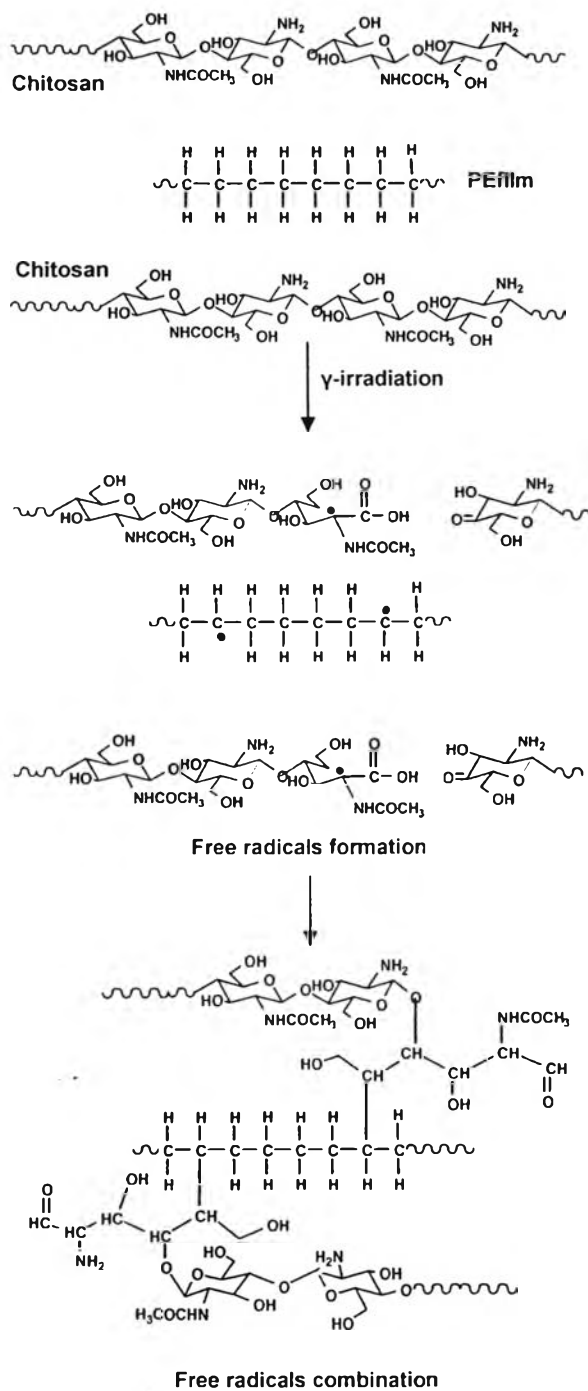
**Fig. 1.** Chemical structure of: (a) chitosan 4-azidobenzoic acid, **1**, (b) chitosan acetate, **2**, and (c) chitosan benzyltriazole salt, **3**.

Here, we applied the derivative and simply dissolved in acetic acid solution so as to prepare **1F** via  $\gamma$ -ray irradiation.

In previous, we found out that chitosan with an equimolar of benzyltriazole forms organic salt and give the water solubility (Fig. 1(c)). This system is not only attractive in terms of dissolving chitosan in water, but also is useful when we consider the conjugating or coupling reaction of chitosan in water. In this work, we apply this solution to prepare **3F**.

The PE films were immersed in solutions of **1-3** followed by  $\gamma$ -ray irradiation for 20, 40, 60, 80, 100 kGy (See *Study on the Effect of  $\gamma$ -Ray Irradiation Dose on Grafting Amount*). After  $\gamma$ -ray irradiation, the films obtained were washed by acetic acid aqueous solution (2 % vol/vol) to remove the physisorbed chitosan and followed by washing with water to remove the trace amount of acetic acid on the PE surface. Here, we focused on the products of  $\gamma$ -ray irradiation with the dose of 100 kGy (**1F-3F**) to determine the most effective solution to graft chitosan onto the PE film.

Fig. 2 shows a possible mechanism in grafting chitosan on PE via  $\gamma$ -ray irradiation. For comparison, blank PE-film was also irradiated. The ATR-FTIR spectra clarify that **1F** and **2F** (Fig. 3A(b) and (c)) show a peak similar to the blank

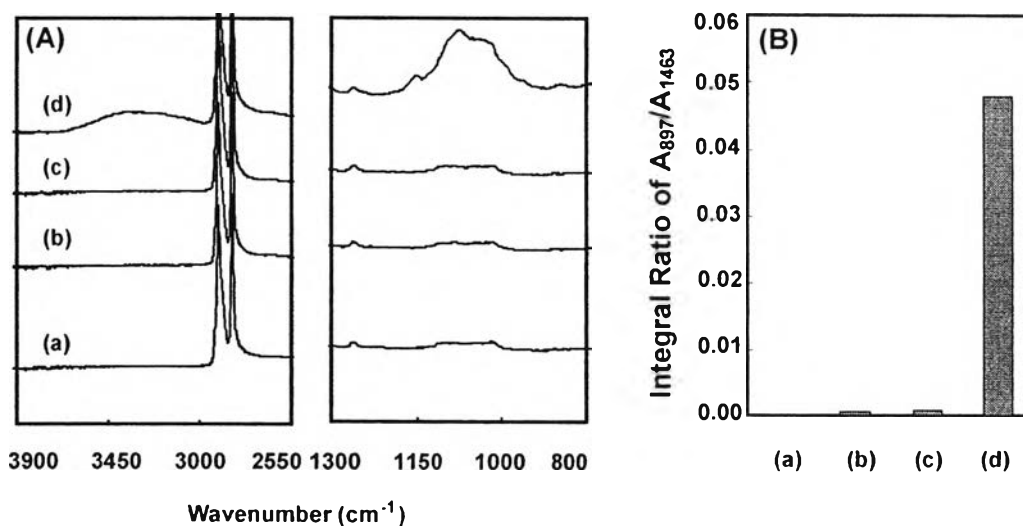


**Fig. 2.** Mechanism of chitosan grafted on PE *via* free radicals formation using  $\gamma$ -ray irradiation technique.

PE film (Fig. 3(a)). However, only **3F** gives an OH peak at  $3440\text{ cm}^{-1}$  together with pyranose peaks at  $1200\text{-}800\text{ cm}^{-1}$  (C-O-C) (Fig. 3A(d)), indicating

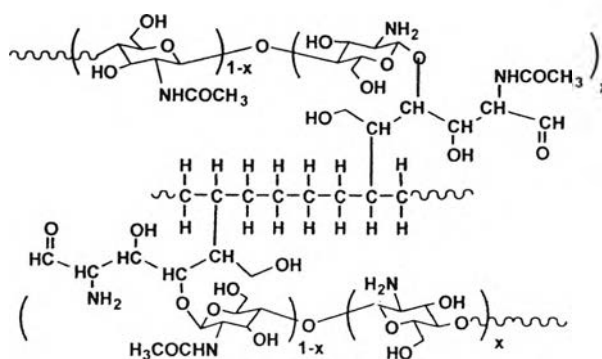


chitosan on PE. A quantitative analysis based on the curve fitting technique to clarify the integral ratios between  $A_{897}$  (pyranose ring of chitosan) and  $A_{1463}$  (C-H bending of polyethylene) was carried out. Fig. 3(B) suggests that only in the case of 3F was successful to graft chitosan on PE film.



**Fig. 3.** Qualitative (A) and quantitative (B) analyses by ATR-FTIR of the films after  $\gamma$ -ray irradiation doses of 100 kGy for (a) PE-blank, (b) 1F, (c) 2F, and (d) 3F.

Based on an ideal structure of chitosan (%DD 95) grafted on PE at carbon of pyranose ring demonstrated in Fig. 4 and Equation (1), the complete chitosan grafted



**Fig. 4.** Ideal structure of chitosan grafted PE for elemental analysis calculation.

on PE gives the %C, H, N, and O for 42.05, 7.04, 7.41, and 34.07, respectively. Here, the %N indicates that the chitosan grafted on **3F** is about 5.1 %.

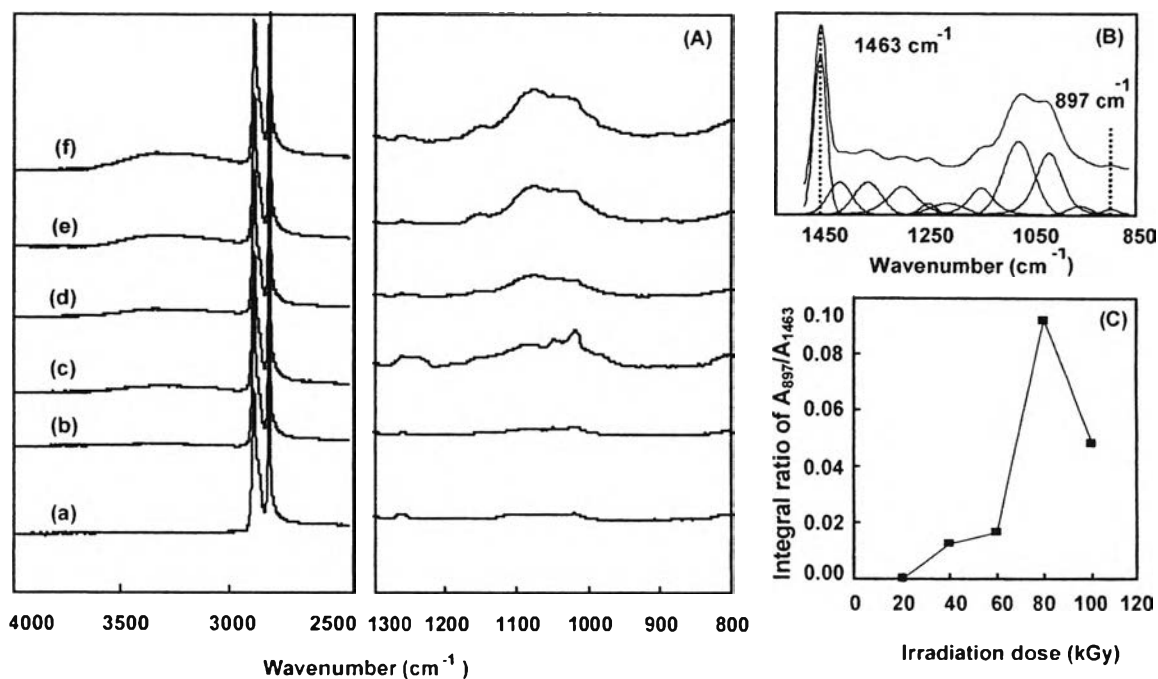
$$\%N = \frac{28X + 28(1 - X)}{378.10} \times 100 \quad (1)$$

The C, H, and N content of the films after  $\gamma$ -ray irradiation at 100 kGy was investigated. In the case of **3F**, the %N was 0.38, whereas the other films show only trace amount of %N. Although HOBt is a compound with nitrogen atom, the ATR-FTIR spectrum (Fig. 3 (B)) showed no peak related to HOBt and insisted the successful removing HOBt. This also confirms us that the solution **3** might be the most appropriate among the three conditions we used.

#### 3.4.2. Study of the effect of $\gamma$ -ray irradiation dosage on grafting amount

It is important to identify the maximal grafting yield for **3F** by varying the irradiation dose from 20-100 kGy. Fig. 5(A) shows the ATR-FTIR spectra of **3F**, which reveals to find that when the  $\gamma$ -ray dose is increased, the hydroxyl group ( $3440 \text{ cm}^{-1}$ ) and pyranose ring ( $1200\text{-}800 \text{ cm}^{-1}$ ) gradually increases, especially when the  $\gamma$ -ray dose was above 40 kGy. In order to quantify the amount of chitosan on the PE, the 2<sup>nd</sup> derivative for curve fitting and for quantitative analysis was carefully done. Fig. 5(B) shows an example of curve fitting at  $1463$  and  $897 \text{ cm}^{-1}$  for **3F** under a  $\gamma$ -ray dose of 80 kGy. The integral ratio (Fig. 5(C)) indicates that the grafting increases as the  $\gamma$ -ray dose increased and is saturated at 80 kGy. For the doses above 80 kGy, the decrease in grafting might relate to the chain scission of chitosan on PE films after exposure to even higher radiation dose.

The C, H, N content analysis of **3F** after various irradiation doses. Based on %C, the grafting percentage for **3F** after the exposures of 20, 40, 60, 80, and 100 kGy could be calculated to be 2.8%, 3.5%, 3.6%, 5.6%, and 5.1%, respectively. The result supports the observations in Fig. 5(C) and confirms that the optimal  $\gamma$ -ray irradiation dose to achieve the highest chitosan grafting yield (5.6%) is 80 kGy.

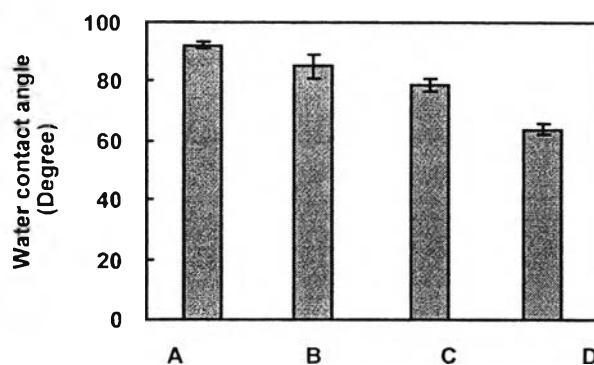


**Fig. 5.** (A) Qualitative, (B) curve fitting of 1463 cm<sup>-1</sup> (C-H bending of polyethylene) and 897 cm<sup>-1</sup> (pyranose ring of chitosan), and (C) quantitative analyses of **3F** by ATR-FTIR by varying the  $\gamma$ -ray doses for: (a) 0 kGy, (b) 20 kGy, (c) 40 kGy, (d) 60 kGy, (e) 80 kGy, and (f) 100 kGy.

### 3.4.3 PE surface analysis

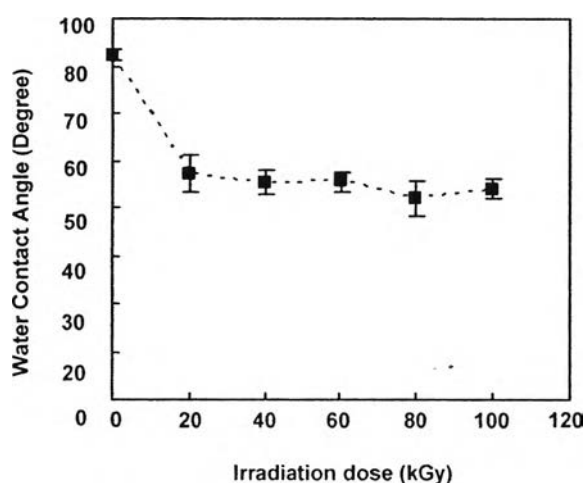
The water contact angle is a good indicator of the hydrophilicity of the film surface. Mao et al. [28] reported that the water contact angle of *O*-butyrylchitosan-grafted PE films was decreased to 43° as compared to the blank-PE film (98°). Fig. 6 shows the water contact angle of the PE-blank to be 92.2±1.2° and slightly decreases after irradiation at 100 kGy (column A). Fig. 6, columns B and C, implies that HOBt slightly affected the surface hydrophobicity (78.7±2.1°), even the  $\gamma$ -ray dose was as high as 100 kGy. In the case of **3F** at 100 kGy, the contact angle is 63.8±2.0° (Fig. 6 column D). The hydrophilicity of the **3F** film suggests the surface is covered with chitosan.

Fig. 7 shows that the contact angles of the **3F** films under various doses (20, 40, 60, 80, and 100 kGy) are 67.2±4.0°, 65.3±2.5°, 65.4±2.0°, 62.0±3.6°, and 63.8±2.0°, respectively. The contact angles decreased for all irradiation doses as



**Fig. 6.** Water contact angle of PE films under various conditions: PE-Blank (A), PE-Blank-100 kGy (B), PE-HOBT-100 kGy (C), **3F**-100 kGy (D).

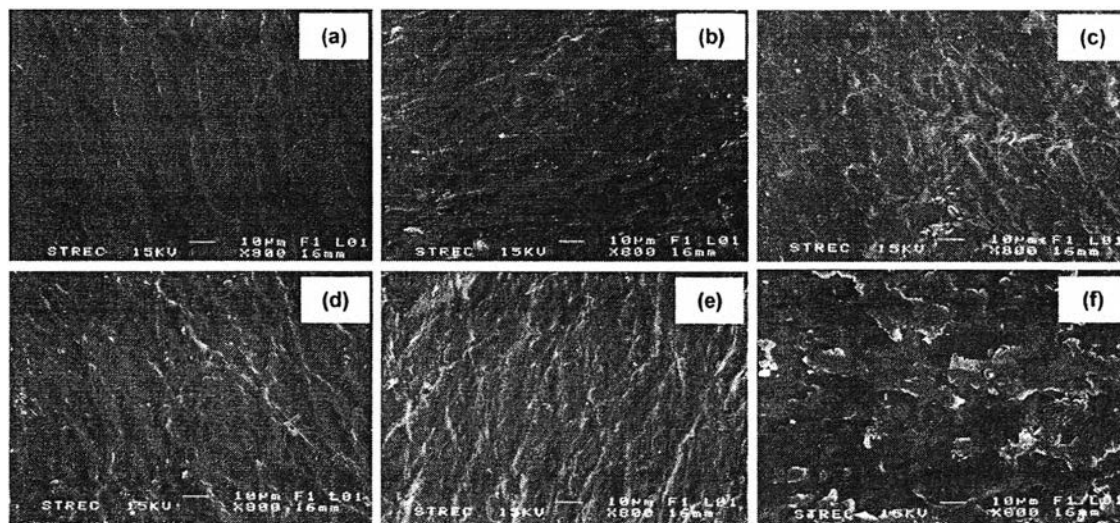
compared to that of the PE-blank. This is most likely be due to the chitosan on PE surface.



**Fig. 7.** Water contact angle of **3F** films under various  $\gamma$ -ray irradiation doses.

#### 3.4.4 Surface morphology

The surface morphology was studied by SEM to identify how the PE surface changed after the grafting of chitosan. Fig. 8 shows the surfaces of **3F** films under various  $\gamma$ -ray irradiation doses. When compared to the blank-PE surface, it is clear that the surfaces of **3F** for every condition are rough. This demonstrated that chitosan



**Fig. 8.** SEM micrographs of **3F** under various  $\gamma$ -ray irradiation doses: (a) 0 kGy (PE-blank), (b) 20 kGy, (c) 40 kGy, (d) 60 kGy, (e) 80 kGy, (f) 100 kGy.

have been grafted on PE film. It is important to note that the roughness is more significant due to the amount of chitosan when the  $\gamma$ -ray doses were increased. For example, when the dose was as high as 100 kGy, the scratched surface could be observed. This might be due to the partial degradation of grafted chitosan at over dose. This strongly confirms that the optimum dose to obtain the highest amount of chitosan is 80 kGy.

#### 3.4.5 Copper ion adsorptivity

The adsorption of copper ions was carried out by immersing PE-blank, **1F**, **2F**, and **3F** in a copper sulfate solution for few days. Fig. 9 shows the XRF spectra in which the copper ion can be identified at 8.04 keV. For PE-blank, **1FC** and **2FC**, the peak at 8.04 keV could not be observed at all (Fig. 9(a), (b), (c)) whereas for **3FC** (obtained from 80 kGy irradiation dose), this peak is significant (Fig. 9(d)).

Now we come to the question of whether the 80 kGy dose is the optimal condition for the copper ion adsorption as mentioned above. Fig. 10(A) shows the XRF spectra of **3FC** obtained from the various  $\gamma$ -ray irradiations. All conditions show a peak at 8.04 keV implying a certain amount of copper ion

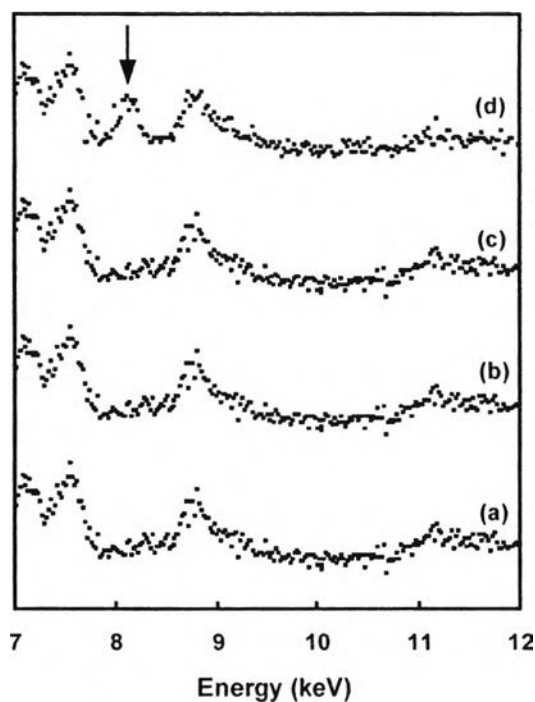


Fig. 9. XRF spectra of: (a) PE- blank, (b) 1FC, (c) 2FC, (d) 3FC.

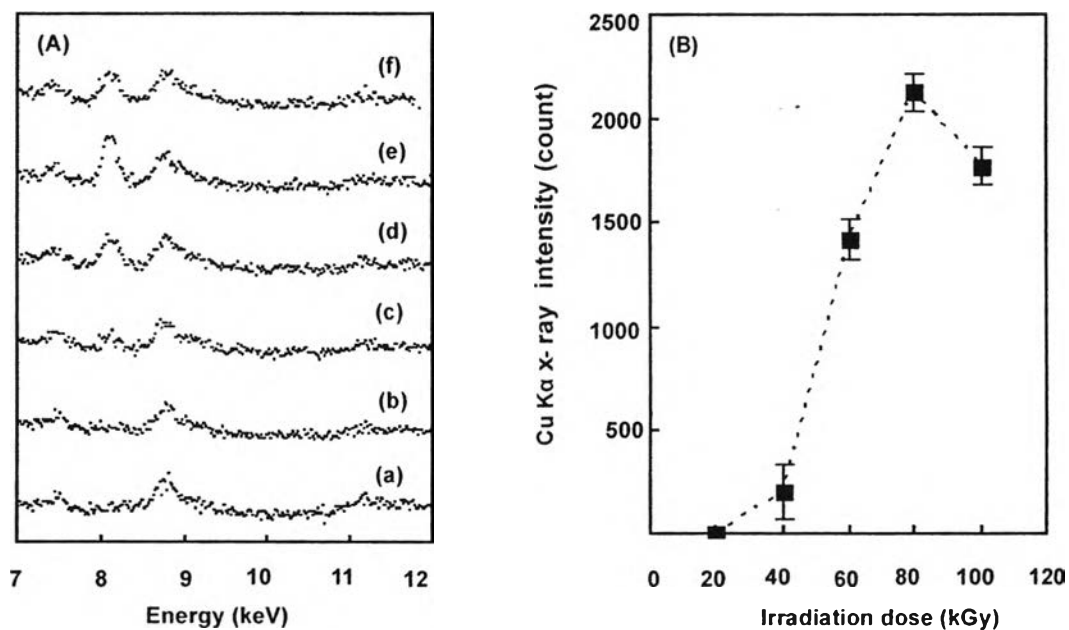
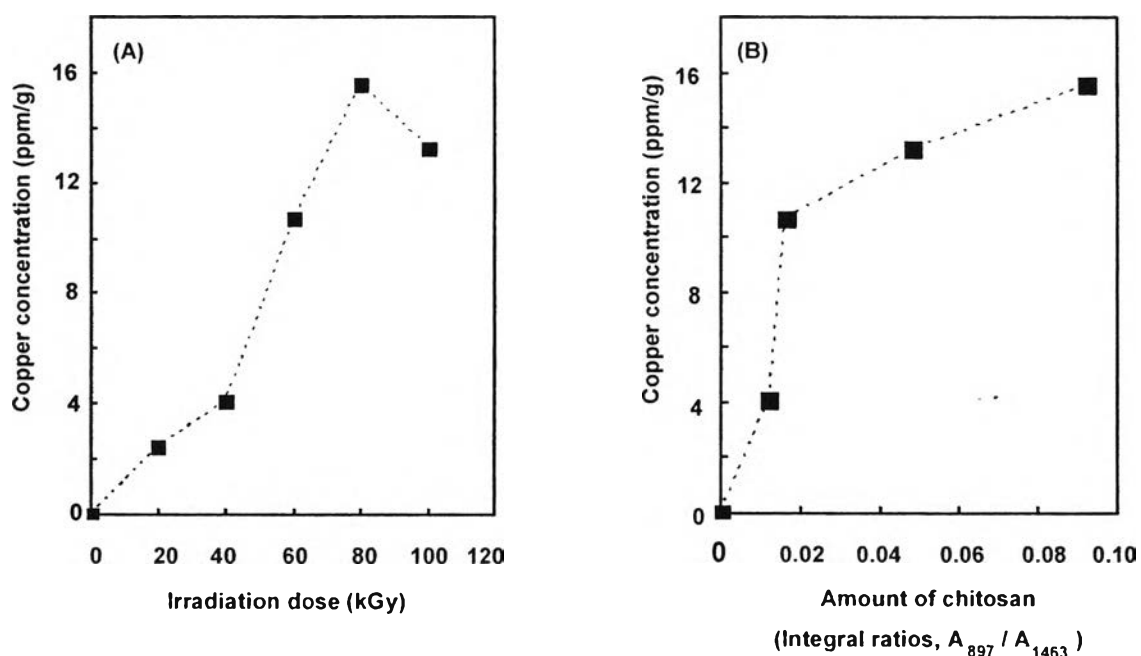


Fig. 10. XRF spectra of 3FC (A) and the quantitative analysis at 8.04 keV (B) for 3FC after (a) 0 kGy, (b) 20 kGy, (c) 40 kGy, (d) 60 kGy, (e) 80 kGy, and (d) 100 kGy.

adsorption. Fig. 10(B) was plotted between the  $\gamma$ -ray dose and the intensity of copper ion as observed from Fig. 10(A). The results clearly indicated that the copper ion adsorption on the film surface was maximized for **3FC** obtained from the irradiation dose of 80 kGy.

The amount of the copper on **3FC** was further quantitatively analyzed by AAS technique. Fig. 11(A) shows that **3FC** films, after irradiation in various doses of 20, 40, 60, 80, and 100 kGy, give a copper concentration of 2.4, 4.1, 10.7, 15.6, and 13.2 ppm/g, respectively. Based on the quantitative analysis of chitosan amount on PE obtained from ATR-FTIR (Fig. 5), copper ion concentration extracted from each film is plotted (Fig. 11(B)). It is clear that the copper concentration increases as the amount of chitosan grafted on PE increased.

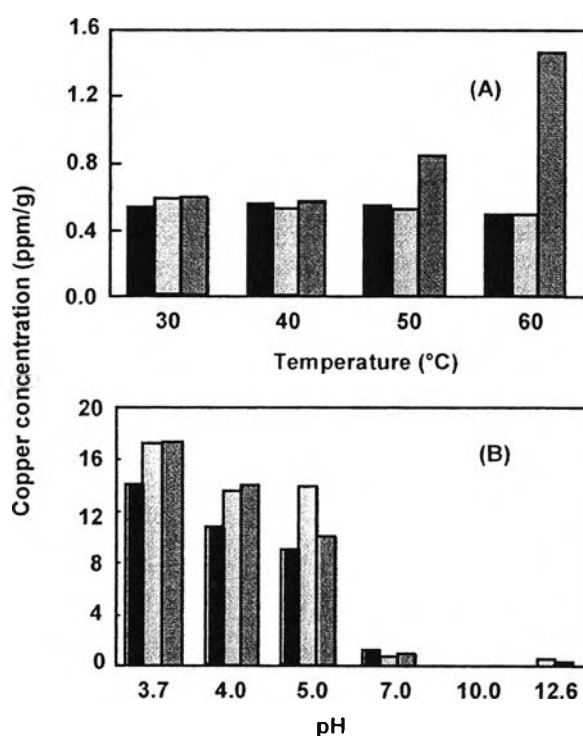


**Fig. 11.** Copper adsorption ability of **3FC** by AAS (A) and the relationship between the amount of chitosan on PE surface and copper ion concentration (B).

### 3.4.6 Study of the stability of copper ions complexed with **3F** films

It is important to note that although the chitosan on the PE surface showed good copper ion adsorption, the stability of the copper ion on the film surface has to be identified. Here, the films were treated under various temperatures and pHs. The amount of copper ion released from the film was identified by AAS.

Based on Fig. 11(A), the maximum copper ion adsorbed on **3FC** is approximately 16 ppm/g. Fig. 12(A) shows that with temperatures up to 40°C only 0.5 ppm/g of copper ion was released, even with a treatment time as long as 14 days. When at 60°C for 14 days, only 1.5 ppm/g was released, which is only about 10% of to the total copper ion adsorbed on **3FC** (16 ppm/g). The acidity significantly affects the release of copper ion (Fig. 12(B)). When **3FC** was treated in pH 3-5 for 14 days,



**Fig. 12.** AA spectra of copper ions adsorption stability of **3F** after  $\gamma$ -ray for 80 kGy for 2 days (■), 7 days (▨), and 14 days (■) under different temperatures (A) and pHs (B).

almost all the copper ions were released. This might be due to the fact that the chitosan on the PE layer was protonated and swelled, and as a result, the copper ion was released.



### 3.5 Conclusions

As chitosan dissolves only in acids and does not show the thermal plasticity, the materialization of chitosan is quite limited. The surface grafting of PE film with chitosan was successful by simply immersing PE film in chitosan chitosan salt with benzyltriazole in aqueous solution followed by carrying out the  $\gamma$ -ray irradiation. Copper ion was used as a model to demonstrate that chitosan enables the PE-film to adsorb metal ions. The treatment of the PE film-chitosan after copper ion adsorption in various pHs confirmed the stability of the metal ions adsorbed on the PE film-chitosan.

### 3.6 Acknowledgments

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