

# RADIATION SYNTHESIS OF POLY(ETHYLENE GLYCOL)-CHITOSAN NANOPARTICLE: A MODIFIED BIODEGRADABLE POLYMER FOR PLA BLENDS

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## 1 Introduction

Polymer blending technology is an effective way to achieve new polymeric materials with optimized properties [1]. Polylactic acid (PLA) is a biodegradable polymer which was approved by the Food and Drug Administration. It has good mechanical, thermal and biodegradable properties, therefore it is a good polymer for various end-use applications. However, other properties such as flexural properties, heat distortion temperature (HDT), gas permeability, impact strength, melt viscosity for processing, etc., are not good enough in processing and applications [2]. Thus, many researchers interested in improving PLA properties by blending with the other biodegradable materials. Chitosan is a naturally occurring biodegradable, biocompatible, bioactivity, and non-toxic biopolymer. It has been reported as a possible material to prepare composite material with PLA [3]. Non-modified chitosan showed non-compatible with PLA [4] because PLA is relatively hydrophobic. The modification of chitosan before blending with PLA may overcome such problem. Since the oligomeric plasticizers, such as poly(ethylene glycol) (PEG) has been reported the good result to improve PLA by lowering glass transition temperature ( $T_g$ ) and increasing the elongation at break [5], PEG modified chitosan has been considered to develop for PLA blend. Li. et al. [1] reported that increasing MPEG-g-chitosan content in composite films, water absorption and degradation rate increase accordingly. It is interesting to note that the particle size of chitosan may also be an important parameter to improve the product's properties. In this view point, it has been

reported that particle size of the filler affected the tensile strength and thermal properties of hydroxypropyl methylcellulose edible films [6]. Modification of chitosan to obtain a wide variety of chitosan derivatives including chitosan nanoparticles has been widely proposed. Chemical modification via chemical conjugation is well known method to improve chitosan properties. Hydrophobic modified chitosan, i.e. deoxycholate-chitosan has also been proposed as a green and compatible additive for polyethylene [7]. Radiation-induced graft copolymerization technique is one of most attractive methods for modifying the chemical and physical properties of polymers via free radical reaction. It has been known as an easy, effective and environmentally friendly method in modifying polymeric materials for various applications [8]. Radiation grafting is an alternative way to improve chitosan properties, such as improving hydrophobic side chain [9] and enhancing absorption properties [10]. As modification chitosan nanoparticle has been successfully prepared via gamma irradiation [11], the strategy therefore is to further modify chitosan nanoparticle with PEG using radiation-induced grafting. Here, the goal of the present work is focused on synthesis and characterization of PEG-grafted-chitosan nanoparticles (PEG-g-CSNPs), via radiation synthesis using  $\gamma$ -irradiation. The product is proposed as a modified biodegradable polymer for PLA blends.

## 2 Experimental

### 2.1 Materials

Chitosan with a degree of deacetylation of 95% was

purchased from Seafresh Chitosan (Lab) Co. Ltd., Thailand. Sodium hydroxide (NaOH) was purchased from Carlo Erba Reagent, Italy. Acetic acid (CH<sub>3</sub>COOH) was purchased from Lab-scan Analytical Science, Thailand. Poly(ethylene glycol) monomethacrylate (H<sub>2</sub>C<sub>2</sub>(CH<sub>3</sub>)CO(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH) (n=400, MW = 17,686 g/mol) was bought from Polysciences, Inc., USA. All chemicals were used without any purification.

## 2.2 Instruments and Equipment

A <sup>137</sup>Cs Gamma irradiator (Mark I), was used as a  $\gamma$ -ray source with the absorbed dose rate of 0.8228 kGy/h. Fourier transform infrared spectroscopy (FTIR) was carried out using a Bruker Tensor 27 with 32 scans at a resolution of 2 cm<sup>-1</sup> in a frequency range of 4000-400 cm<sup>-1</sup>. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were obtained from a Bruker III Avance 500 MHz using CD<sub>3</sub>COOD/D<sub>2</sub>O (2% v/v) at room temperature. Nanoparticle formation and particle size were analyzed using a Hitachi H7650 transmission electron microscope (TEM). The samples were diluted to suitable concentrations (1 × 10<sup>-5</sup>% w/v). Vigorous stirring and sonication were carried out before dropping the solution onto the copper grid. Morphology within cross section was observed by a JEOL JSM-5410 LV scanning electron microscope (SEM). Atomic force microscope (AFM), Nano world (NCHR-50), was carried out to confirm the particle shape and size. Five  $\mu$ l of 1 × 10<sup>-5</sup>% (w/v) colloid solution were dropped onto a mica slide and were air dried before analysis.

## 2.3 Radiation Synthesis of PEG-g-CSNPs

Chitosan (CS) aqueous solution was prepared according to Pasanphan et al. [10]. The 0.2% (w/v) CS solution and 0.2% (w/v) poly(ethylene glycol) monomethacrylate (PEG) were mixed in distilled water and  $\gamma$ -irradiated with the different  $\gamma$ -ray doses of 1-4 kGy using <sup>137</sup>Cs source. After  $\gamma$ -irradiation, the solution was precipitated in 1% (w/v) NaOH to obtain colloidal product. The product was dialyzed and PEG-grafted-CS nanoparticles (PEG-g-CSNPs) were achieved.

## 2.4 Compatibility of PEG-g-CSNPs with PLA

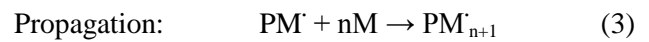
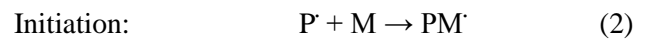
PEG-g-CSNPs powder (2 %wt) was blended with PLA at 170°C. The compatibility of PEG-g-CSNPs was analyzed by a JEOL scanning electron

microscope (SEM). The blended sheet was fractured in liquid nitrogen to observe the morphology within the cross section.

## 3 Results and Discussion

### 3.1 Radiation Grafting of PEG onto Chitosan (PEG-g-CSNPs)

Radiation-induced graft copolymerization process is carried out in the simultaneous reaction which is the simplest irradiation technique for preparation of graft copolymers. The radiation grafting mechanism can be represented as follows



where P is the polymer matrix, M is the monomer units and P<sup>·</sup> and M<sup>·</sup> are their primary radicals, respectively. PM<sup>·</sup> is the initiated graft chain. PM<sup>·</sup><sub>n</sub> and PM<sup>·</sup><sub>m</sub> are the graft growing chain of the copolymer [12].

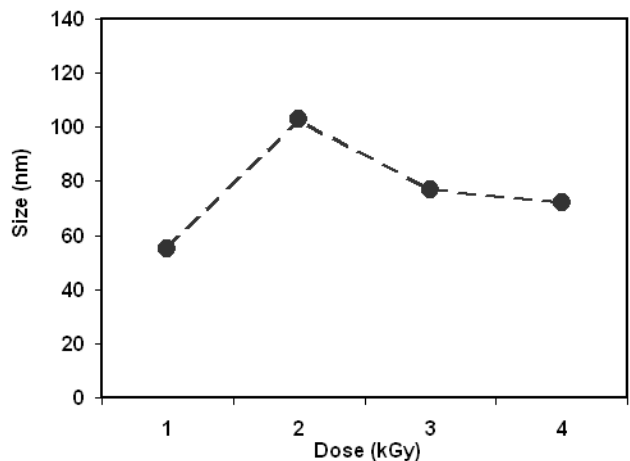


Fig. 1. Effect of  $\gamma$ -ray irradiation dose on grafting yield (%) of PEG-g-CSNPs.

Grafting yield (%) was determined by the following relation:

$$\% \text{ Grafting yield} = \frac{\text{wt. of graft copolymer} - \text{wt. of chitosan}}{\text{wt. of chitosan}} \times 100 \quad (5)$$

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The result in Fig. 1 shows that the grafting yield (%) increased when the  $\gamma$ -ray dose increased to a certain dose of 2 kGy. The maximum grafting yield of 100% was achieved when the grafting reaction was carried out under the irradiation dose of 2 kGy. The grafting yield tend to decrease when the  $\gamma$ -ray dose was higher than 2 kGy.

FTIR was used to identify the chemical structure of all irradiated samples. FTIR spectra as seen in Fig. 2(a) shows the major peaks of CS at  $3450\text{ cm}^{-1}$  (hydroxy group),  $1654\text{ cm}^{-1}$  (amide linkage), and  $1200\text{-}800\text{ cm}^{-1}$  (pyranose ring). Compared with CS, FTIR spectra of PEG-*g*-CSNPs show the new peak at  $1730\text{ cm}^{-1}$  indicating the ester linkage of grafted PEG (Fig. 2(c)-(f)). Increasing the peaks at  $2920$ ,  $2883$  and  $1093\text{ cm}^{-1}$  of C-H stretching and C-O-C bond of PEG structure also confirmed the successful grafting of PEG onto CS.

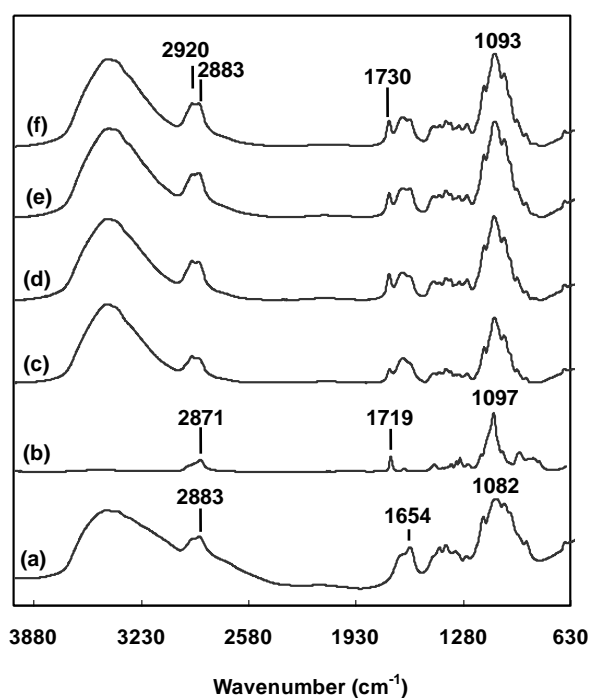


Fig. 2. FTIR spectra of CS (a), PEG (b) and PEG-*g*-CSNPs synthesized using  $\gamma$ -ray irradiation doses of 1 kGy (c), 2 kGy (d), 3 kGy (e), and 4 kGy (f).

The formation of the molecular structure of PEG-*g*-CSNPs was further confirmed by  $^1\text{H}$  NMR (Fig. 3). The  $^1\text{H}$  NMR spectrum of CS in Fig. 3 (a) shows at  $\delta$

$= 2.1$  (H-Ac),  $3.1$  (H-2), and  $3.5\text{-}3.9$  ppm (H-3 to H-6 of pyranose ring). The peak at  $2.1$  ppm (H-Ac) and  $3.1$  ppm (H-2) were attributed to  $-\text{CHNH}_2$  and  $-\text{COCH}_3$  from chitosan [13].

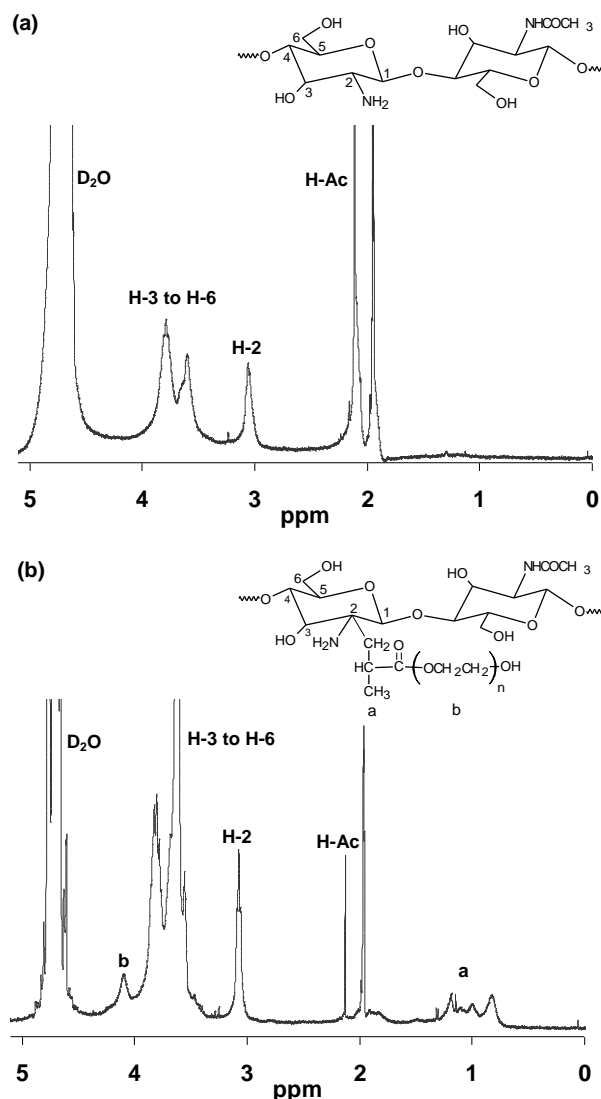


Fig. 3.  $^1\text{H}$  NMR spectra of (a) CS and (b) PEG-*g*-CSNPs synthesized using  $\gamma$ -ray irradiation dose of 2 kGy irradiation.

Compared with CS, the  $^1\text{H}$  NMR spectrum of PEG-*g*-CSNPs (Fig. 3 (b)) indicates the new peaks at  $0.7\text{-}1.3$  (H-a) and  $4.1$  ppm (H-b) belonging to the methylene group of PEG as also been reported by Fangkangwanwong et al. [14]. Increasing the methylene proton peak at  $3.6$  ppm of PEG

macromonomer also confirms the successful grafting of PEG onto CS.

### 3.2 Nanoparticle Formation of PEG-g-CSNPs

The observation from transmission electron microscope (TEM) gave the information on the particle shape and the determination of the particle size. The PEG-g-CSNPs synthesized using 2 kGy irradiation formed circle-like shape with two layers (Fig. 4(a)) and it formed particle containing the inner-core of CS and the outer-shell of PEG in the present of water. The particle sizes were  $153\pm 16$ ,  $79\pm 8$ ,  $116\pm 15$ , and  $123\pm 40$  nm when the samples were irradiated with the dose of 1, 2, 3 and 4 kGy, respectively. One can be seen that the highest grafting yield generated using 2 kGy irradiation brought the smallest particle size.

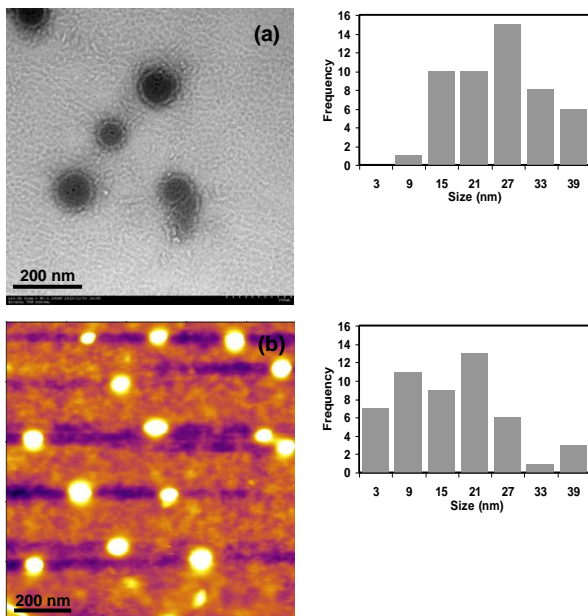


Fig. 4. (a) TEM image and size distribution plot, and (b) AFM image and size distribution plot of PEG-g-CSNPs synthesized from 2 kGy irradiation.

The particle information from AFM image (Fig. 4(b)) confirmed the spherical shape of PEG-g-CSNPs. The particle sizes determined from AFM image was  $71\pm 9$  nm, which is consistent to that observed from TEM.

### 3.3 Compatibility of PEG-g-CSNPs/PLA blends

This work aimed to modify CS as a modified biodegradable polymer for PLA blends. Therefore, clarification of its compounding with PLA, especially its compatibility is also important. Fig. 5A shows the images obtained by an ordinary digital camera, of pure PLA (Fig. 5A(a)), the blended PLA with CS powder (Fig. 5A(b)) and the blended PLA with PEG-g-CSNPs synthesized using 2 kGy irradiation (Fig. 5A(c)). In the case of the PLA blended with CS, the white traces along the samples can be observed, indicating phase separation. The PLA blended with PEG-g-CSNPs shows homogeneous and transparent sheet.

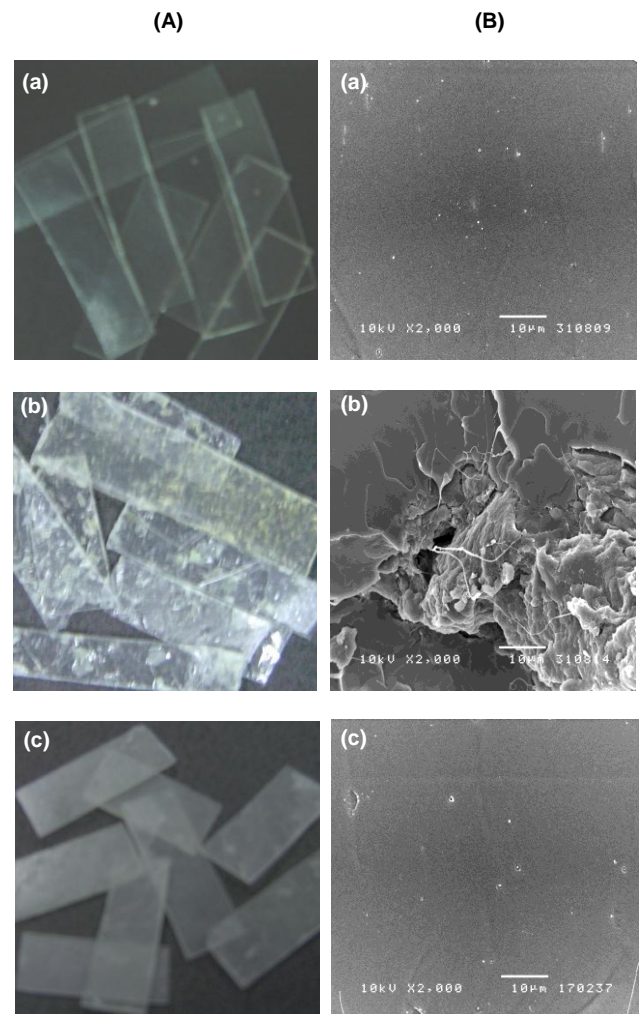


Fig. 5. (A) Images and (B) SEM of cross sections of (a) pure PLA (b) 2 %wt CS powder blended PLA, and (c) 2 %wt PEG-g-CSNPs synthesized from 2 kGy irradiation blended PLA.

SEM was also used to confirm the miscibility of the blends. In the case of PLA blended with 2 %wt CS powder Fig. 5B(b), it was clearly seen the phase separation between the PLA and the CS. Compared with PLA blended with non-modified CS, PLA blended with 2 %wt of PEG-g-CSNPs as seen in Fig. 5B(c) indicates homogeneous morphology, implying the miscibility of the system.

#### 4 Conclusions

PEG can be radiation grafted onto CS to obtain PEG-g-CSNPs. The present work reports an effective pathway to synthesize the PEG-g-CSNPs by  $\gamma$ -irradiation. FTIR and  $^1\text{H}$  NMR confirmed the successful grafting of PEG onto CS. The highest grafting yield (%) with the smallest particle size of  $79\pm 8$  nm can be achieved when the  $\gamma$ -ray dose of 2 kGy was used to synthesize. The PEG-g-CSNPs showed the compatibility with PLA. The PEG-g-CSNPs is expected to be a modified biodegradable polymer for PLA blends in order to improve mechanical property of PLA. Our work to a study of the performance of PEG-g-CS/PLA blends will be extended in the future.

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