

# GAMMA-RAYS INDUCED STEARYL-GRAFTED-CHITOSAN AS A NOVEL NANOFILLER FOR PLA BLENDS

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## 1 Introduction

Recently, biodegradable thermoplastic plastics become a great concern and popular plastic because it can reduce the impact of plastic waste. Polylactic acid (PLA) is aliphatic polyester, which can be produced from fermentation of renewable resources such as corn and cassava to lactic acid and subsequent chemical polymerization [1]. Although PLA has the advantage of renewable resources, such as biocompatibility, biodegradability, energy savings and environmental friendliness, it has limitations in the cost for production and some mechanical properties [2]. Blending of PLA with biodegradable polymer for reducing the cost of material and improving its properties is one of the most important ways. PLA-biodegradable blends have been extensively studied because they offer property improvements without obstructing biodegradable property. Chitosan (CS) is a naturally polymer occurring, biodegradable, biocompatible, edible, and non-toxic biopolymer [3-5]. It has also been reported as filler for PLA by solution blending and it was found to be non-compatible. It was suggested that PLA is a hydrophobic polymer with a static water contact angle of  $\sim 80^\circ$  [6]. This causes non-compatible blend between hydrophilic CS and PLA. CS/PLA blends showed that the tensile strength is increased whereas the %elongation at break is not significant improved [7]. As CS is one of the most abundant biopolymer next to cellulose and exhibits many unique properties as mentioned, it is interesting to improve CS by suitably modifying to use as biodegradable filler for PLA. It has also been reported that CS/tripolyphosphate nanoparticles improved the mechanical properties of edible polymeric films. The smaller particle size of 85 nm gave the higher thermal stability with increasing of

the tensile strength than that of 110 nm, 221 nm and non-nanoparticles. Addition of the nanoparticles has been reported the reinforce effect in the polymeric matrix [8]. Stearyl methacrylate (SMA) is a monomer obtained from renewable plant oil. Its structure consists of long chain alkyl terminated with double bond, which is reactive to radiation [9]. Furthermore, the structure of SMA contains ester group, which is similar to aliphatic polyester of PLA. As radiation grafting is well known in the field of radiation chemistry and processing, it is interesting to modify CS with SMA via free radical reaction using gamma-ray induced grafting because gamma-ray irradiation is an easy and effective tool for carrying out the reaction.

In the present work, stearyl-grafted-chitosan (SMA-grafted-CS) was synthesized by  $\gamma$ -irradiation grafting technique. The effects of  $\gamma$ -ray doses and monomer concentrations on %grafting yield, particle shape and size of SMA-g-CSNPs were studied. The compatibility of the nanoparticle with PLA and the thermal property was also investigated.

## 2 Experimental

### 2.1 Chemical

Chitosan with a degree of deacetylation (%DD) of 95 ( $M_v = 7 \times 10^5$  Da) was obtained from Seafresh Chitosan (Lab) Co. Ltd., Thailand. Stearyl methacrylate (SMA) was purchased from Aldrich Chemical Co., USA. Acetic acid ( $\text{CH}_3\text{COOH}$ ) and acetone ( $(\text{CH}_3)_2\text{CO}$ ) were supplied from Lab Scan Analytical Science Co. Ltd., Thailand. Sodium hydroxide (NaOH) was purchased from Carlo Erbar reagent, USA. Methanol ( $\text{CH}_3\text{OH}$ ) was bought from Mallinckrodt Baker, Inc., USA. Polylactic acid

(PLA) pellets were kindly supported by Thailand Institute of Nuclear Technology, Ministry of Science and Technology, Thailand. All chemicals were used without further purification.

## 2.2 Instruments and Equipment

Gamma irradiation was carried out in a  $^{60}\text{Co}$  Gammacell 220 irradiator with the dose rate of  $7.7 \text{ kGy}\cdot\text{h}^{-1}$ , which was supported by the Office of Atoms for Peace, Ministry of Science and Technology, Bangkok, Thailand. Fourier transform infrared (FTIR) spectra were recorded using a Bruker Tensor27 FTIR spectrometer with 32 scans at a resolution of  $2 \text{ cm}^{-1}$  in a frequency range of  $4000\text{--}400 \text{ cm}^{-1}$ . Power X-ray diffraction (XRD) pattern were collected by a D8 Advance, Bruker AXS over  $5^\circ\text{--}45^\circ 2\theta$ . Particle shape and size were determined by a Hitachi H7650 transmission electron microscope (TEM) (Hitachi High-Technology Corporation, Japan). A Nanoworld (NCHR-50) atomic force microscope (AFM) was also used to confirm the particle formation. Morphology of PLA blends was observed using a JEOL JSM-5410LV scanning electron microscope (SEM). Thermal property of the blends was carried out in thermo gravimetric analyzer (TGA) with a heating rate of  $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  over the temperature range of  $250\text{--}550 \text{ }^\circ\text{C}$ , which kindly provided by Thailand Institute of Nuclear Technology, Ministry of Science and Technology, Thailand.

## 2.3 Radiolytic Synthesis of SMA-g-CSNPs

Chitosan (CS) solution was prepared by dissolving CS flakes (1% w/v) in aqueous acetic acid (2% v/v). The solution was reprecipitated in NaOH (1% w/v) and washed with water to obtain colloidal CS. SMA was pre-dissolved in methanol and mixed with colloidal CS with the different CS:SMA ratios of 1:1, 1:3, 1:5 and 1:7. The mixtures were  $\gamma$ -ray irradiated with the doses of 3, 5, 10, 25 and 40 kGy under ambient temperature. The products were rigorously washed with methanol and dried at room temperature to obtain stearyl-grafted-CS nanoparticles (SMA-g-CSNPs). %Grafting yield (%GY) was evaluated as follows:

%Grafting yield (%GY)

$$= \frac{(\text{wt. of graft copolymer} - \text{wt. of chitosan})}{\text{wt. of chitosan}} \times 100$$

Chemical structure and morphology of SMA-g-CSNPs were characterized by FTIR and XRD, respectively. TEM and AFM were used to observe the particle shape and size of SMA-g-CSNPs.

## 2.4 Blending of SMA-g-CSNPs with PLA

The SMA-g-CSNPs (2% w/w) was blended with PLA at  $170 \text{ }^\circ\text{C}$ . The sample was pressed and rapidly cooled down to obtain a blended sheet. The blended sheet was cut in liquid  $\text{N}_2$  to observe the morphology within the cross section by SEM. The blended sheet of 8–10 mg was used to evaluate the thermal properties using TGA.

## 3 Results and Discussion

### 3.1 Effect of $\gamma$ -ray Doses and CS:SMA Ratios on %Grafting Yield

The effect of  $\gamma$ -ray doses on %GY is presented in Fig. 1A. By increasing  $\gamma$ -ray doses, %grafting yield increased and subsequently saturated or reduced after reaching a certain  $\gamma$ -ray dose. It can be explained that the higher irradiation dose induced the higher radiolytic products (e.g.,  $e_{\text{aq}}^-$ ,  $\text{H}^\cdot$ ,  $\text{HO}^\cdot$ ) resulting in the higher grafting amount.

The amount of the monomer presented in the solution is also a parameter affecting the %GY. To consider the effect of monomer concentration on the amount of grafting, the %GY was plotted against the SMA concentrations as indicated in Fig. 1B. The effect of the SMA concentrations on the %GY is similar to the effect of  $\gamma$ -ray dose. Increasing SMA concentration induced increasing the %GY. This behavior has also been reported when the 2-hydroxyethyl methacrylate (HEMA) monomer was grafted onto CS via  $\gamma$ -ray irradiation [10]. However, increasing monomer concentration over a suitable amount can also induce the decreasing of the %GY due to a homopolymerization [11]. Fig. 1 also indicates decreasing of the %grafting yield when using CS:SMA ratio as high as 1:7. This is consequence of the homopolymerization of SMA monomers. The SMA-g-CSNPs obtained from the conditions of CS:SMA ratios of 1:1, 1:3, 1:5 and 1:7 and using  $\gamma$ -ray irradiation dose of 25 kGy produced the %GY of 11%, 36%, 59% and 37%, respectively.

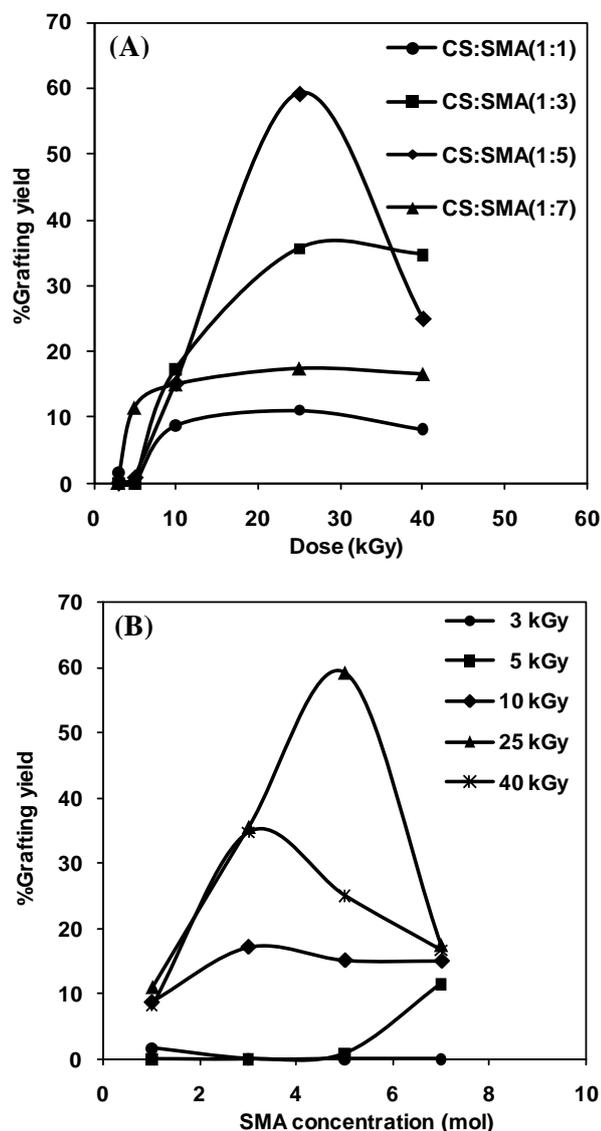


Fig.1. %Grafting yield of SMA grafted onto CS. Effect of (A)  $\gamma$ -ray doses and (B) SMA concentration.

### 3.2 Chemical Structure and Morphology of SMA-g-CSNPs

Fig. 2 shows the FTIR spectra of chitosan, SMA, and SMA-g-CSNPs. FTIR spectra of SMA-g-CSNPs indicates the increasing of the peaks at 2850, 2920 and 1156  $\text{cm}^{-1}$  belonging to C-H stretching and ether bond (C-O-C) of SMA structure. It is obviously observed with the higher %GY of 59% (Fig 2 (d)). The new ester peak at 1731  $\text{cm}^{-1}$ , shifting from 1726

to 1731  $\text{cm}^{-1}$  and an increasing peak at 1156  $\text{cm}^{-1}$ , shifting from 1166 to 1156  $\text{cm}^{-1}$  evidently confirmed the successful grafting of SMA onto CS. Moreover, the peaks at 1011-817  $\text{cm}^{-1}$  and at 1639  $\text{cm}^{-1}$  belonging to the double bond of alkene structure ( $\text{H}_2\text{C}=\text{CH}-$ ) of methacrylate functional group disappeared after radiation grafting due to an addition reaction. The appearance of a new peak at 752  $\text{cm}^{-1}$  was suspected to be a new alkene bond occurring after the addition reaction and subsequent radical rearrangement.

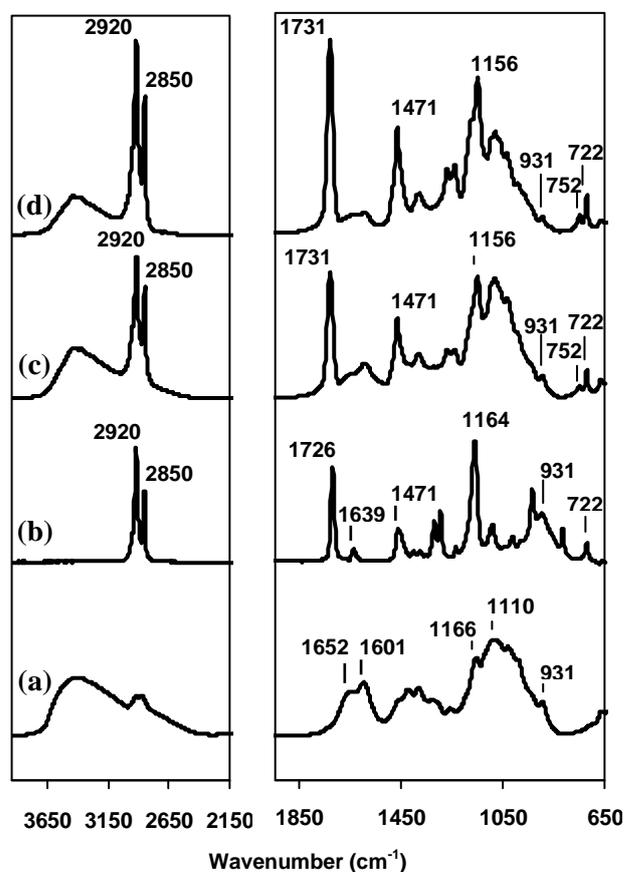


Fig.2. FTIR spectra of (a) CS, (b) SMA, (c) SMA-g-CSNPs from CS:SMA ratio of 1:1 (11%GY) and (d) SMA-g-CSNPs from CS:SMA ratio of 1:5 (59%GY) after  $\gamma$ -ray irradiation with the dose of 25 kGy. The XRD results were used to confirm the grafting products.

The XRD pattern of chitosan (Fig. 3(a)) shows three major peaks at  $2\theta$ : 13°, 19.5° and 21°. After grafting with SMA, a sharp peak at 21°  $2\theta$  significantly increased especially in the case of the higher %GY

of 59% (Fig. 3(c)). The XRD pattern of SMA-g-CSNPs reflected the increase of crystalline structure due to long chain alkyl of SMA structure. The chemical structure and morphological changes observed from FTIR and XRD confirms the successful grafting of SMA onto CS via radiolytic synthesis using  $\gamma$ -irradiation.

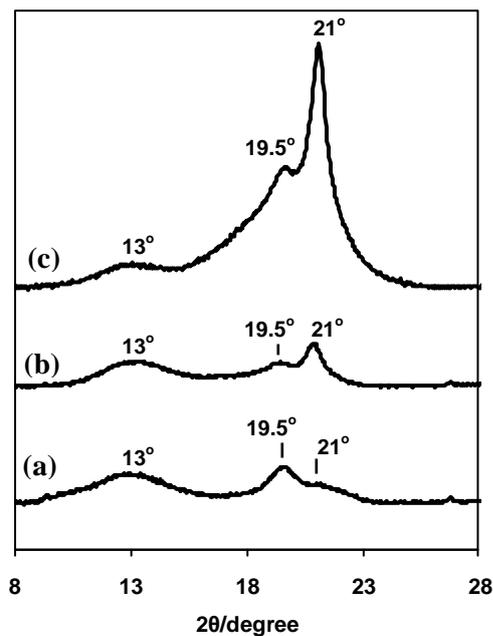


Fig.3. XRD pattern of (a) CS, (b) SMA-g-CSNPs from CS:SMA ratio of 1:1 (11%GY) and (c) SMA-g-CSNPs from CS:SMA ratio of 1:5 (59%GY) after  $\gamma$ -ray irradiation with the dose of 25 kGy.

### 3.3 Particle Formation of SMA-g-CSNPs

The particle shape and size of SMA-g-CSNPs synthesized using  $\gamma$ -ray irradiation was observed from TEM and AFM images as illustrated in Fig. 4. The SMA-g-CSNPs formed circle-like particles with two distinct layers. It is known that the SMA structure consists of a long chain alkyl and exhibits highly hydrophobic. Therefore, it was suspected that the particles comprised of CS-core and SMA-shell since the samples were dispersed in methanolic solution.

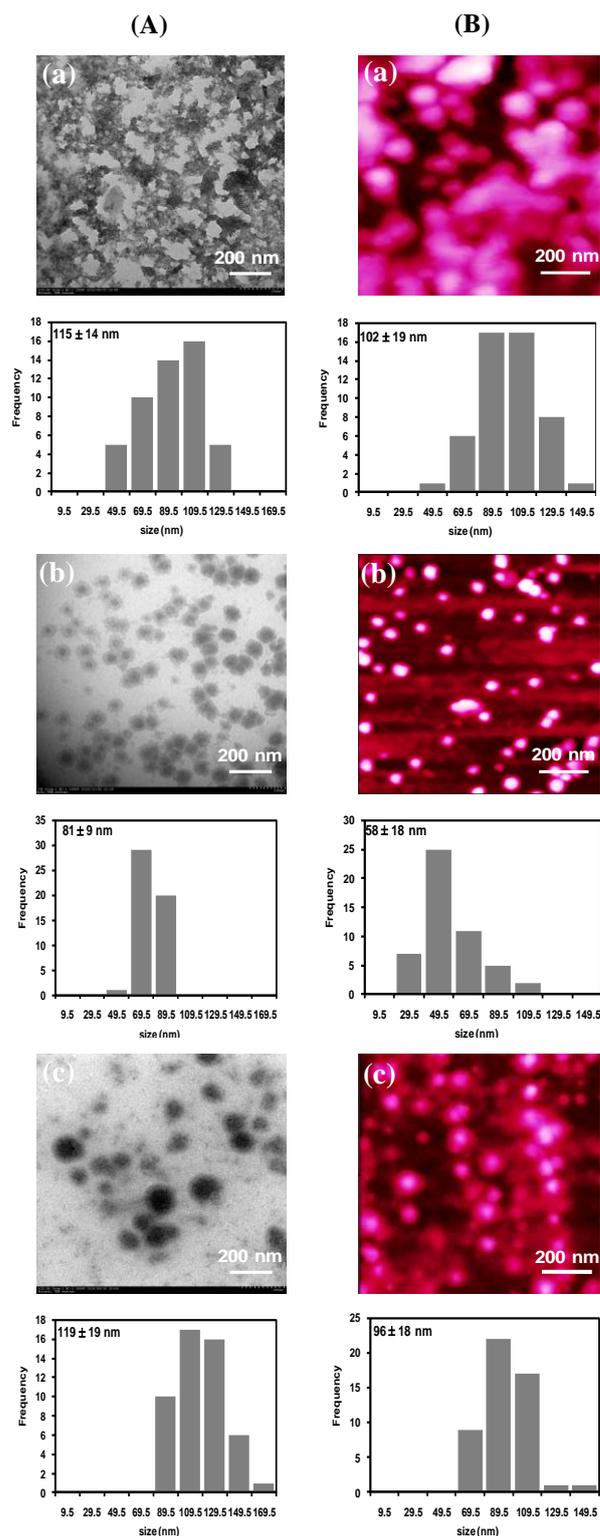


Fig.4. The micrographs of (A) TEM and (B) AFM from (a) CS, (b) SMA-g-CSNPs from CS:SMA ratio of 1:1 (11%GY) and (c) SMA-g-CSNPs from CS:SMA ratio of 1:5 (59%GY) after  $\gamma$ -ray irradiation with the dose of 25 kGy.

The irregular-shape particles were also observed in some conditions, especially the condition using a high SMA:CS ratio. This may be due to the homopolymerization of the SMA monomers leading to inappropriate amount of %GY in forming particle. The particle sizes of SMA-g-CSNPs were measured from TEM images. For CS:SMA ratios of 1:1 and 1:5 at 25 kGy, the particle sizes were determined to be  $81 \pm 9$  nm and  $119 \pm 19$  nm, respectively. Fig. 5 represents the relationship between the %GY and the particle size. The larger particle size was observed when the %GY increased.

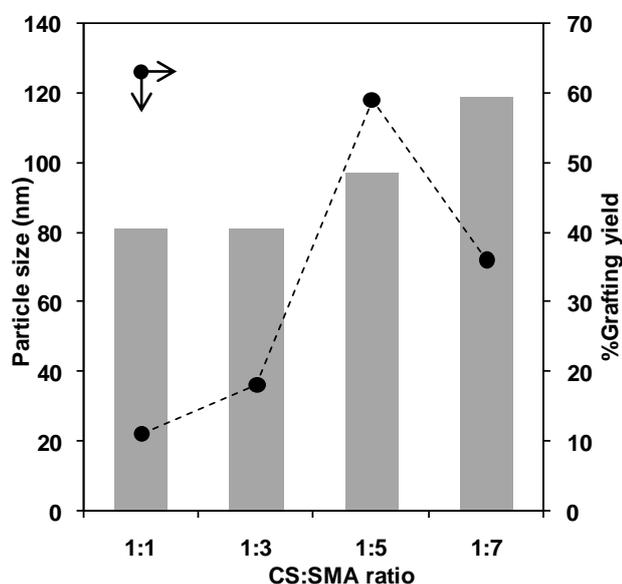


Fig.5. Relationship between CS:SMA ratio, particle size and %grafting yield.

### 3.4 Compatibility and Thermal Property of SMA-g-CSNPs/PLA Blends

SEM was employed to observe the compatibility of SMA-g-CSNPs/PLA blends. Fig. 6 shows the morphology of pure PLA, PLA blended with 2% of CS and PLA blended with 2% of SMA-g-CSNPs from CS:SMA ratios of 1:1 and 1:5 at 25 kGy. The blended PLA with 2 wt% of non-modified CS obviously exhibited the phase separation between CS and PLA (Fig. 6(b)). Comparing the miscibility in term of %GY, SMA-g-CSNPs with the higher %GY of 59% (CS:SMA = 1:5) showed the

better miscible blending than that of 11% (CS:SMA = 1:1)

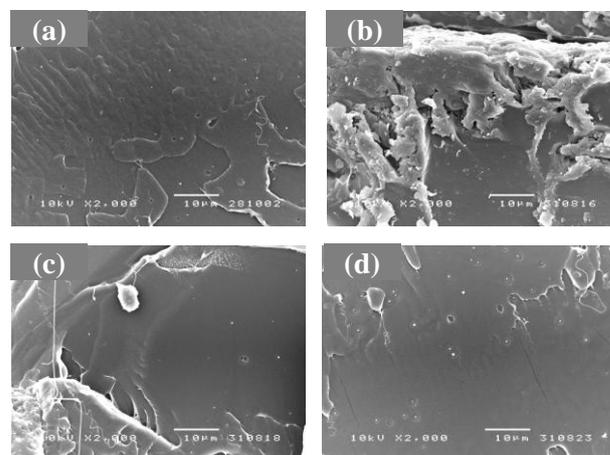


Fig.6. SEM images of (a) pure PLA, (b) PLA blended with 2% CS, (c) PLA blended with 2% SMA-g-CSNPs from CS:SMA ratio of 1:1 (11%GY) and (d) SMA-g-CSNPs from CS:SMA ratio of 1:5 using  $\gamma$ -ray irradiation dose of 25 kGy (59%GY).

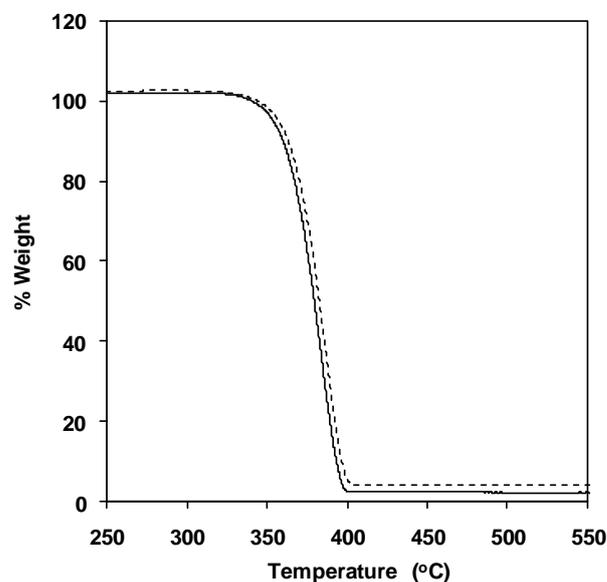


Fig.7. TGA curve of (—) pure PLA and (----) PLA blended with 2%wt of SMA-g-CSNPs synthesized from CS:SMA ratio of 1:5 for using  $\gamma$ -ray dose of 25 kGy (59% GY).

The thermal property of pure PLA and SMA-g-CSNPs/PLA blends was determined by TGA. Fig. 7

shows the %weight loss curve of pure PLA and SMA-g-CSNPs/PLA blends. The curves represent single step decomposition. By blending only small amount of SMA-g-CSNPs of 2% (w/w) with PLA, the initial decomposition temperature (IDT) and final decomposition temperature (FDT) of SMA-g-CSNPs/PLA blends shifted from 318.67 °C to 320.10 °C and from 399.50 °C to 320.10 °C, respectively in comparison to that of the pure PLA. The blending PLA with 2%(w/w) of SMA-g-CSNPs shown the increase of the IDT and FDT. The result implied the possibility to improve thermal property of PLA by composite with SMA-g-CSNPs.

#### **4 Conclusions**

The fabrication of the biodegradable polymer-bound natural monomer as a nanofiller for PLA was accomplished by grafting SMA onto CS via  $\gamma$ -irradiation. The  $\gamma$ -ray doses and CS:SMA ratios influence the %GY, particle shape, particle size as well as the compatibility with PLA. The samples containing CS:SMA ratio of 1:1 and 1:5 and irradiated with the  $\gamma$ -ray dose of 25 kGy produced the core-shell structure particle with the sizes of ~80 and 120 nm, respectively. The SMA-g-CSNPs can be miscible blended with PLA. We propose that the multifunctional SMA-g-CSNPs would be applicable to use as a nanofiller for PLA to overcome its limitation due to the mechanical properties. The performance of SMA-g-CSNPs/PLA blends will be extended to study in our future work.

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