

# Synthesis, Characterization, and Enzymatic Degradation of Starch-Grafted Poly(methyl methacrylate) Copolymer Films

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**ABSTRACT:** Graft copolymerization of methyl methacrylate (MMA) onto the corn starch (CS) backbone was carried out in an aqueous medium using ceric ammonium nitrate as an initiator under nitrogen atmosphere. The weight ratio of CS/MMA varied with their composition, as 7/3, 6/4, 5/5, 4/6, and 3/7 were used in this study of the graft efficiency and graft percentage (GP); thus, five different GP CS-g-PMMA copolymers were obtained. The molecular weight of CS-g-PMMA copolymers were measured by using gel permeation chromatography. The structure of CS and CS-g-PMMA copolymer were confirmed by infrared spectra. CS and CS-g-PMMA copolymers were characterized by thermal gravimetric analysis, differential scanning calorimetry, and scanning electron microscopy (SEM). Horowitz-Metzger and Broido methods were

applied to investigate the thermal decomposition kinetics of CS-g-PMMA copolymers. The effect of GP on the activation energy of decomposition, crystallization behavior, and morphology was investigated. In addition, the biodegradability of CS-g-PMMA films were also studied by  $\alpha$ -amylase treatment with different times. The weight loss of CS-g-PMMA films after  $\alpha$ -amylase treatment were calculated. Finally, the morphology of CS-g-PMMA films before and after  $\alpha$ -amylase treatment were observed by SEM photograph. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 405–414, 2012

**Key words:** biodegradable; crystallization; graft copolymers; enzymes; modification

## INTRODUCTION

Biodegradable polymers from renewable resources have a great attention for research because of its non-pollution and environmental friendly. Among lots of natural raw resources, starch is considered one of most important and promising candidates because of its properties of abundant, renewable, low cost, and completely biodegradable.<sup>1</sup> Therefore, starch-based materials, such as starch-based copolymer plastic,<sup>2,3</sup> starch/rubber compound,<sup>4–6</sup> and starch/clay nanocomposites<sup>7,8</sup> have been studied by many research groups for last 2 decades. Unfortunately, pure starch without any modification is not suitable for most uses because of its poor physical properties, high hydrophilicity, high recrystallization behavior, and low decomposition temperature. Thermoplastic starch was prepared by using various plasticizers, such as glycerol, glycol, urea, formamide, acetamide, and citric acid.<sup>9</sup> Although the processing properties have been

improved, the mechanical properties of starch/hydrophobic polymer were not enhanced. Chemical modification of starch via grafting of appropriate vinyl monomer is an effective method to improve the compatibility between hydrophilic starch and hydrophobic polymer matrix. The polymer grafts could restrain the crystallinity of starch. Liu et al.<sup>5</sup> reported the grafting of butyl acrylate onto starch backbone not only restrained the crystallinity of starch but also improved the interaction between starch and natural rubber matrix. Ge et al.<sup>10</sup> reported that grafting of methyl acrylate led to an improvement in the thermal and mechanical properties of poly(propylene carbonate)/starch composites. Therefore, starch-grafted vinyl copolymer have wide application as a biodegradable filler or compatibilizer in the field of thermoplastic and rubber composites.

Starch-grafted vinyl copolymer can be prepared by many methods, such as free-radical method, microwave irradiation, and  $\gamma$ -ray irradiation.<sup>11–13</sup> Initiator ceric ammonium nitrate (CAN) is widely used in the grafting of vinyl monomer onto starch because of some advantages such as the simple mechanism of single electron transfer, formation of free radicals on the backbone polymer itself, production of pure graft copolymer, and ease of application at an ambient temperature in aqueous medium.<sup>14</sup> There are many reports on starch-grafted vinyl copolymers, such as

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starch-*g*-poly(methacrylic acid), starch-*g*-polystyrene, starch-*g*-polyacrylonitrile, starch-*g*-polymethacrylonitrile, and starch-*g*-polyacrylamide.<sup>15–19</sup> Most of reports focused on the influence of reaction time, temperature, concentration of starch, vinyl monomer, and initiator on the GE and GP. Still now, there are few investigations on the correlation of GP to various properties such as morphology, thermal stability, crystallization behavior, and biodegradability.<sup>18–20</sup>

In this study, CS-*g*-PMMA copolymers with different GP were successfully synthesized by CAN-initiated radical polymerization. The effect of GP on the thermal stability, crystallization behavior, and morphology of copolymers was investigated. Moreover, the biodegradability of CS-*g*-PMMA films were also studied by  $\alpha$ -amylase treatment.

## EXPERIMENTAL

### Materials

Corn starch (amylose content 25%, insoluble in water at room temperature) was kindly supplied by Samyang Genex Company, South Korea. Methyl methacrylate (MMA), ceric ammonium nitride (CAN), and nitric acid were purchased from Dae Jung Chemical and metal co., Ltd, South Korea. Termamyl 120L, a thermostable  $\alpha$ -amylase of *Bacillus licheniformis* origin, were purchased from Novozymes Company, Denmark. The enzymatic activity of Termamyl 120L was 120 KNU/g. The Kilo Novo  $\alpha$ -amylase Unit (KNU) was defined as the amount of enzyme which can break down 5.26 g of starch 1 h at pH 5.6 and 37°C. All the chemicals were used as received without further purification.

### Synthesis of CS-*g*-PMMA copolymer

Corn starch was dissolved in excess deionized water under nitrogen atmosphere and stirred at 40°C for 1 h to obtain the starch slurry. After that, MMA was added during 30 min. The initiator CAN was first dissolved in 10 mL of 0.1 mol/L nitric acid solution and then added into the mixture. The weight ratio of CS/MMA were 7/3, 6/4, 5/5, 4/6, and 3/7, and other parameters kept constant. The graft copolymerization was carried out under nitrogen atmos-

phere at 40°C for 3 h. The product was cooled at room temperature and then poured into excess methanol solution. The precipitate was filtered, washed with methanol and water, and then dried at 50°C in an oven.

To remove the ungrafted poly(methyl methacrylate) homopolymer, 1 g product was extracted with chloroform and dried in an oven at 50°C for 24 h. Grafted poly (methyl methacrylate) can be separated from the CS-*g*-PMMA by oxidation of starch. Pure CS-*g*-PMMA copolymer was added into 100 mL of glacial acetic acid at 90–100°C for 1 h. Then, 2 mL perchloric acid (60%) was added dropwise for 2 min.<sup>21</sup> The product was poured into cold water, washed and dried in an oven at 50°C. The graft percentage (GP) and graft efficiency (GE) are calculated by the following equation:

$$GP = \frac{W_1}{W_2} \times 100\% \quad (1)$$

$$GE = \frac{W_1}{W_3} \times 100\% \quad (2)$$

where  $W_1$  is the weight of PMMA grafts in the CS-*g*-PMMA copolymer,  $W_2$  is the weight of starch in the CS-*g*-PMMA copolymer, and  $W_3$  is the initial weight of monomer MMA.

### Preparation of CS-*g*-PMMA films

The obtained pure copolymer was dissolved in dimethyl sulfoxide solution, casted into a petri dish, and dried in an oven at 70°C for 5 days.

### Biodegradation of CS-*g*-PMMA films

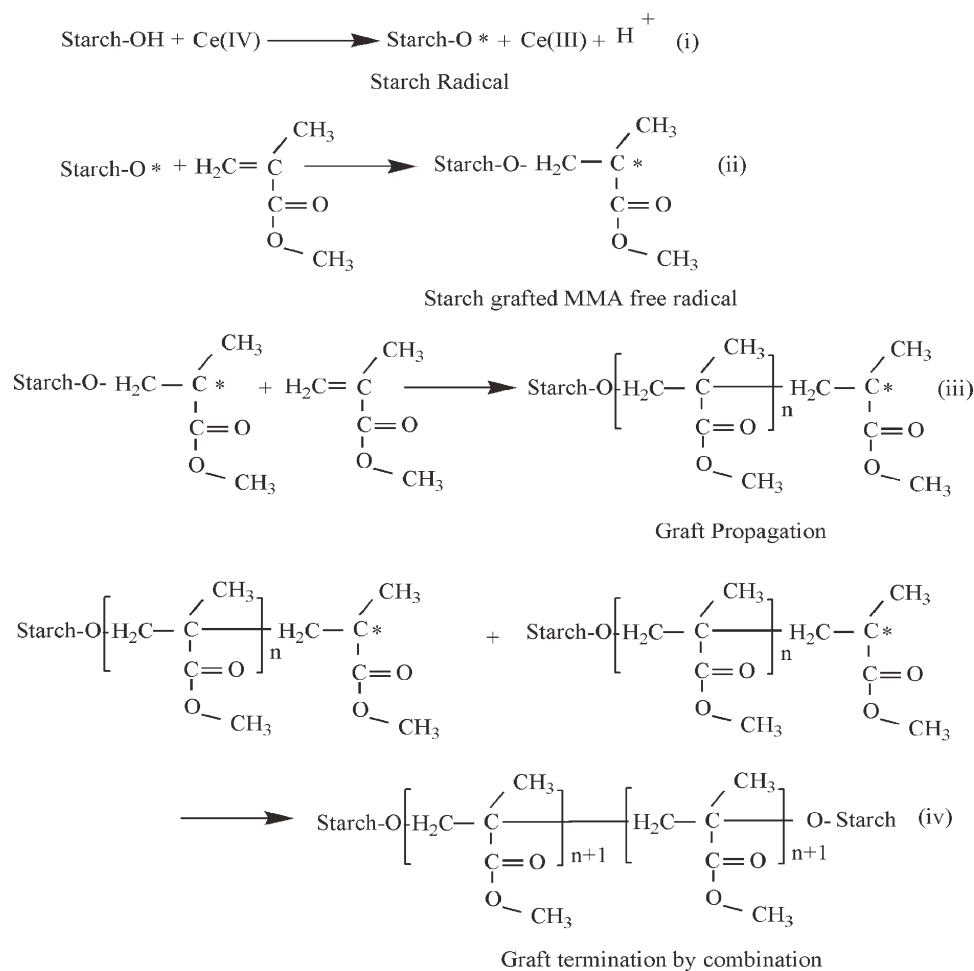
Biodegradation studying was carried out according to Shah et al.<sup>22</sup> CS-*g*-PMMA films were weighted accurately to 0.1 mg and placed in a bowl containing 3 g of  $\alpha$ -amylase in 3 L of distilled water. The bowl was heated in a water bath at 95°C. The CS-*g*-PMMA films after 24, 72, and 120 h treatment with  $\alpha$ -amylase were dried and weighted accurately. The weight loss percentage was calculated as follow:

$$\text{Weight loss \%} = \frac{\text{original weight} - \text{weight after } \alpha - \text{amylase treatment}}{\text{original weight}} \times 100\% \quad (3)$$

### Characterization

Infrared spectra were recorded on a PerkinElmer spectrum 1000. The frequency range of Infrared spectra was 4000–400  $\text{cm}^{-1}$  with a resolution of 4.0  $\text{cm}^{-1}$ . Molecular weight of poly(methyl methacrylate) was measured on an Agilent gel permeation

chromatography (GPC, 1200 series, Agilent Technologies) equipped with a Refractive Index Detector calibrated with polystyrene standards. The poly (methyl methacrylate) grafts after separation from CS-*g*-PMMA copolymers were dissolved in THF solvent and then injected into the GPC test cells.



Scheme 1 Mechanism of grafting polymerization.

Thermal properties were evaluated by thermogravimetric analysis (PerkinElmer TGA 4000) and differential scanning calorimetry (PerkinElmer DSC 4000). TGA analysis was carried out at a heating rate of 10°C/min from 25 to 700°C under nitrogen atmosphere. DSC analysis was operated with a heating rate 10°C/min from 20 to 200°C under nitrogen atmosphere. Scanning electron microscopy (SEM) morphologies were used to observe the surface morphology of starch and copolymer granules using a CX-100S SEM from COXEM Company. The samples were coated with gold before testing. The surface morphology of films before and after  $\alpha$ -amylase treatment were also performed.

## RESULTS AND DISCUSSION

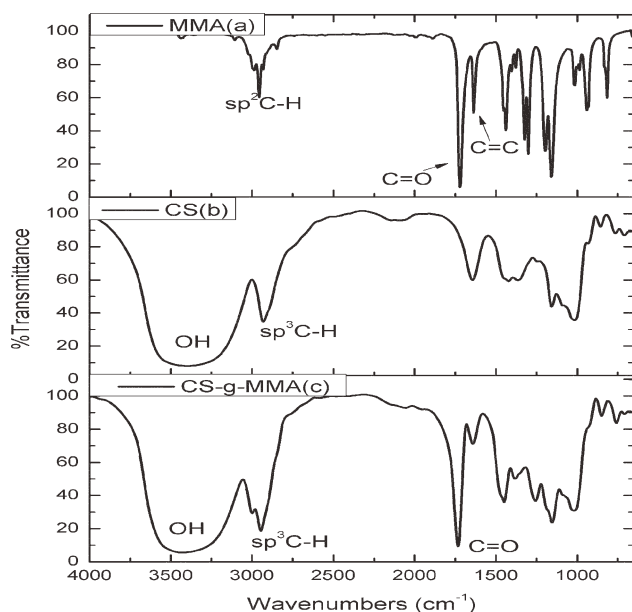
### Mechanism of grafting copolymerization

Scheme 1 gives the proposed mechanism for this grafting polymerization. At low temperature, CAN is an efficient initiator because of its instability at elevated temperature.<sup>23</sup> After addition of the initiator CAN in an inert atmosphere of nitrogen, starch-

macro radicals were produced by donating hydrogen atoms, as shown in reaction (i). In the presence of monomer MMA, these reactive starch radicals were easily added to the double bond of monomer MMA, producing starch-grafted MMA free radicals, as shown in reaction (ii). Reaction (iii) shows that many more MMA molecules were successively added to continuously propagate the reactive chain. Finally, this grafting copolymerization might be terminated by a combination of two reactive starch-grafted MMA chains, as shown in reaction (iv).

### Evidence of grafting

Figure 1 shows the infrared spectra of MMA, corn starch, and CS-g-PMMA copolymer. In the infrared spectrum of MMA [Fig. 1(a)], the absorption peaks found at 1625 and 1720  $\text{cm}^{-1}$  were attributed to C=C and carbonyl groups (C=O) stretching of MMA, respectively. The infrared spectra of pure corn starch [Fig. 1(b)] were characterized as follows: absorption peaks at 998, 1077, and 1148  $\text{cm}^{-1}$  for C—O stretching; a broad absorption peak at 3313  $\text{cm}^{-1}$  for O—H stretching. In the case of CS-g-



**Figure 1** The infrared spectra of (a) MMA, (b) CS, and (c) CS-g-PMMA.

MMA [Fig. 1(c)], compared to pure corn starch, new absorption peak appeared at  $1726\text{ cm}^{-1}$  was attributed to C=O stretching of MMA. This new peak gave supporting evidence that the monomer MMA was successfully grafted onto starch backbone.

### Grafting parameters and molecular weight

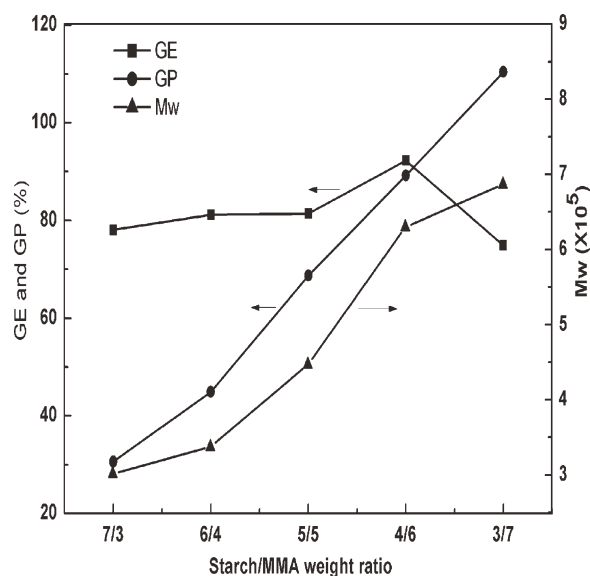
The different weight ratio of CS/MMA might influence the GE and GP. Thus, the effect of CS/MMA in the weight ratio on the GE and GP was investigated. Figure 2 shows the GE and GP values with the different weight ratio of CS/MMA. GE increased from 78.1 to 92.3% with decreasing the molar ratio of CS/MMA from 7/3 to 4/6. Further decreasing from 4/6 to 3/7, GE decreased to 74.9%. It is well known that at a higher weight ratio of CS/MMA, monomer MMA could be highly grafted onto the starch backbone. At a lower molar ratio of CS/MMA, most monomers could be used for homopolymer formation, resulting in decreasing of GE. However, GP increased gradually with decreasing the weight ratio of CS/MMA from 7/3 to 3/7. The GPs were 30.6%, 44.9%, 68.7%, 89.2%, and 110.4% for the CS/MMA weight ratio of 7/3, 6/4, 5/5, 4/6, and 3/7, respectively. The increase in GP may be attributed to increasing supply of monomer MMA to starch-macro radicals. Sen et al.<sup>12</sup> indicated that an increase in monomer concentration led to the accumulation of monomer molecules in close proximity to the starch backbone, result in increasing of GP.

The molecular weight of a polymer has a vital importance in its application. Some properties, such as mechanical strength and processability, show a sig-

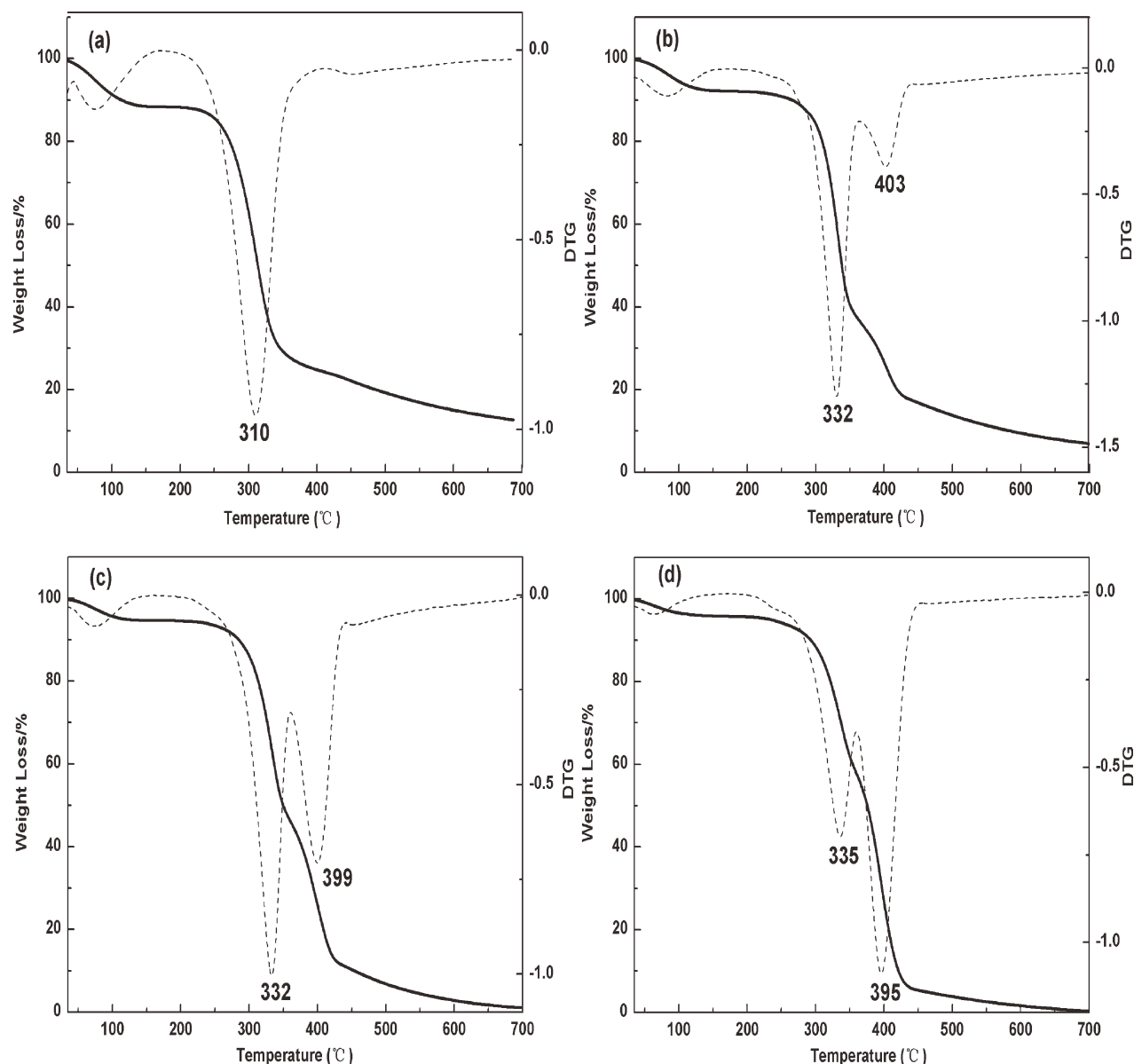
nificant dependence on the molecular weight. Thus, it is essential to study the molecular weight of a polymer. Here, the weight-average molecular weight ( $M_w$ ) of PMMA grafts in the CS-g-PMMA copolymer was investigated as shown in Figure 2. It is clear that the  $M_w$  of PMMA grafts and graft chain length increased gradually with decreasing the weight ratio of CS/MMA from 7/3 to 3/7. Namely, the  $M_w$  increased as increasing the concentration of monomer MMA. This result is agreed with the traditional radical chain polymerization theory. As reported by Odian,<sup>24</sup> the kinetic chain length is directly dependent on the monomer molecular concentration and inversely dependent on the radical concentration or the polymerization rate. Moreover, it is well known that corn starch is difficult to dissolve in water phase at  $40^\circ\text{C}$ , so the grafting copolymerization might take place at the surface of the starch granules. Cho and Lee<sup>25</sup> assumed that there were a fixed number of grafting sites available for graft copolymerization at the surface of the starch granules. If this assumption was correct, then when the whole available grafting sites were fully covered by PMMA grafts, the further addition of MMA monomer would increase the graft chain length continuously, resulting in an increase in the  $M_w$  of PMMA grafts.  $M_w$  results confirmed this assumption and also indicated that this grafting copolymerization occurred in heterogeneous system.

### Thermal properties of corn starch and CS-g-PMMA copolymer

Thermogravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) were applied to



**Figure 2** Effect of weight ratio of CS/MMA on the graft parameters and the molecular weight of PMMA grafts.



**Figure 3** TGA and DTG curves of (a) pure corn starch, (b) CS-g-PMMA copolymer with GP = 30.6%, (c) 68.7%, and (d) 110.4%.

assume the effect of PMMA grafts on the thermal properties of these obtained copolymers.

Figure 3 shows the TGA curves of corn starch and CS-g-PMMA copolymer with different GP. Pure corn starch [Fig. 3(a)] showed a three-stage characteristic decomposition. The first stage occurring from 35 to 165°C was attributed to the water evaporation. The moisture of corn starch was about 11.6% as shown in Table I. The second stage occurred from 165 to 420°C, which was the major weight loss (64.2%). From the differential thermogravimetric (DTG) curve of corn starch, the maximum decomposition temperature was about 310°C. The third stage occurring from 353 to 700°C was attributed to formation and evaporation of some volatile compounds. The char residue was 11.7% at 700°C.

All of CS-g-PMMA copolymers show four-stage decomposition. In case of CS-g-PMMA copolymer with PG = 30.6% PG [Fig. 3(b)], compared to pure corn starch, a new stage appearing from 365 to 439°C was attributed to the decomposition of PMMA grafts, which demonstrated monomer MMA were successfully grafted onto the starch backbone again. It was observed that the maximum decomposition temperature of starch portion increased up to 332°C, which was 22°C higher than that of pure corn starch. It indicated the CS-g-PMMA copolymers had significant higher thermal stability than that of pure starch. It was probably due to the addition of PMMA grafts that had much higher thermal stability than pure corn starch. Similar result was also observed for starch-g-poly(methyl acrylate).<sup>10</sup> Table I

TABLE I  
Thermal Decomposition Data of Corn Starch and CS-g-PMMA Copolymer

Sample	Number of degradation stage	Temperature range (°C)	$T_{\max}$	Weight loss (%)
(a) Corn starch	1	35–165	78	11.6
	2	165–420	310	64.2
	3	420–700	–	11.5
CS-g-PMMA copolymer (b) GP = 30.6%	1	35–161	84	7.8
	2	161–365	332	54.9
	3	365–439	403	20
	4	439–700	–	10.8
(c) GP = 68.7%	1	35–141	74	5.6
	2	141–362	332	48.3
	3	362–442	399	35
	4	442–700	–	9.2
(d) GP = 110.4%	1	35–137	64	3.8
	2	137–359	335	38.2
	3	359–461	395	52.7
	4	461–700	–	3.9

summarizes the thermal decomposition data of corn starch and CS-g-PMMA copolymer.

The effect of GP on the thermal decomposition kinetics of CS-g-PMMA copolymer was studied. The thermal decomposition kinetics were investigated utilizing both the Horowitz-Metzger and Broido methods. According to Horowitz-Metzger method,<sup>26</sup> the temperature dependence of the thermal decomposition reaction could be expressed in terms of eq. (4)

$$\ln[\ln(1 - \alpha)^{-1}] = E_a q / RT_{\max}^2 \quad (4)$$

where  $\alpha$  represents the decomposed reaction,  $E_a$  represents the activation energy of decomposition,  $T_{\max}$  is the temperature of maximum decomposition rate,  $\theta$  is  $(T - T_{\max})$ . By plotting  $\ln[\ln(1 - \alpha)^{-1}]$  against  $\theta$ , straight lines could be obtained as shown in Figure 4(a). The slope of this straight line is  $E_a/RT_{\max}^2$ ; thus, the activation energy of decomposition  $E_a$  could be calculated.

According to Broido method,<sup>27</sup> the temperature dependence of the thermal decomposition reaction could be expressed in terms of eq. (5)

$$\ln[\ln(1 - a)^{-1}] = -E_a/RT + \text{const} \quad (5)$$

where  $\alpha$  represents the decomposed reaction,  $E_a$  represents the activation energy of decomposition, and  $T$  is the temperature. Thus, by plotting  $\ln[\ln(1 - \alpha)^{-1}]$  against  $1/T$ , straight lines could be obtained as shown in Figure 4(b). The activation energy of decomposition  $E_a$  could be also calculated from the slope of the straight line of the plots.

Figure 5 shows the effect of GP on the decomposition activation energy  $E_a$  of starch composition

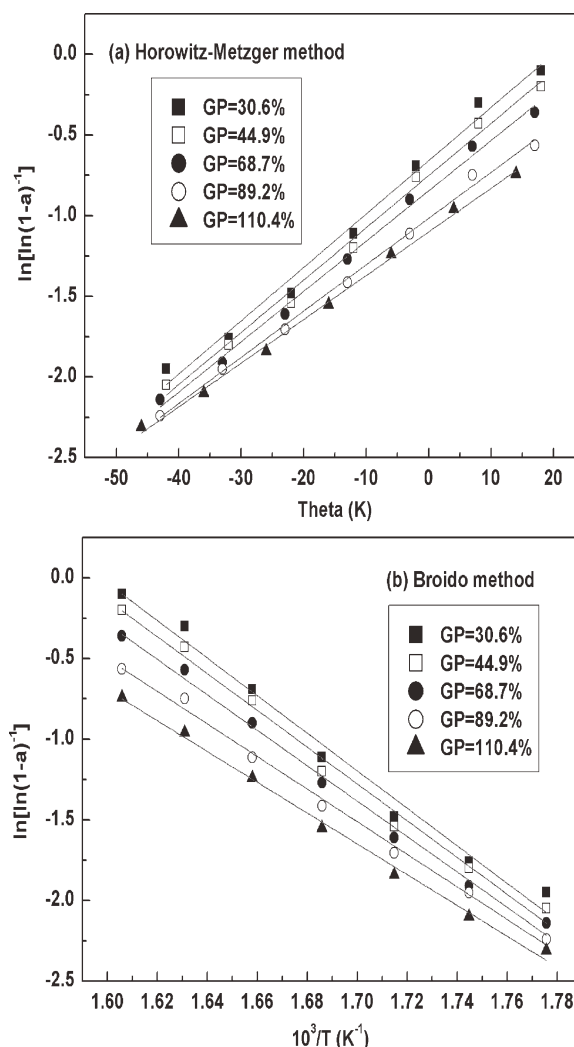
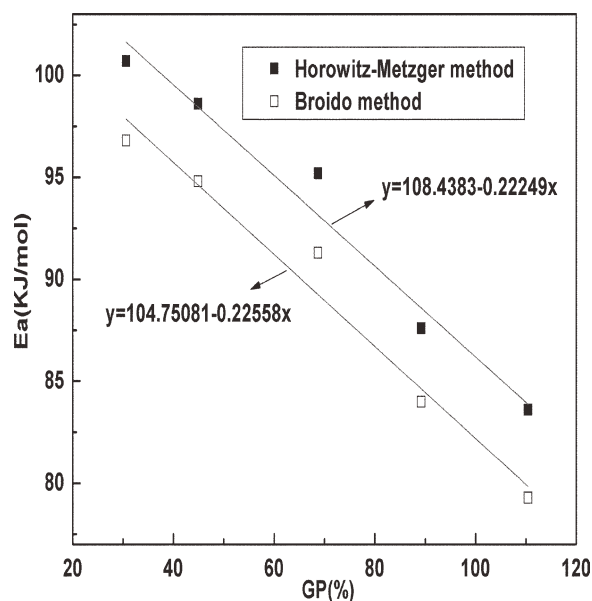


Figure 4 Results of (a) plots of  $\ln[\ln(1 - a)^{-1}]$  versus  $\theta$  using Horowitz-Metzger methods and (b) plots of  $\ln[\ln(1 - a)^{-1}]$  versus  $1/T$  using Broido method.



**Figure 5** Decomposition activation energy of starch composition as a function of GP.

calculated by both Horowitz-Metzger and Broido methods. As calculated from Horowitz-Metzger method, as the GP was increased from 30.6 to 110.4%, the decomposition activation energy  $E_a$  of starch composition decreased successively from 100.7 to 83.6 KJ/mol. Calculated from Broido method, the decomposition activation energy  $E_a$  of starch composition was also decreased successively from 96.8 to 79.3 KJ/mol. This was indicated that the  $E_a$  of starch composition decreased successively as increasing of GP, which could be attributed to the plasticizing effect of PMMA grafts.

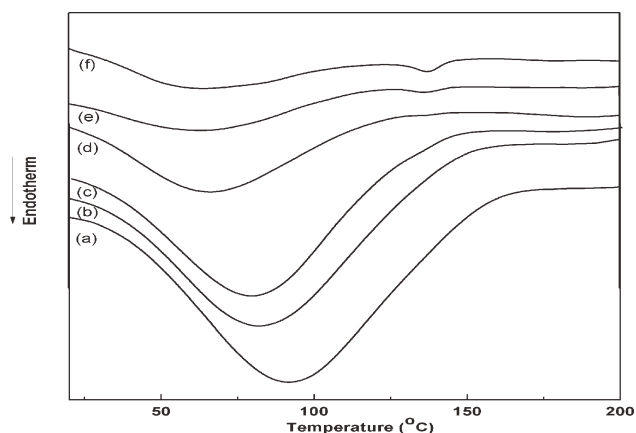
By correlation of the activation energy  $E_a$  of starch composition with the GP, it was observed that the decomposition activation energy  $E_a$  of starch composition was a linear function of the GP. The relationship between the decomposition activation energy  $E_a$  of starch composition and GP calculated by both Horowitz-Metzger and Broido methods were  $y = 108.4383 - 0.22249x$  and  $y = 104.75081 - 0.22558x$ , respectively. Therefore, the GP shows significant effect on the thermal stability of CS-g-PMMA copolymer.

Figure 6 shows the DSC curves of pure corn starch and CS-g-PMMA copolymers with different GP. As shown in Figure 4(a), Pure corn starch showed a very strong and broad endothermic hill from 40 to 155°C, which was indicated its highly recrystallization behavior. The peaks at 89.2°C could be considered as the melting temperature ( $T_m$ ) of pure corn starch. Hamdan et al.<sup>28</sup> reported that this broad peak was due to the melting of the amylopectin fraction in the starch. Ge et al.<sup>10</sup> suggested that this broad peak was attributed to the crystalline melting,

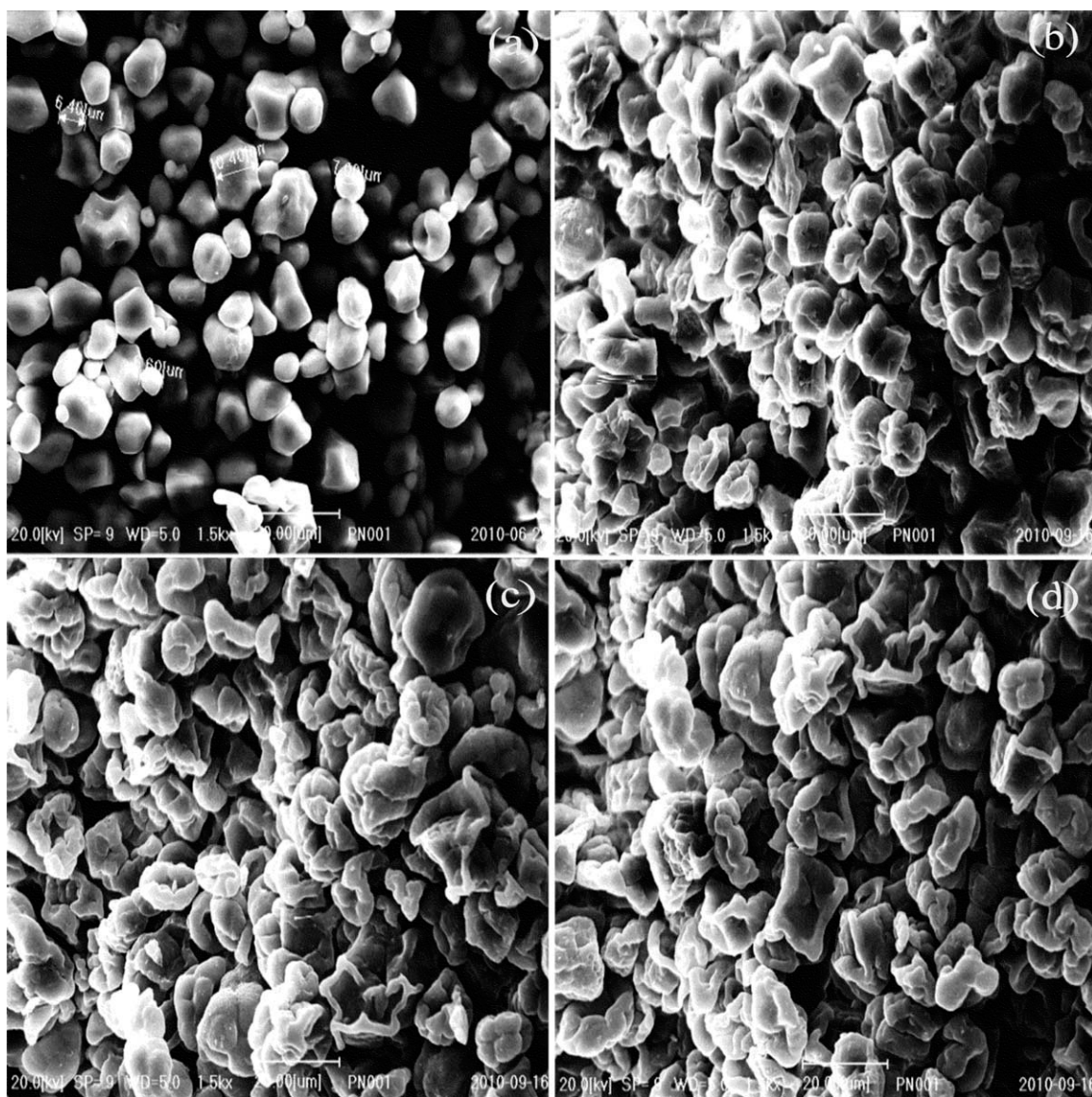
which was formed between residue water and molecular chains of starch via hydrogen bonding. In case of CS-g-PMMA with GP of 30.6% [Fig. 6(b)] and 44.9% [Fig. 6(c)], the  $T_m$  were decreased a little. Further increasing of GP up to 68.7% [Fig. 6(d)], 89.2% [Fig. 6(e)], and 110.4% [Fig. 4(f)], the endothermic hills and melting temperature were highly decreased. Therefore, the crystallization behavior was greatly restrained by grafting of PMMA onto starch backbone, forming amorphous structure. The grafting of PMMA onto starch backbone was leading the destruction or reduction of hydrogen bonding between starch molecules and a decrease in crystallinity of starch. The glass temperature ( $T_g$ ) of CS-g-PMMA copolymer was hard to be detected in DSC curves. However, according to literature,<sup>29</sup> in polymers with a higher degree of crystallization, there was more restriction of segmental motion, resulting in increased  $T_g$ . Therefore, the  $T_g$  of CS-g-PMMA copolymers might be decreased with increasing of GP because of the decreasing of crystallization.

#### Morphology of corn starch and CS-g-PMMA copolymer

Figure 7 shows the granule morphology of corn starch and CS-g-PMMA copolymer with different GP. The pure corn starch granules had a spherical or polyhedral shape with a very smooth surface as shown in Figure 6(a). The particle size of corn starch ranged from 5 to 15  $\mu\text{m}$ . The Figure 6(b–d) showed the CS-g-PMMA copolymers exhibited a different surface morphology. Because of grafting copolymerization occurred in heterogeneous system, the surface of starch granules were covered with a layer of PMMA grafts. The biggest structural difference happened at the less organized central core region of starch granules. At low GP% (30.6%), the CS-g-PMMA granules were slightly deformed, indicating



**Figure 6** DSC curves of (a) pure corn starch, and CS-g-PMMA copolymer with GP: (b) 30.6%, (c) 44.9%, (d) 68.7%, (e) 89.2%, and (f) 110.4%.



**Figure 7** SEM photographs of (a) CS, and CS-g-PMMA copolymer with GP: (b) 30.6%, (c) 68.7%, and (d) 110.4%. (at magnification 1500 $\times$ ).

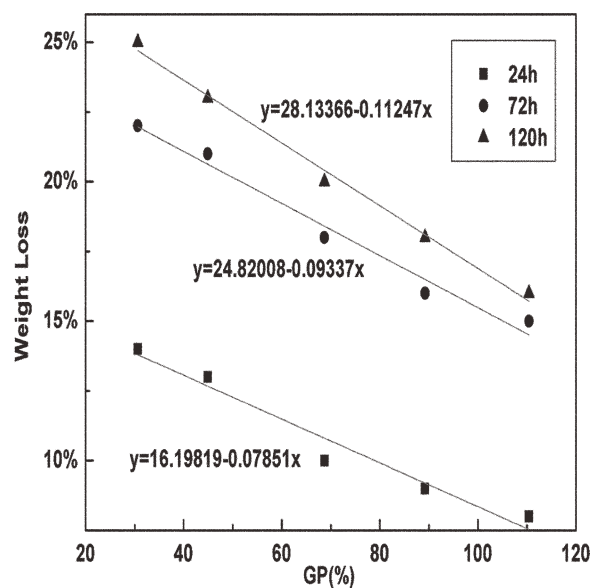
its strong recrystallization behavior and high resistance toward deformation. With increasing the GP up to 68.7% [Fig. 6(c)] and 110.4% [Fig. 6(d)], the CS-g-PMMA granules were heavily deformed to fragmentation or the formation of a deep groove in the central core region, indicating the development of plasticity presumably because of the entanglement of amorphous amylopectine.<sup>5</sup> This observation was agreed with the DSC result that the grafting of MMA restrains crystallization behavior of corn starch.

#### Biodegradability of CS-g-PMMA films

$\alpha$ -Amylase enzymatic hydrolysis is an effective way for studying the biodegradability of starch-based polymer. The enzymatic hydrolysis of starch could

be divided into three steps<sup>30</sup>: (1) Diffusion of enzyme molecules from the bulk aqueous phase to the gel surface. (2) Adsorption of the enzyme onto the gel substrate, resulting in the formation of enzyme-substrate complex. (3) Hydrolysis of the  $\alpha$ -1,4-glucose bond, and finally diffusion of the soluble degradation products from the gel substrate into the bulk aqueous phase. Imam et al.<sup>31</sup> suggested that enzyme preferentially catalyzed the anhydroglucose units in amorphous regions of the granule. Therefore, the lower crystallinity and higher starch content were benefited for biodegradation. Figure 8 shows the weight loss as function of GP and enzymatic treatment time. It was observed that the weight loss decreased gradually as increasing of GP%. After 120 h enzymatic treatments, the weight loss of CS-g-PMMA films with GP of 30.6%, 44.9%,





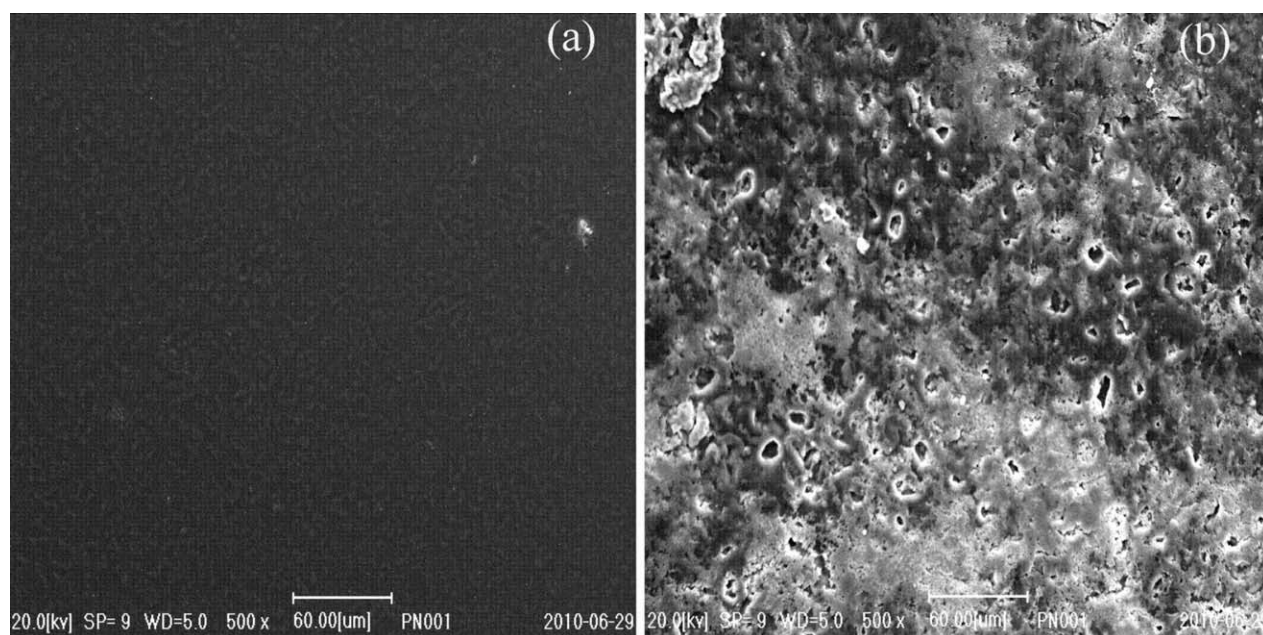
**Figure 8** Weight loss of CS-g-PMMA films as function of GP and enzymatic treatment time.

68.7%, 89.2%, and 110.4% were 25.2%, 23.1%, 20.1%, 17.8%, and 15.8%, respectively. It was probably attributed to the decreasing of starch content.<sup>32</sup> Moreover, it was observed that weight loss increased rapidly at the first day of hydrolysis; however, the rate of increase reduced at the 5th day of hydrolysis. It was probably due to some factors such as decreasing of starch content, inhibition of enzyme action by the accumulated products, and partial enzyme inactivation.<sup>33–35</sup> The surface morphology of CS-g-PMMA film with GP = 110.4% before and after

120 h enzymatic treatment are shown in Figure 9. It was clearly observed that the surface of CS-g-PMMA film appears many holes randomly, demonstrating its biodegradability.

## CONCLUSIONS

CS-g-PMMA copolymers with five GP of 30.6%, 44.9%, 68.7%, 89.2%, and 110.4% were successfully prepared by CAN-initiated radical polymerization. Results showed that the GP significantly influenced on its properties, such as the molecular weight of PMMA grafts, thermal stability, crystallization behavior, morphology, and biodegradability. TGA results indicated the presence of PMMA grafts improved the thermal stability of starch; however, the decomposition activation energy decreased as increasing of GP. DSC results showed that the crystallinity of starch was restrained by grafting of MMA, and further decreased with increasing of GP value. SEM micrograph exhibited a strongly deformed structure of CS-g-PMMA copolymer granules. All of these observations were explained by considering the plasticizing effect of PMMA grafts.  $\alpha$ -Amylase biodegradation studies indicated the weight loss increased with increasing of treatment time, while decreased with increasing of GP value. Thus, because of its low crystallinity and biodegradability, CS-g-PMMA copolymers can be widely applied in biodegradable plastic or rubber industry. Moreover, the desirable properties of this copolymer can be obtained by tailoring the GP value properly.



**Figure 9** SEM photographs of CS-g-PMMA film with PG = 110.4%: (a) before enzymatic treatment and (b) after 120 h enzymatic treatment. (at magnification 500 $\times$ ).

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