The Study on the Grafting of Glycidyl Methacrylate onto Poly(lactic acid) in an Internal Mixer

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Abstract

Glycidyl methacrylate (GMA) was grafted onto poly(lactic acid) (PLA) by melt mixing in an internal mixer using dicumyl peroxide (DCP) as an initiator. The results from nuclear magnetic resonance (^{1}H-NMR) and Fourier transform infrared (FTIR) spectroscopy indicated that the grafting reaction of GMA onto PLA took place successfully. After grafting, the brittle behaviour of PLA was changed to ductile behaviour of glycidyl methacrylate grafted poly(lactic acid) (PLA-g-GMA). The elongation at break and impact strength of PLA-g-GMA were significantly higher than those of pure PLA. In order to obtain the optimal mixing conditions, the mixing time was varied from 7, 10 to 14 min. PLA-g-GMA prepared by mixing for 10 and 14 min showed melt crystallization upon cooling. This was different from PLA and PLA-g-GMA prepared by mixing for 7 min, which did not undergo crystallization upon cooling from the melt. A mixing time of 10 min was found to give the optimum grafting yield, elongation at break and impact strength of PLA-g-GMA. With the significantly improved mechanical properties compared to those of pure PLA, the new, biodegradable PLA-g-GMA obtained from this study can be used to replace pristine PLA which has many drawbacks in many industrial applications.

Keywords: Poly(lactic acid), PLA, bioplastic, grafting, mechanical properties, GMA

Introduction

Due to environmental issues related to non-degradable plastic wastes, research and development of biodegradable polymers has recently received considerable attention. Poly(lactic acid) (PLA), a synthetic aliphatic polyester derived from biomasses, is an environmentally friendly polymer and has emerged as an alternative to conventional petroleum-based polymeric materials because of its renewability, biodegradability and greenhouse gas neutrality. Moreover, PLA also possesses good mechanical properties and can be easily processed [1]. However, PLA is still more expensive than many petroleum-derived commodity plastics. It has some poor physical properties such as slow crystallization rate, high brittleness, which hinder PLA to be used for various end-use applications.

Free radical grafting of PLA with monomers containing reactive groups has been considered to be a potential approach to modify the basic properties of pristine PLA. In addition, it is an effective method to produce compatibilizing agent for PLA-based polymer blends. So far, in addition to solution copolymerization, a melt grafting process by using an internal mixer has been extensively used in order to prepare many functionalized reactive polymers because of the relative simplicity and cost efficiency of this method. This grafting method can be applied for industrial scale production. The reactive grafting of glycidyl methacrylate (GMA) onto non-polar polyolefins such as polypropylene (PP) backbones via

reactive extrusion was carried out successfully [2,3]. Cho *et al.* investigated the melt grafting of GMA onto high-density polyethylene (HDPE) in the presence of free radical initiators in the batch mixer [4]. The results showed that the grafting reaction was significantly influenced by reaction time. It is one of the important variables for the preparation of functional polymers.

Recently, GMA has been increasingly used as a grafting monomer because of its dual functionality, which consists of epoxy and acrylic groups. It is believed that the epoxy group of GMA can react with many other groups, such as hydroxyl and carboxyl groups. Meanwhile, acrylic groups show the capability of free-radical grafting of GMA onto the polymer chain [5]. Even the radical grafting of GMA onto polyolefin in the melt mixing process has been investigated extensively, there have been very few studies focusing on the grafting of GMA onto PLA and the effect of reaction time on the physical properties of prepared PLA-g-GMA. Therefore, in this study, we report the grafting of GMA onto PLA with different mixing times using dicumyl peroxide (DCP) as an initiator in the internal mixer.

PLA-g-GMA obtained from this study can be used as a potentially biodegradable material used in various applications such as packaging materials, textile materials, environmental technology including wastewater treatment and bioremediation. Moreover, with the chemical structure containing hydrophilic and oleophylic chains, the obtained PLA-g-GMA can be used as a potential compatibilizer in natural fibers reinforced PLA-based biocomposites.

Materials and methods

Materials

Commercial PLA (PLA 4043D) was purchased from NatureWorks LLC. Dicumyl peroxide (DCP, 99 %), glycidyl methacrylate (GMA, 99 %), dichlorobenzene (DCB), chloroform (HPLC grade) and methanol were supplied from Sigma-Aldrich®. Before being used for grafting, GMA was purified by basic alumina pack column to remove inhibitor and stored in the refrigerator at about 5 ºC.

Preparation of glycidyl methacrylate grafted poly (lactic acid)

The grafting of GMA onto the PLA chain was carried out by an internal mixer (Hakke Rheomix, 3000p). Before being used, PLA pellets were dried at 70 ºC for 2 h. The grafting reaction was carried out under constant temperature at 170 ºC. The mixing speed was held at 60 rpm. A GMA content of 10 wt% of PLA was used. The mixing time was varied from 7, 10 to 14 min. The obtained grafted samples were labeled as PLA-g-GMA7min, PLA-g-GMA10min and PLA-g-GMA14min, respectively with the number indicating the mixing time used. Before being used for grafting, GMA was stored in the refrigerator at 5 ºC. The concentration of DCP used was 0.2 wt% of PLA. The grafting procedure is described as follows:

First, appropriate amounts of PLA and DCP were premixed by hand in a small plastic bag before being charged into the mixing chamber. After 2 min of mixing, GMA was added into the chamber. After the addition of GMA, the mixing chamber was closed immediately in order to minimize the loss of GMA due to vaporization.

Purification of glycidyl methacrylate grafted poly (lactic acid)

In order to remove unreacted GMA and possible homopolymer of GMA, which can be generated during the grafting reaction, after completion of mixing, the obtained samples were dissolved in DCB (5 wt% solution) at 120 ºC. After that, the solution was poured into a large excess of methanol to precipitate PLA-g-GMA. The obtained white PLA-g-GMA precipitate was washed several times with methanol to completely remove the residual GMA and homopolymer of GMA. After the purification process, the pure white PLA-g-GMA was dried in a vacuum oven at 70 ºC for 24 h.

Characterization of glycidyl methacrylate grafted poly (lactic acid)

Nuclear Magnetic Resonance (NMR): The percentage of GMA grafted onto PLA was determined by ^{1}H-NMR analysis. It was determined by calculating the relative area of the characteristic peaks of PLA and GMA. Its value was examined by Eq. (1) [9]. The ^{1}H-NMR spectra of PLA, PLA-g-GMA and GMA

monomer were recorded on a Varian model Inova 300 NMR spectrometer at 25 ºC using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

$$\%\text{grafting} = \frac{relative-area-of-characteristic-peak-of-GMA}{relative-area-of-characteristic-peak-of-PLA} \times 100 \tag{1}$$

Fourier Transform Infrared (FTIR) Spectroscopy: The measurements of structural characterization of PLA and PLA-g-GMA were recorded on a Bruker Tensor 27 spectrometer using attenuated total reflectance (ATR) equipped with a platinum diamond crystal (TYPE A225/QL). Spectra were obtained at 4 cm^{-1} resolution and 32 scans in the wavenumber range from 4000 to 400 cm^{-1}. All samples were dried in a vacuum oven at 60 ºC for 24 h before testing.

Mechanical properties: In order to prepare the test specimens for mechanical properties testing, samples were compression molded at 170 ºC for 10 min. PLA-g-GMA was dried in an oven at 70 ºC for 2 h to eliminate moisture before being compressed. Tensile properties of all compression molded samples were obtained according to ASTM D638 using an Instron Universal Testing Machine (UTM 5565) with a load cell of 5 kN. The unnotched Izod impact strengths of pure PLA and PLA-g-GMA were obtained by using an Instron CEAST 9050 Pendulum Impact System according to ASTM D256.

Thermal properties: The nonisothermal crystallization behavior of pure PLA and PLA-g-GMA was investigated using differential scanning calorimetry (DSC) (model: DSC204F1 Phoenix). The samples were first heated to 200 ºC with the rate of 5 ºC/min and kept at 200 ºC for 5 min (First heating scan). After that, they were cooled to 40 ºC with the rate of 5 ºC/min (Cooling scan). Then they were heated again to 200 ºC with the rate of 5 ºC/min (Second heating scan). Enthalpy of crystallization (ΔH_c) was determined from the area under the peak of the thermograms from the cooling scan. Enthalpy of cold crystallization (ΔH_{cc}) was obtained from the area under the recrystallization peak of the thermograms from the second heating scan. Enthalpy of melting (ΔH_m) was determined from the area under the melting peak of the thermograms from the second heating scan. The degree of crystallinity ($\%X_c$) of pure PLA and PLA-g-GMA was determined by Eq. (2) [6]:

$$\%X_c = \frac{\Delta H_m}{\Delta H_{mo}} \times 100 \tag{2}$$

where, ΔH_m is the measured melting enthalpy (in J/g) from the second heating scan and ΔH_{mo} is the theoretical melting enthalpy of completely crystalline PLA (93.7 J/g) [7].

Results and discussion

The FTIR spectra of pure PLA and PLA-g-GMA are shown in **Figure 1**. The spectrum of pure PLA showed peaks at 3000 - 2940 cm^{-1}, 1761 cm^{-1} and 1190 - 1090 cm^{-1}, which are associated with CH_3 stretching, C=O stretching and the O–C=O stretching, respectively [8]. The peaks at 910, 1150, 1761 and 3000 cm^{-1} were observed in the spectrum of PLA-g-GMA. Compared to the spectrum of pure PLA, the spectrum of PLA-g-GMA presented a small new peak appeared at 910 cm^{-1}, which is attributed to the asymmetric stretching of the epoxy group. This evidence demonstrates that the GMA was successfully grafted onto the PLA chain.

The NMR analysis also confirmed the result above. As seen in **Figure 2**, the ^{1}H-NMR spectra of PLA and PLA-g-GMA showed 2 peaks at 5.2 and 1.6 ppm, which represent the methylene and methyl protons of the PLA chain, respectively. However, compared to the spectrum of pure PLA, the spectrum of PLA-g-GMA exhibited the new and weak peaks at 0.9 - 4.3 ppm. These peaks represent the protons 1 - 7 in the chemical structure of GMA as shown in **Figure 3**. Moreover, from the ^{1}H-NMR spectrum of GMA, it can be observed that the chemical shifts of all peaks, which are associated with the GMA constitutional unit of proton CH, CH_2 and CH_3, are different from those in the spectrum of PLA-g-GMA. This observation demonstrates that the new multiplet belongs to GMA grafted onto the PLA chain (not

unreacted GMA). These results again confirmed that the GMA was successfully grafted onto the PLA chain. Similar results were also reported in another study [9].
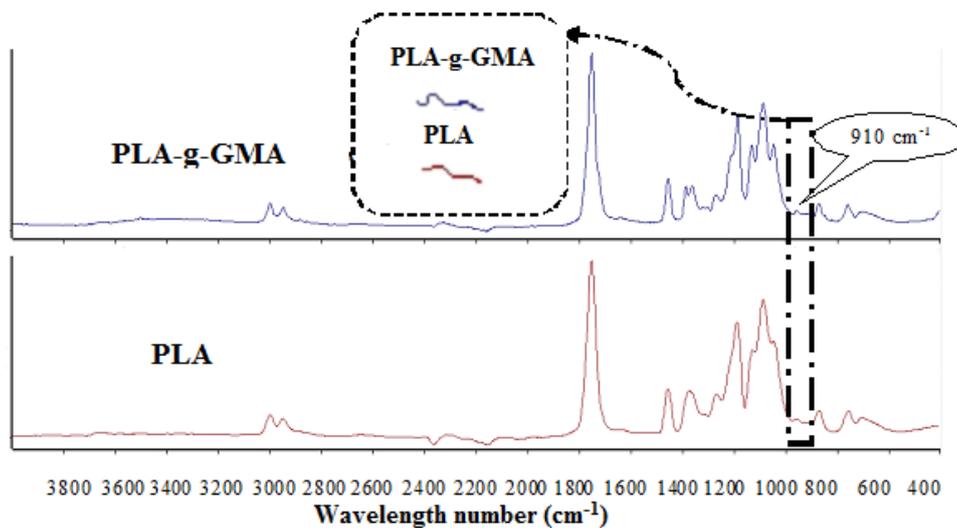

Figure 1 FTIR spectra of pure PLA and PLA-g-GMA with mixing time of 10 min.
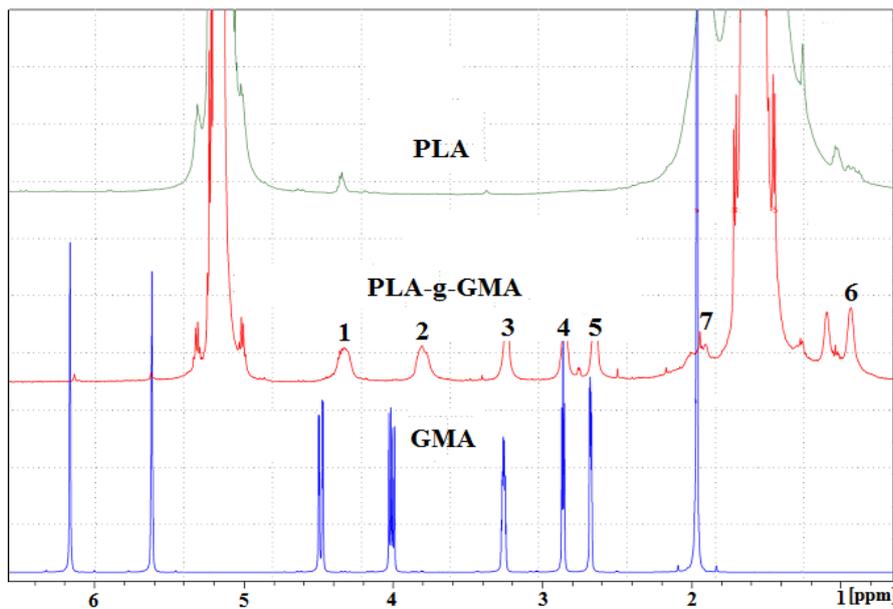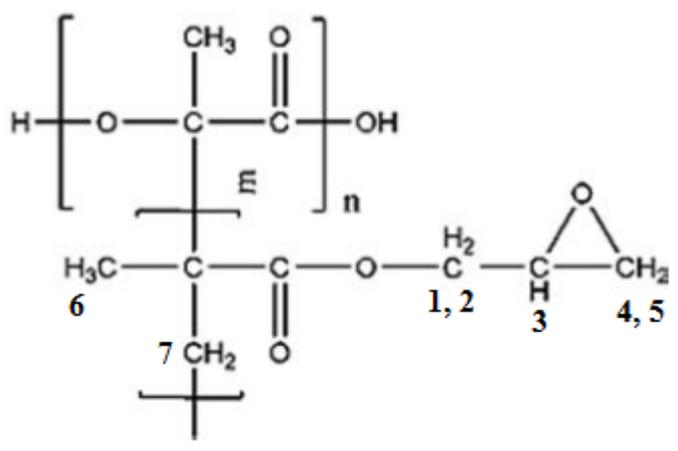

Figure 2 ^{1}H-NMR spectra of pure PLA, GMA and PLA-g-GMA at a mixing time of 10 min.

**Figure 3** The probable structure of PLA-g-GMA.

The effect of mixing time on grafting yield was determined by calculating the relative area of the characteristic peaks of GMA and PLA from the ^{1}H-NMR spectra. Calculated results are shown in **Table 1** and **Figure 4**. It indicates that the percentage of GMA grafted onto PLA chain increased from 1.123 to 1.379 % as the mixing time increased from 7 to 10 min. However, further increases in the mixing time to 14 min, led to a decrease from 1.379 to 1.128 %. The reason for this decrease may be attributed to depolymerization of GMA which takes place if the mixing time is too long.

Table 1 The relative area of characteristic peaks of GMA and PLA calculated from ^{1}H-NMR spectra of PLA-g-GMA at different mixing times.

Samples	Relative area	
	Characteristic peak of PLA	**Characteristic peak of GMA**
PLA-g-GMA7min	4.275	0.048
PLA-g-GMA10min	4.279	0.059
PLA-g-GMA14min	4.345	0.049

The effect of mixing time on the mechanical properties of PLA-g-GMA is shown in **Figure 5** and **Figure 6**. From **Figure 5**, PLA-g-GMA showed ductile fracture with necking and cold drawing in the stress-strain curve. In contrast, brittle fracture of pure PLA was demonstrated. The elongation at break of PLA-g-GMA was considerably higher than that of PLA. From this result, it can be thought that a re-orientation of the molecular chain of PLA-g-GMA can occur under tensile force. This phenomenon did not occur in the case of pure PLA, which indicates a difference in crystallization behavior between pure PLA and PLA-g-GMA under applied tensile force. However, the tensile strength at break of PLA-g-GMA decreased significantly compared to that of pure PLA. This decrease is attributed to the decrease of crystallinity of PLA after grafting. Moreover, **Figure 5** also shows that elongation at break of PLA-g-GMA increased slightly with an increase in mixing time from 7 to 10 min. This is due to the increase of GMA grafting yield as the mixing time increases from 7 to 10 min as observed in **Figure 4**. On the other hand, it decreased significantly when the mixing time reached 14 min. It has been known that PLA is highly sensitive to heat, therefore, if the mixing time was too long, degradation of the PLA chain can

occur easily. Furthermore, the GMA grafting yield had a tendency to drop at certain mixing time as observed in **Figure 4** and where GMA was grafted onto HDPE [4].
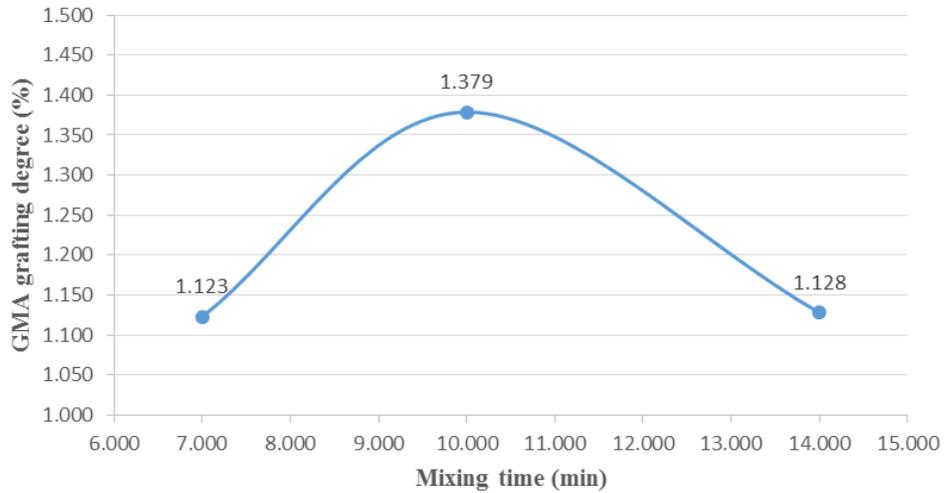
Figure 4 Effect of mixing time on GMA grafting yield.
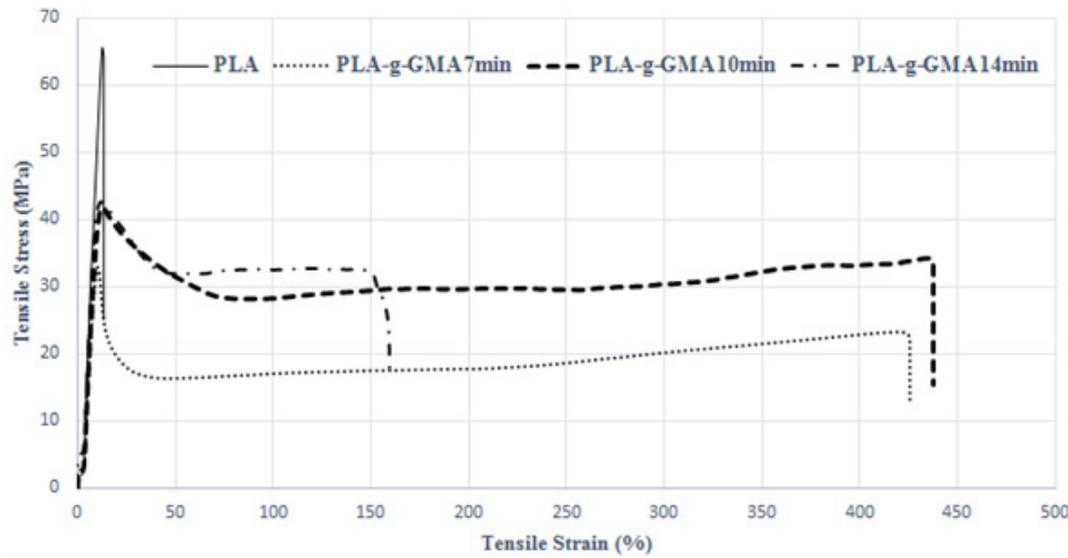
Figure 5 Stress-strain curves of pure PLA and PLA-g-GMA at different mixing times.

Figure 6 demonstrates that the impact strength of PLA-g-GMA was considerably higher than that of pure PLA. However, it was not significantly influenced by the mixing time. The impact strength of PLA-g-GMA increased slightly as mixing time increased from 7 to 10 min. Conversely, it decreased as mixing time increased from 10 to 14 min. This decrease is due to the decrease of GMA grafting yield and

degradation of the PLA chain as the mixing time became too long. The results above indicate that a mixing time of 10 min was optimal for the elongation at break and impact strength of PLA-g-GMA.
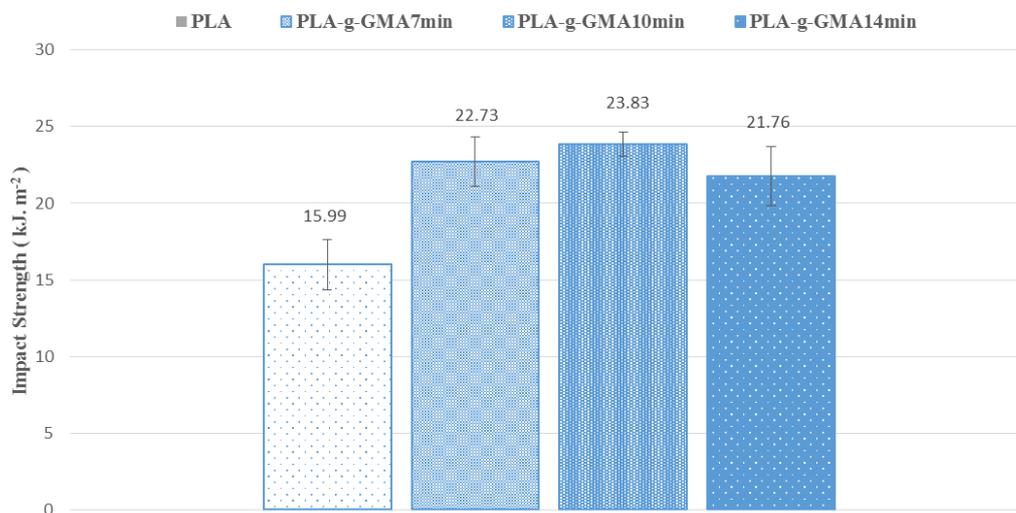

Figure 6 Effect of mixing time on impact strength of PLA-g-GMA.

DSC thermograms during cooling and heating of PLA and PLA-g-GMA with different mixing times are shown in **Figure 7** and **Figure 8**, respectively. As observed from the cooling scan (**Figure 7**) pure PLA and PLA-g-GMA7min did not show crystallization from melt upon cooling. PLA-g-GMA10min and PLA-g-GMA14min samples, however, underwent melt crystallization upon cooling. This indicates a difference in crystallization behavior between pure PLA and PLA-g-GMA as the mixing time was long enough so that the grafting reaction could take place effectively.

As seen in the heating scan (**Figure 8**) pure PLA and PLA-g-GMA7min present strong cold crystallization peaks upon heating. Meanwhile, PLA-g-GMA10min and PLA-g-GMA14min showed very weak cold crystallization peaks. The reason for this difference is due to the fact that PLA and PLA-g-GMA7min did not undergo melt crystallization under cooling (**Figure 7**). Therefore, the reorientation of their chain can occur easily upon heating. Conversely, the packed crystals of PLA-g-GMA10min and PLA-g-GMA14min, which were generated under cooling could not rearrange upon heating. As a result, very weak cold crystallization peaks were observed with respect to PLA-g-GMA10min and PLA-g-GMA14min samples.

Moreover, the double melting peak located at lower and higher temperature was observed in **Figure 8** for pure PLA, which related to less organized crystals and well-organized crystals, respectively [10]. The lower temperature peak (T_{m1}) is attributed to melting of the primary crystals formed upon cooling from the melt, and the higher one (T_{m2}) which corresponds to the melting of the crystals generated from recrystallization upon heating [11]. Besides that, **Figure 8** also shows that the melting temperature of PLA-g-GMA was lower than that of pure PLA. This implied that the crystals formed upon cooling from the melt of PLA-g-GMA are thermally less stable than those of pure PLA, which were almost formed from recrystallization upon heating [12]. In addition, as can be seen clearly from **Figure 8** the melting temperature of PLA-g-GMA did not change considerably with respect to the increase of mixing time from 7 to 14 min. The values of enthalpy of crystallization (ΔH_c), enthalpy of cold crystallization (ΔH_{cc}), enthalpy of melting (ΔH_m), crystallization temperature (T_c), cold crystallization temperature (T_{cc}), melting temperatures (T_{m1} and T_{m2}) and degree of crystallinity ($\%X_c$) of pure PLA and PLA-g-GMA at various

mixing times are shown in **Table 2**. The degree of crystallinity of PLA-g-GMA did not change significantly with respect to mixing time.
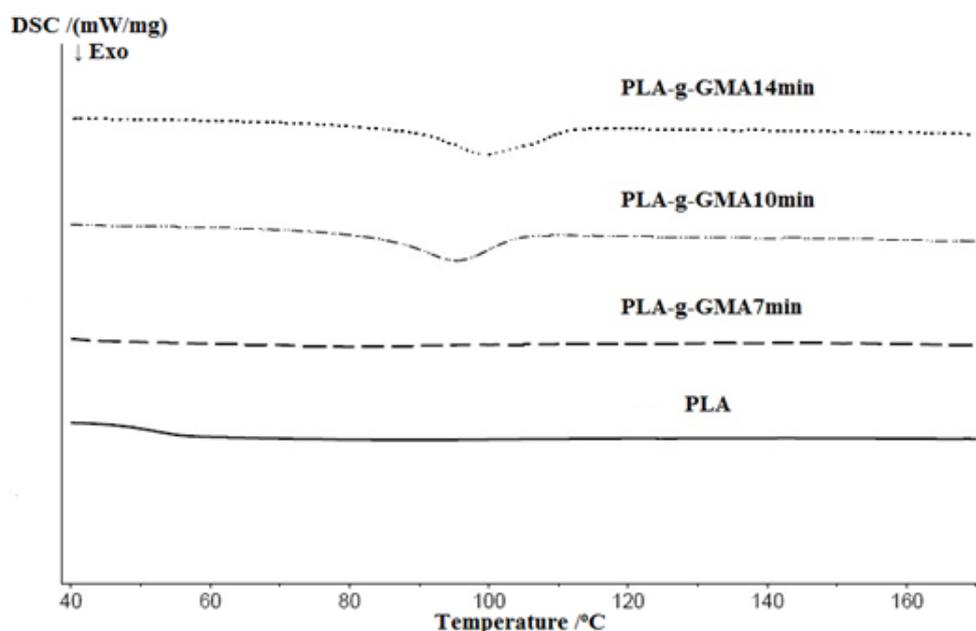
Figure 7 DSC thermograms of PLA and PLA-g-GMA at various mixing times (cooling scan).

Table 2 Thermal properties of PLA and PLA-g-GMA at different mixing times.

Samples	Thermal properties							
	T_c (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_c (J/g)	ΔH_{cc} (J/g)	ΔH_m (J/g)	$\%X_c$ (%)
PLA	-	100.2	145.3	155.5	0.00	29.80	31.23	33.33
PLA-g-GMA7min	-	86.3	135.2	148.2	0.00	21.50	24.52	26.17
PLA-g-GMA10min	95.3	87.3	139.4	148.3	13.26	7.34	22.96	24.50
PLA-g-GMA14min	99.5	84.9	139.6	147.9	14.38	5.38	23.88	25.49
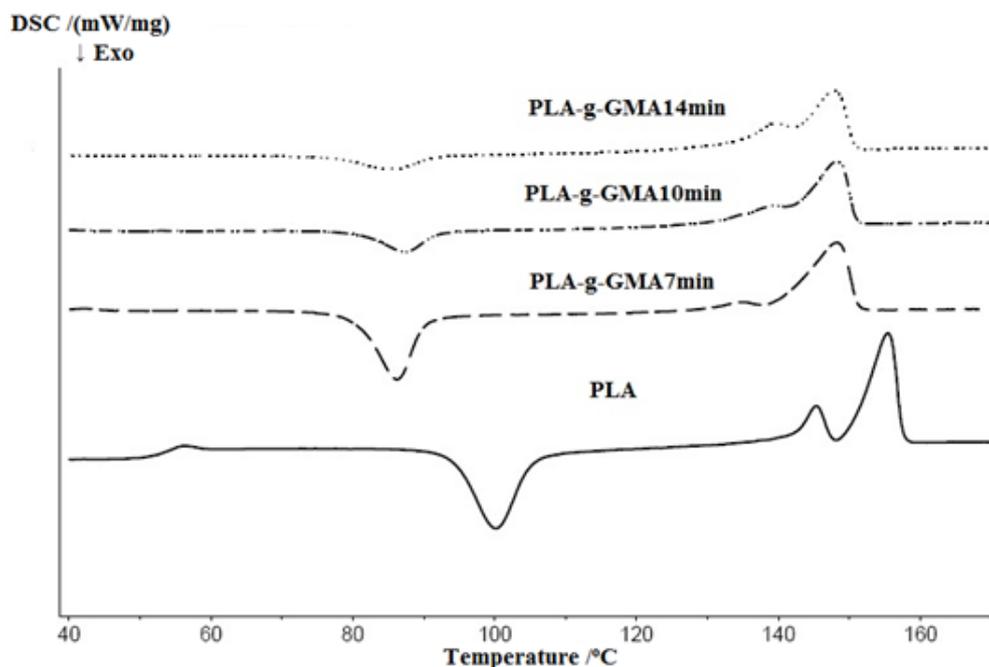
Figure 8 DSC thermograms of PLA and PLA-g-GMA at various mixing times (second heating scan).

Conclusions

FTIR and ^{1}H-NMR analyses demonstrate that glycidyl methacrylate can be successfully grafted onto poly(lactic acid) in an internal mixer using dicumyl peroxide as an initiator. The mechanical properties and thermal properties of PLA-g-GMA were found to be considerably different from those of pure PLA. It changed from brittle PLA to ductile PLA-g-GMA. The elongation at break and impact strength of PLA-g-GMA were significantly higher than those of pure PLA. Moreover, it was also found that GMA grafting yield, mechanical properties and crystallization behavior of PLA-g-GMA were affected by melt mixing time. The optimal grafting yield, elongation at break and impact strength of PLA-g-GMA was achieved at a mixing time of 10 min.

Acknowledgements

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