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Melt Free-Radical Grafting of Maleic Anhydride onto Biodegradable Poly(lactic acid) by Using Styrene as a Comonomer

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Abstract: Maleic anhydride (MA) was grafted onto poly(lactic acid) (PLA) in the presence of styrene (St) by using a free-radical grafting methodology. The grafting degree (D_g) of MA was increased from 0.65 wt % to 1.1 wt % with the St/MA ratio up to 2/1, where the grafting efficiency (E_g) of MA was 27%. However, both D_g and E_g were decreased with further increasing of the St/MA ratio to 4/1. The D_g of MA increased with MA concentration and showed a maximum at 180 °C in the temperature range of 165 °C–190 °C. The grafting mechanisms of MA in the presence of St are analyzed based on titration, thermogravimetric analysis and infrared results, *i.e.*, MA is grafted onto PLA chains via single monomers and a charge-transfer-complex (CTC) at St/MA ratios of $\leq 1/1$, while dominantly via St-*co*-MA oligomers at St/MA ratios of around 2/1. Copolymerization rather than grafting of St and MA occurs at St/MA ratios of around 4/1. The thermal stability of PLA was compromised to a certain extent by the grafting of MA, resulting in reductions in the decomposition temperature ($T_{d-5\%}$) and molecular weight of the PLA. In addition, the crystallization and melting temperatures of the PLA were slightly reduced after the grafting.

Keywords: biodegradable polymers; grafting; maleic anhydride; styrene; thermal properties

1. Introduction

Bio-based and biocompostable materials have received considerable attention because of the environmental concerns and the sustainability issues associated with petroleum-based polymers [1]. Poly(lactic acid) (PLA) is both bio-based and biocompostable, and several favorable properties such as high strength and stiffness at room temperature, make it the most promising as a substitute for conventional petroleum-based polymers [2]. However, some limitations, notably low heat distortion temperature, brittleness and relatively high prices restrict its application [3,4].

Property improvement and cost reduction of PLA can be obtained by making PLA-based blends. If blended with natural materials the renewability and/or biocompostability can be retained [5]. PLA is hydrophobic polyester whereas natural materials, such as celluloses, starch, protein, lignin and inorganic fillers, are generally hydrophilic. Consequently, blends of PLA with natural additives usually exhibit coarse morphology and poor mechanical performances, due to the lack of affinity [5–7]. The affinity can be improved by using a compatibilizer or by the functionalization of PLA chains such as grafting.

Maleic anhydride (MA) [5,7], amide [8], glycidyl methacrylate [9], *N*-vinyl pyrrolidone [10], PEG [11] and chitosan [12] were grafted onto PLA. MA is popular among these grafting pendants due to its difficulty in homopolymerization and the benefit of cell attachment and proliferation [13]. MA was grafted onto PLA by the melt free-radical grafting method with a maximum grafting degree (D_g) of 0.52 wt % [14]. Wu [15] grafted MA onto PLA chains via the solvent free-radical grafting method and the maleated PLA was subsequently used to make PLA-g-MA/green coconut fiber (GCF) blends. The resulting materials showed much better mechanical properties and biodegradation behavior than the normal PLA/GCF blends. These results were ascribed to ester formation between PLA and GCF via the grafted MA, leading to a strong increase in compatibility. Electrospun fibrous bio-nanocomposite scaffolds reinforced with cellulose nanocrystals (CNCs) were fabricated by using MA grafted PLA as a matrix. The interfacial adhesion between the CNC and PLA was improved by the graft of MA, leading to superior tensile strength [16]. PLA-g-MA was also widely used as a compatibilizer in the compounding of PLA and hydrophilic polymer/additives such as starch [5–7], cellulose nano-whiskers (CNWs), clay [17] and protein [18], to improve the performances of their blends.

Apparently grafting of MA onto PLA is promising for the modification of PLA. However, the D_g of MA on the PLA is usually low, e.g., lower than 0.52 wt % [14]. Furthermore, the D_g and the grafting parameters were not systematically reported in some literatures. Therefore, it would be of interest to develop an eco-friendly route to achieve a high D_g for MA on the PLA.

To obtain a high D_g , it is essential that the macroradicals react with the MA monomers before undergoing side reactions, e.g., recombination and chain scission [19]. The low D_g of MA results from the poor activity of MA toward macroradicals, which is inherently due to its structural symmetry and low electron density around the $-\text{CH}=\text{CH}-$ bonds. An effective way to promote the activity of MA is by the addition of co-monomer(s). The co-monomer(s) generally have higher activity toward both of the macroradicals and the MA monomer. An example is the grafting of MA on poly(butylene succinate-*co*-adipate) being promoted by the addition of cinnamic co-agents [20].

Styrene (St) with an electro-donating feature can easily interact/react with the electron-attracting monomers (*i.e.*, MA) via a charge transfer complex (CTC) or copolymerization [21]. The St could activate MA, leading to an unsymmetrical structure and Π bonds of radical-anion. As a result, the gap

between macroradicals and MA monomers could be bridged by St, resulting in higher D_g of MA on polyolefins [21–23]. Although considerable work has been devoted to polyolefin-g-MA/St systems rather less attention has been paid to St-assisted free-radical grafting of MA onto polyesters. It was reported in a recent study that the D_g of MA on poly(hydroxybutyrate) was increased from 0.24 wt % to 0.83 wt % by the assistance of St co-monomer [24]. In another study, MA was grafted onto PLA in the presence of St (MA/St = 2/1) and the resulting PLA-g-MA/St was used as a compatibilizer in PLA/soy protein blends. The D_g of MA was increased from 0.25 wt % to 0.90 wt % by the addition of St, however, the grafting process and the grafting mechanism was not reported in detail.

The prime objective of this work is to provide a systematic investigation of the grafting of MA onto PLA chains by using styrene as the co-monomer. This method would enable the creation of PLA with high functionality and could possibly broaden its application range. A deep insight into the styrene-assisted grafting mechanism in the PLA/MA/St/dicumyl peroxide (DCP) systems is revealed based on the relationship of grafting degree and product structures. In addition, the effect of grafting on the thermal properties of PLA is investigated as well.

2. Experimental Section

2.1. Materials

PLA was provided by Zhejiang Hisun Biomaterials Co., Ltd., Taizhou, China, with a melt flow index of 3–4 g·10 min^{−1} (190 °C × 2.16 Kg). The content of L-lactide is approximately 99.3%. Its molar mass was measured based on viscosity in chloroform at 25 °C and yielded $M_\eta = 110$ KDa, according to the equation $[\eta] = K \times M_\eta^\alpha$ ($K = 2.48 \times 10^{-4}$, $\alpha = 0.77$ [25]), where $[\eta]$ is the intrinsic viscosity. Maleic anhydride (MA) and styrene (St) were supplied by Fluka and Aldrich respectively. The MA was first dried at 180 °C for 2 h and then recrystallized from acetone before use. Dicumyl peroxide (purity ≥ 99.5%) with a half-life time of 1 min at 171 °C was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The styrene and DCP were used as received.

2.2. Sample Preparation

PLA was dried in a vacuum oven at 50 °C for 12 h before use. The MA, St and DCP were first dissolved in a small amount of acetone and then sprayed onto the surface of PLA pellets to obtain a uniform distribution of the chemicals in the mixtures. After complete evaporation of acetone the mixtures were fed into a twin-screw mini-extruder where the grafting reactions occurred. The mixtures were processed at 160 °C–190 °C and at a fixed screw speed of 35 rpm. The recipes and grafting temperatures are shown in Table 1. For comparison, neat PLA was also processed under the same conditions.

2.3. Purification

Around 1.5 g of each sample was refluxed in 25 mL chloroform for 1 h, and the samples were precipitated in 250 mL acetone. The precipitates were filtrated and washed twice with fresh acetone and then dried in a vacuum oven at 70 °C for 12 h. The purified samples were used for further characterizations.

Table 1. Formulation and grafting temperature of the poly(lactic acid) (PLA)/maleic anhydride (MA)/styrene (St)/dicumyl peroxide (DCP) systems.

Samples Code	Formulation				Grafting Temperature °C
	PLA	MA	St	DCP	
1	100	0	0	0	180
2	100	4.50	0.00	0.50	180
3	100	4.50	2.25	0.50	180
4	100	4.50	4.50	0.50	180
5	100	4.50	9.00	0.50	180
6	100	4.50	18.00	0.50	180
7	100	4.50	9.00	0.50	165
8	100	4.50	9.00	0.50	170
9	100	4.50	9.00	0.50	190
10	100	1.50	3.00	0.17	180
11	100	3.00	6.00	0.33	180
12	100	6.00	12.00	0.67	180

Note: the formulation in Table 1 is expressed by weight parts.

The intermediate products were obtained via selective precipitation, *i.e.*, (1) the acetone filtrates obtained from the above purification process were concentrated, which contains the MA and St residues, low molecular weight PLA portions and MA-St copolymers; (2) the concentrated acetone filtrates were precipitated in excess methanol. The precipitates (*i.e.*, intermediate products) were finally collected by centrifugation (10,000 rpm for 10 min) and dried at 70 °C for 12 h.

2.4. Characterizations

2.4.1. Fourier Transform Infrared Spectroscopy (FT-IR)

The intermediate products were dissolved in chloroform and cast to form thin films. All the films were analyzed on an FT-IR spectrometer (FTLA2000 spectrometer, ABB, Zurich, Switzerland) in transmission mode. The final spectrum of each sample was an average of 50 scans at a resolution of 4 cm^{−1}.

2.4.2. Titration

The grafting degrees (D_g) of MA were determined by titration. Each sample was weighted and completely dissolved in chloroform (approximately. 0.02 g·mL^{−1}) in a flask. The titration started with a standardized NaOH ethanol solution (0.06 mol·L^{−1}). The titration end was judged by using phenolphthalein as an indicator. The processed PLA was titrated first to determine the blank value (D_{g0}) via Equation (1):

$$D_{g0} = \frac{98.06 \times V_0 \times C_{\text{NaOH}}}{2000 \times m_0} \times 100\% \quad (1)$$

where V_0 is the titrant volume (mL), C_{NaOH} is the concentration of titrant (mol·L^{−1}), and m_0 is the weight of PLA (g).

The grafting degrees (D_g) of the MA on PLA chains were obtained via Equation (2):

$$D_g = \frac{98.06 \times V \times C_{\text{NaOH}}}{2000 \times m} \times 100\% / D_{g0} \quad (2)$$

where V is the titrant volume (mL), C_{NaOH} is the concentration of titrant ($\text{mol} \cdot \text{L}^{-1}$), m is the weight of grafted PLA (g).

The grafting efficiency (E_g) was then calculated via Equation (3):

$$E_g = \frac{m_2}{m_1} \times 100\% \quad (3)$$

where m_2 is the weight of grafted MA calculated via the grafting degree and m_1 is the weight of initially added MA.

2.4.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a TGA 1/1100SF (METTLER, Greifensee, Switzerland) to characterize the thermal stability of the PLA and maleated PLA. The samples were heated from 20 °C to 700 °C at 20 °C·min⁻¹ in a nitrogen atmosphere. The weight of the samples was recorded as a function of temperature.

2.4.4. Molar Mass Characterization

The molar mass of PLA and grafted PLA was measured based on viscosity in chloroform at 25 °C and yielded a viscosity average molecular weight (M_η) according to the Mark-Houwink equation $[\eta] = K \times M_\eta^\alpha$ ($K = 2.48 \times 10^{-4}$, $\alpha = 0.77$) [25], where $[\eta]$ is the intrinsic viscosity.

2.4.5. Differential Scanning Calorimetry (DSC)

The thermal properties of maleated PLA were studied by using a DSC 8000 calorimeter (PerkinElmer, Inc., Waltham, MA, USA). The samples were first heated to 190 °C and equilibrated for 3 min to erase the thermal history, then cooled to 0 °C and reheated to 190 °C at 10 °C·min⁻¹. The cooling and re-heating DSC curves were recorded to study the thermal behavior of the samples. The crystallinity (X_c) of PLA was calculated based on the crystallization enthalpy via Equation (4):

$$X_c = \frac{\Delta H_c}{\Delta H_0} \times 100\% \quad (4)$$

where ΔH_0 is the fusion enthalpy of 100% crystalline PLA (93 J·g⁻¹) [26], ΔH_c is the measured crystallization enthalpy of the samples, and W is the weight percentage of PLA in the samples.

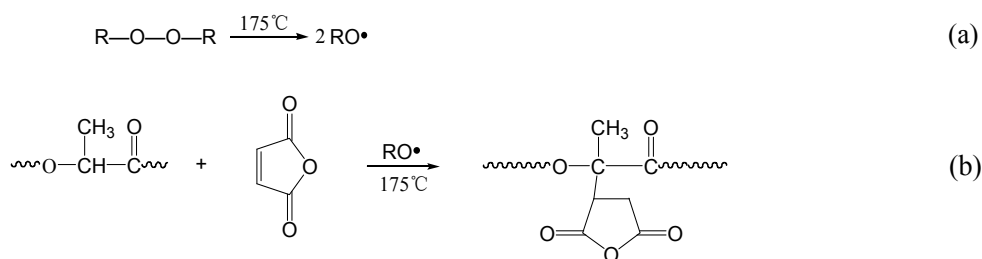
3. Results and Discussion

3.1. Analysis on PLA Grafting MA System

The first step of grafting is the formation of primary radicals (RO•) via the decomposition of dicumyl peroxide (DCP), which then initiates macroradicals (PLA•) by a hydrogen abstraction mechanism [5]. The macroradicals subsequently react with maleic anhydride (MA), resulting in

PLA-g-MA. The grafting reactions are schematically shown in Scheme 1. However, the grafting reaction is not so active, because of the low reactivity of MA toward macroradicals. The low reactivity is ascribed to its structural symmetry and low electron density around the $-\text{CH}=\text{CH}-$ bond [21–23]. As a result, styrene was used as a co-monomer in this study to enhance the grafting degree of MA. The mechanism of St-assisted free radical grafting of MA onto PLA will be discussed below.

Scheme 1. Proposed grafting reactions of MA onto PLA chains in the presence of dicumyl peroxide (R represents C_9H_{11}). Some possible side reactions such as combination or chain scission are not shown here.



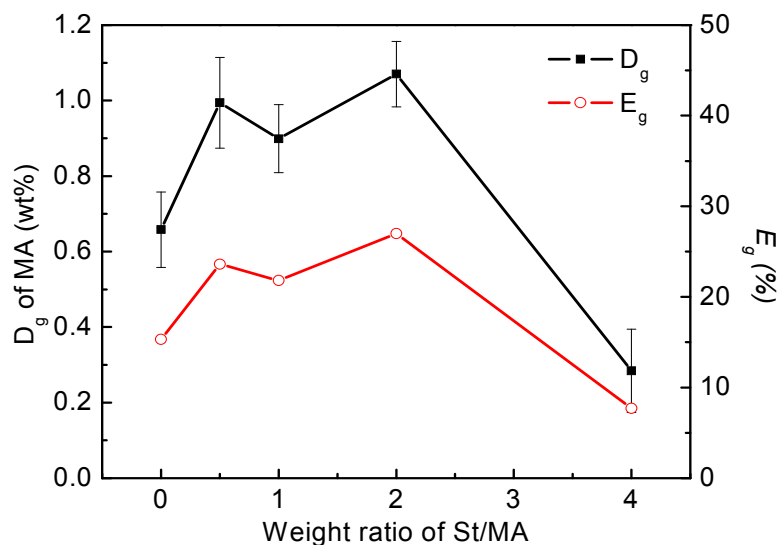
FT-IR is an effective technique to analyze the structures of maleated polyolefins. However, the MA on PLA-g-MA was not clearly detected by FT-IR because of: (1) the overlap of the characteristic absorption peaks of MA (1780 cm^{-1} and 1850 cm^{-1} corresponding to the symmetric and asymmetric stretching of carbonyl groups of cyclic MA respectively [21,24]) and the strong absorption peak of PLA (around 1756 cm^{-1} corresponding to the carbonyl groups); and (2) the relatively low grafting degree (D_g) of MA. The FT-IR spectra of PLA and maleated PLA in the range of $1700\text{--}1900\text{ cm}^{-1}$ were provided as supporting data (Figure S1). Therefore, the titration methodology was used to determine the D_g of MA.

3.2. Grafting Degree and Grafting Efficiency of MA on PLA Chains

The grafting degree (D_g) and grafting efficiency (E_g) of MA on polymer chains are associated with chain structures, recipe parameters and processing conditions [27,28]. In this paper, the D_g and E_g of MA on the PLA chains are investigated as a function of the styrene/MA ratio, MA concentration and processing temperature.

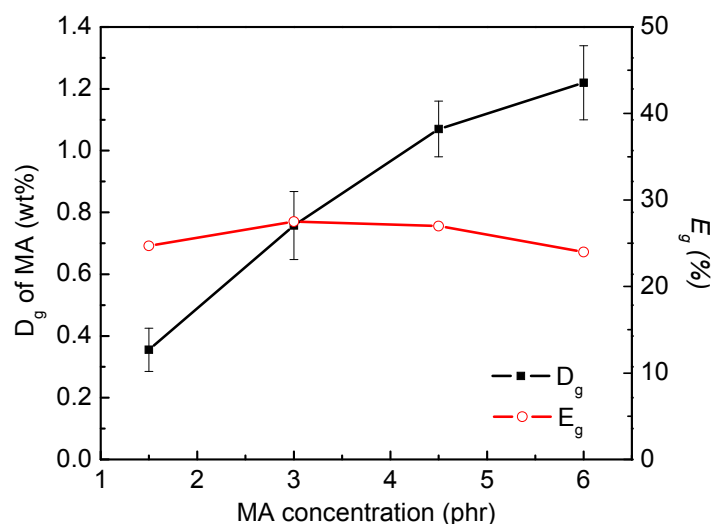
The effect of St on the D_g and E_g of MA is shown in Figure 1. The D_g in the absence of St is 0.65 wt %, which is increased to 1.1 wt % with a St/MA ratio up to 2/1 and then dramatically reduced at a St/MA ratio of 4/1. It was reported in polyolefin systems that co-monomer would be beneficial for enhancing the D_g of MA if the co-monomer reacts with macroradicals more rapidly than the monomer and the resulting macroradicals are capable of copolymerizing with the grafting monomer. However, the optimal St/MA ratio for D_g in the poly(propylene) system was reported to be 1/1 [21,23]. In St-assisted melt grafting of MA onto the poly(hydroxybutyrate) (PHB) system, the highest D_g of MA was achieved at the St/MA ratio of 2/1 [24]. Apparently, the St-assisted grafting mechanism of MA in the polyester system (e.g., PLA) is different from that in the polyolefin system. Moreover, the trend of D_g of the MA on PLA is different from that on PHB as a function of the St/MA ratio, indicating a varied grafting mechanism between the PLA and PHB as well. The E_g shows a similar trend as the D_g , since MA concentration is constant in this part.

Figure 1. The grafting degree (D_g) and efficiency (E_g) of maleic anhydride on PLA chains as a function of the St/MA ratio. The MA and DCP are fixed at 4.5 and 0.5 phr, respectively.



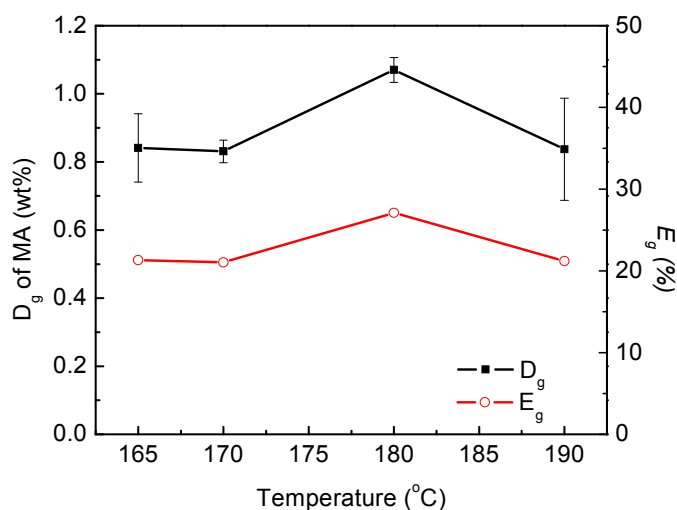
A St/MA ratio of 2/1 was applied for other formulations since it gave the highest D_g . Figure 2 shows the effect of MA concentration on its D_g and E_g . The D_g increases from 0.35 wt % up to 1.2 wt % with the increasing of the MA concentration from 0.5 to 6.0 phr. The grafting mechanism is dominated by the St/MA ratio, thus it is not changed with varying the MA concentration, due to the fixed St/MA/DCP ratio. Consequently, the D_g is mainly associated with the total amount of reactive species and MA concentrations, *i.e.*, the possibility of a combination between macroradicals and MA monomers. The total amount of reactive species is proportional to the DCP content, *i.e.*, proportional to the MA concentration here due to the fixed MA/DCP ratio. Hence, a linear relationship between the D_g and MA concentration is observed. It is also found that the E_g fluctuates slightly around 25% with the MA concentration.

Figure 2. Grafting degree (D_g) and efficiency (E_g) of maleic anhydride on PLA chains as a function of maleic anhydride concentration. The St/MA/DCP ratio is fixed at 2/1/0.1.



Temperature is important in the grafting reactions because the initiator (DCP) cannot be decomposed completely in a short time span if the temperature is too low. On the other hand, the radicals would be initiated too fast and inefficiently consumed if the temperature is too high. The D_g and E_g of MA were studied as a function of processing temperature, as shown in Figure 3. As expected, the D_g and E_g of MA are first increased with temperature and then decreased. The highest D_g and E_g are obtained at 180 °C. Thus the optimal grafting temperature for PLA-g-MA system is determined as 180 °C.

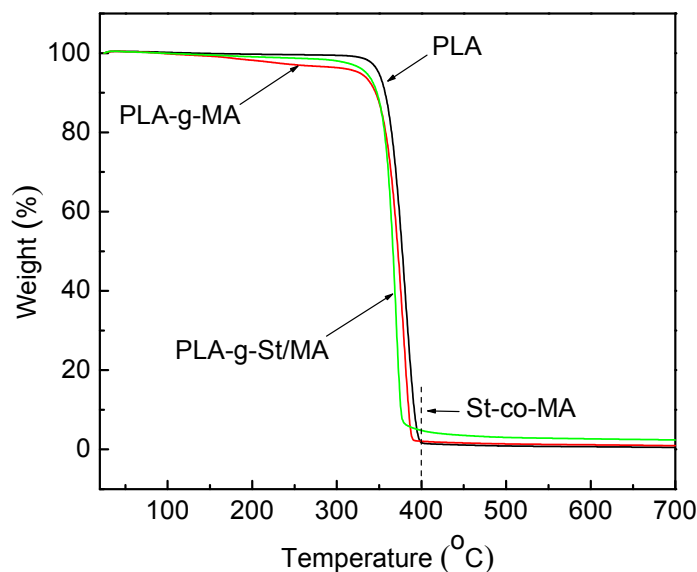
Figure 3. Grafting degree (D_g) and efficiency (E_g) of maleic anhydride on PLA chains as a function of grafting temperature. The MA and the St/MA/DCP ratio are fixed at 4.5 phr and 2/1/0.1, respectively.



3.3. Thermogravimetric Analysis of Maleated PLA

The thermal decomposition of PLA and maleated PLA was studied as a function of temperature, as shown in Figure 4. PLA is thermally instable with a decomposition temperature ($T_{d-5\%}$) of 350 °C. The thermal degradation of PLA is mainly associated with the hydrolysis of the ester groups and accelerated by the end groups ($-\text{COOH}$) [29]. The $T_{d-5\%}$ of PLA was reduced by 27 °C after grafting with 0.65 wt % MA, indicating that the presence of anhydride (MA) is not beneficial to the thermal stability of PLA. These results are different from PHB grafting MA systems where the decomposition temperature of PHB was greatly improved by grafting MA. The differences should result from different degradation mechanism between the two polymers [24,29,30]. In addition, the styrene monomer did not improve the thermal decomposition behavior of the PLA. Both PLA and PLA-g-MA are almost decomposed at 400 °C (2 wt % residue), while around 5 wt % of the PLA-g-St/MA was retained at this temperature, which corresponds to the grafted St-co-MA side chains [24]. Taking the grafting degree of MA (1 wt %) into account, the grafting degree of St can be roughly calculated to be 2 wt % for Sample #5.

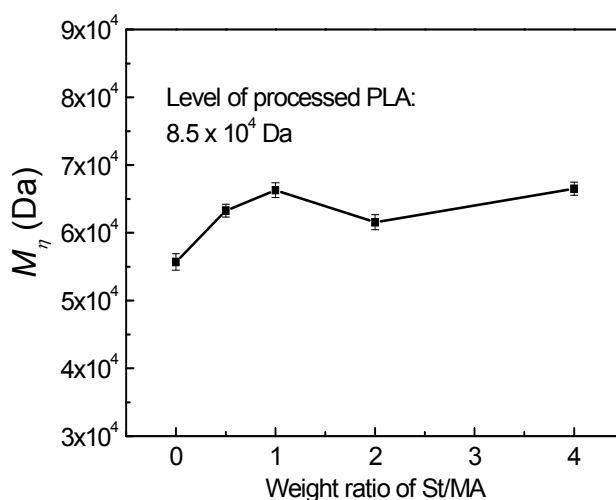
Figure 4. TGA curves of the purified samples as a function of temperature: (a) neat PLA-; (b) PLA-g-MA and (c) PLA-g-St/MA corresponding to Samples 1, 2 and 5 in Table 1, respectively.



3.4. Influence of Grafting on the Molecular Weight of PLA

The average molecular weight of the PLA and maleated PLA was measured by using an Ubbelodhe viscometer based on the viscosity in chloroform (25 °C). The yielded viscosity average molecular weight (M_η) according to the Mark-Houwink equation, $[\eta] = K \times M_\eta^\alpha$ ($K = 2.48 \times 10^{-4}$, $\alpha = 0.77$) [25] is shown in Figure 5, where $[\eta]$ is the intrinsic viscosity.

Figure 5. Viscosity average molecular weight (M_η) of the neat PLA and the maleated PLA samples as a function of the St/MA ratio.



The degradation of PLA is generally ascribed to the hydrolysis of ester bonds in the presence of an even ppm level of water. The M_η of the PLA raw material is around 110 kDa, which was decreased to 85 kDa after processing. Moreover, the M_η of PLA was decreased further after grafting with MA which might be due to the following: (1) the anhydride facilitates the hydrolysis of PLA and/or (2) the

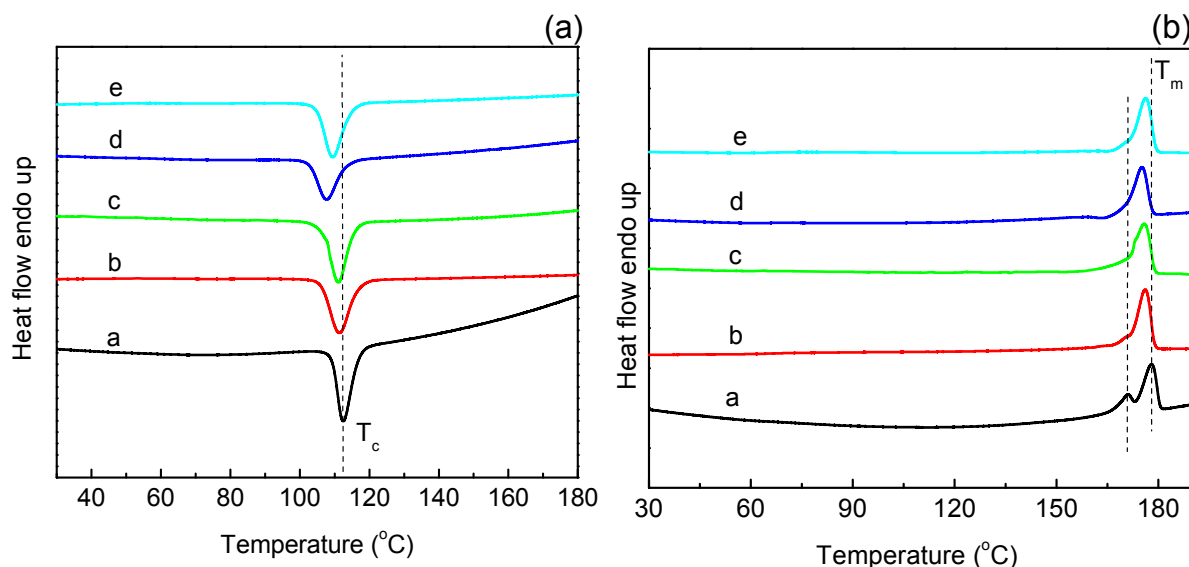
PLA macroradicals initiated by DCP are not so stable. Interestingly, the M_n of PLA was increased after the addition of St as a co-monomer. It was found in a previous study that PP macroradicals could be stabilized by the addition of St co-monomers, reducing the possibility of chain scission [21–23]. This might be also a reason for the improved thermal stability of the PLA in the PLA-g-St/MA system.

3.5. Crystallization and Melting Behavior of PLA and Maleated PLA

The crystallization and melting behavior of the maleated PLA is studied by using DSC, as shown in Figure 6a,b, respectively. The corresponding thermal parameters such as crystallization peak temperature (T_c), crystallization starting temperature (T_{onset}), crystallinity (X_c) and melting temperatures (T_m) are summarized in Table 2.

The PLA chain consists of short and rigid segments, leading to low crystallization rate. The crystallization is also strongly affected by the optical purity, e.g., poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) are semi-crystalline polyesters while poly(D,L-lactic acid) (PDLLA) can be completely amorphous. In this study, all of the samples exhibited notable crystallization peaks during cooling, as shown in Figure 6a, which is due to the high optical purity (99.3% of L-lactide). The neat PLA shows T_{onset} and T_c at 117 °C and 113 °C, respectively. The T_{onset} and T_c are decreased after grafting with MA or St/MA. These results indicate that the crystallization of PLA was restricted to a certain extent, probably due to the steric hindrance of the grafted pendants. Consequently, the lowest T_{onset} and T_c were observed at a St/MA ratio of 2/1, where the highest D_g was obtained.

Figure 6. (a) DSC cooling curves and (b) DSC sencond heating curves of the purified samples: **a**, neat PLA and **b–e**, PLA-g-MA/St samples with St/MA ratios of 0/1, 1/1, 2/1 and 4/1 respectively. The MA and DCP content is fixed at 4.5 and 0.5 phr, respectively. The scanning rate is fixed at 10 °C·min^{−1}.



The double melting-peak phenomenon of the PLA sample (Figure 6b) is observed, which is usual for polyesters and can be explained by a melt/crystallization/re-melt mechanism [31,32]. It indicates that PLA contains crystals with different perfections. The neat PLA chains without grafting pendants have higher mobility and a high T_c . Thus, crystals of neat PLA have better organization and larger

lamellar thickness, thus a higher T_m . The presence of St and the St/MA ratio have only a little influence on the melting behavior of the grafted PLA.

Table 2. Thermal parameters of the neat and maleated PLA samples.

Samples	St/MA ¹ (wt/wt)	Crystallization Process		Melt Process	
		T_{onset} °C	T_c °C	X_c %	T_{m1} °C
PLA ²	-	117	113	30	178
	0/1	117	111	32	176
Maleated PLA	1/1	116	111	31	175
	2/1	112	107	26	175
	4/1	114	109	28	176

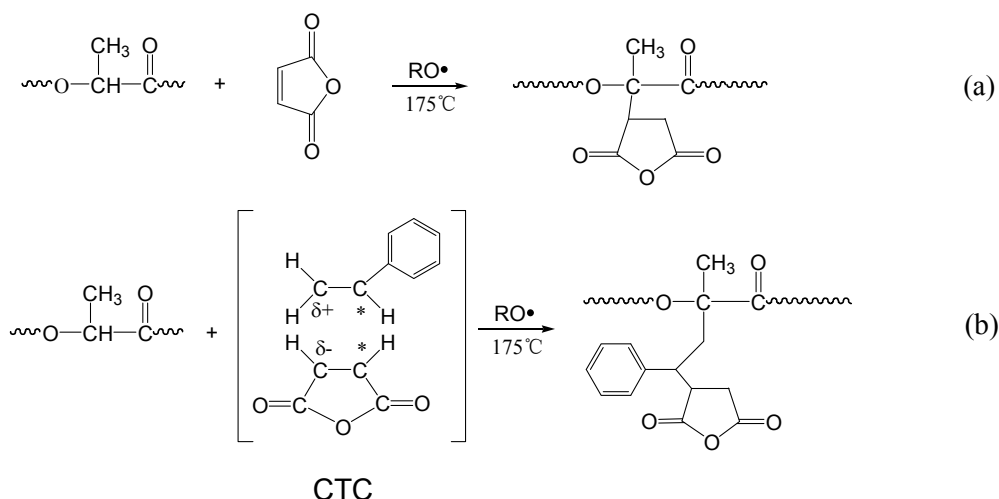
Notes: 1. the weight ratio of St to MA in the initial PLA/MA/St/DCP mixtures; 2. underwent the same processing conditions as maleated PLA; T_{onset} is the starting crystallization temperature; T_c represents the crystallization peak temperature; X_c represents the crystallinity of PLA as calculated via Equation (1); T_m represents the melting peak temperature.

3.6. Grafting Mechanism of MA onto PLA in the Presence of Styrene

The first step of grafting is the formation of primary radicals (RO•) via the decomposition of DCP, which then initiate macroradicals (PLA•) by hydrogen abstraction [5]. The macroradicals then either react with grafting monomers or undergo side reactions (e.g., combination or chain scission). Most PLA macroradicals would be consumed prior to the reaction with MA, due to the inert feature of MA toward macroradicals, thus a relatively low D_g . Styrene as a co-monomer in grafting originated from the analysis of poly(propylene) (PP) grafting glycidyl methacrylate (GMA) systems [19,22,23]. St preferentially reacts with PP macroradicals, forming stable styryl macroradicals (*i.e.*, PP-St•) which subsequently copolymerize readily with GMA, leading to an increase in grafting degree. St can interact with MA forming a charge transfer complex (CTC) which enhances the electric asymmetry on the $-\text{CH}=\text{CH}-$ bond of MA, thus a higher reactivity and a higher D_g . On the other hand, MA may copolymerize with St into oligomer-radicals (St-co-MA•) in the presence of free radicals. The St-co-MA• could react with macroradicals (PLA•) by combination. Consequently, more than one MA can be grafted at one site of the PLA chains, leading to a notable increase in the D_g . However, too much St may result in (co-)polymerization of St and MA or the grafting of St rather than MA, leading to a reduction in D_g of the MA, as shown in Figure 1. Therefore, the St-assisted grafting mechanism of MA onto PLA depends on the St/MA ratio which is proposed according to experimental data. It has to be remarked that the weight ratio of St/MA is close to the molar ratio due to its very similar molar mass. (1) In the case of the St/MA ratio $< 1/1$: being only a part of MA forms CTC with St. The St-MA co-oligomer is seldom generated because of the low St concentration, as confirmed by TGA results (Figure 6). Consequently, MA was mainly grafted onto PLA in terms of single MA and CTC, as shown in Scheme 2a,b, respectively. The CTC concentration increases with the St/MA ratio and the reaction (b) is easier to occur than reaction (a), thus the D_g increases with the St/MA ratio up to 1/1. (2) In the case of $1/1 \leq \text{St/MA ratio} \leq 2/1$, in principle, all MA and St can form CTC when the molar ratio of St/MA equals 1/1. Consequently, the maximum D_g of MA was reported at an St/MA ratio of

1/1 in the PP-g-MA/St system [21,23]. However, the maximum D_g occurs at 2/1 in the PHB-g-MA/St system [24] and the studied PLA-g-MA/St system. Therefore, the grafting mechanisms are not only associated with the St/MA ratio, but also with the polymer chain structures.

Scheme 2. The main grafting reactions proposed at low St/MA ratios ($R = C_9H_{11}$). Some possible side reactions are not present here.



When the St/MA ratio is lower than 2/1, MA preferentially reacts with a part of St, forming CTC before grafting. The excess St could react with macroradicals (PLA•) generating relatively stable styryl macroradicals (PLA-g-St•) or copolymerize with MA forming short oligomer-radicals (St-co-MA•) in the presence of primary radicals (RO•). The PLA-g-St• could then react with CTC, MA or short St-co-MA• to form branching structures, *i.e.*, PLA-g-(St-co-MA•). The grafting of shot St-MA• (co-)oligomers onto PLA chains is proposed to be the dominating mechanism at an St/MA ratio of around 2/1, as shown in Scheme 3. It has to be remarked that the St-co-MA is a kind of random co-oligomer rather than a block co-oligomer, due to the uncontrollable feature of the free radical reactions. The proposed grafting mechanism is supported by the above TGA results (the residues of the maleated PLA at 400 °C). (3) In the case of the St/MA ratio $> 2/1$, polymerization of St and copolymerization of St/MA are the dominating reactions when the amount of St is in far excess, *e.g.*, St/MA = 4/1. Long oligomer-radicals (St-co-MA•) would be obtained in such a case. The long St-co-MA• could be terminated with free radicals such as St•, MA• or another St-co-MA•. Moreover, excess St consumes primary radicals and PLA macroradicals, as well, resulting in a decline in the total amount of grafting reactive species. Consequently, the D_g of MA is reduced (Figure 1), and St-co-MA copolymers are obtained, which are evidenced by infrared analysis (FT-IR, see Figure 7).

The intermediate products were obtained via selective precipitation as described in the experimental part. The FT-IR spectra of the intermediate products in the range of 1650–1900 cm^{-1} and 525–825 cm^{-1} are shown in Figure 7a,b, respectively.

Scheme 3. Main grafting reactions proposed at high St/MA ratios ($R = C_9H_{11}$). The St_n-MA_m represents random St-MA co-oligomers. Some possible side reactions are not present here.

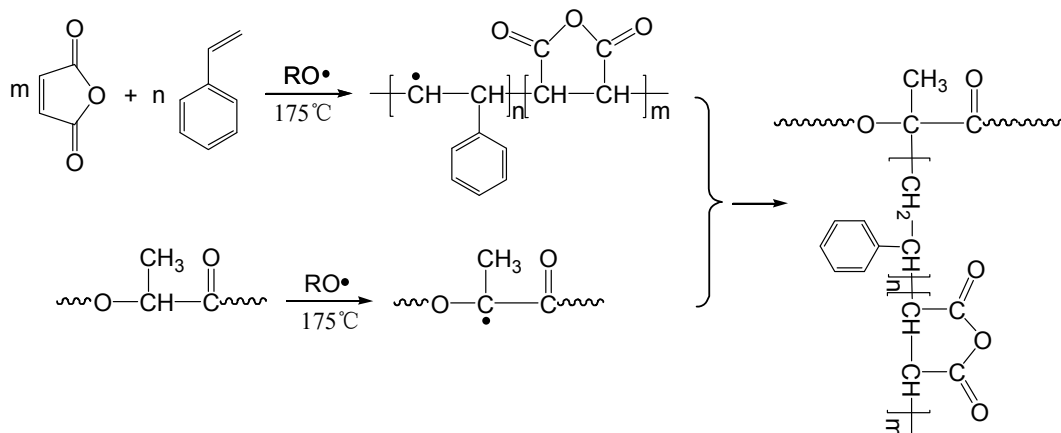
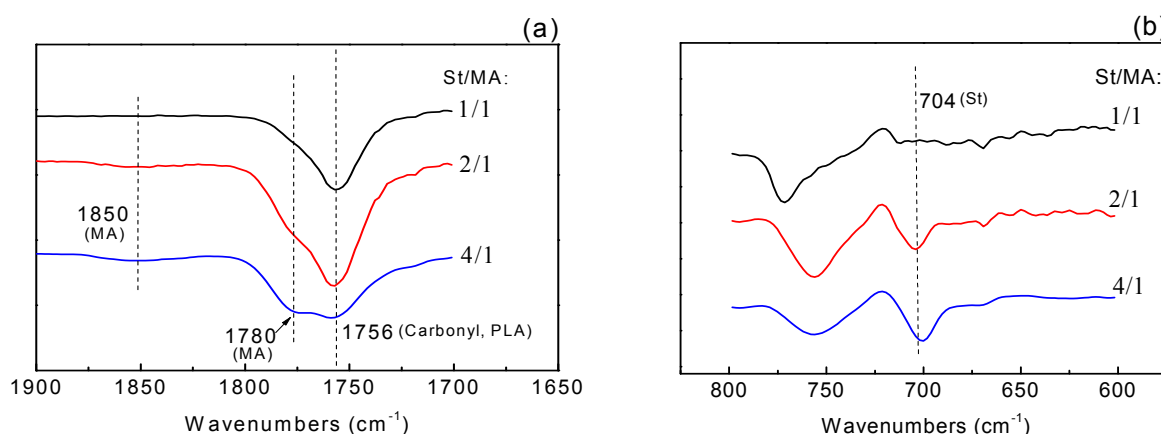


Figure 7. FT-IR spectra of the intermediate products of the PLA-g-MA/St samples (St/MA = 1/1, 2/1 and 4/1).



The FT-IR spectra of intermediate products exhibit characteristic absorption peaks, e.g., 1780 cm^{-1} and 1850 cm^{-1} for cyclic anhydride and 704 cm^{-1} for the benzene ring [24]. The intermediate products also show a notable peak at 1756 cm^{-1} which corresponds to the low molecular weight PLA which was dissolved in acetone. Moreover, the relative intensity of peaks 1780 cm^{-1} and 1850 cm^{-1} to peak 1756 cm^{-1} was increased with the increasing of the St/MA ratio. These results confirm that the component of St-MA co-oligomers in the intermediate products and the content of MA in the intermediate products increase with the St/MA ratio.

In summary, the D_g of MA is enhanced by the grafting of St-co-MA• onto PLA chains at a St/MA ratio of around 2/1; however, too high of the St concentration shows a negative effect on the grafting of MA.

4. Conclusions

A styrene-assisted melt free-radical grafting of maleic anhydride (MA) onto poly(lactic acid) (PLA) chains was investigated. The grafting degree (D_g) and grafting efficiency (E_g) of MA were studied as a function of the St/MA ratio, MA concentration and processing temperature by using titration methodology. Both D_g and E_g were enhanced by the addition of a certain amount of St (St/MA \leq 2/1)

implying that the interaction and/or reaction between MA and St play an important role in the grafting reaction. The maximum D_g of MA was obtained at a St/MA ratio of 2/1. The D_g of MA was increased with the MA concentration, while the E_g was only slightly influenced. The D_g and E_g were affected by the processing temperature, as well. An optimal temperature for the PLA-g-MA/St system is determined at 180 °C. The intermediate products of the PLA grafting MA/St system were successfully obtained via selective purification. The composition of the intermediate products, *i.e.*, St-MA co-oligomers and degraded PLA are confirmed by FT-IR analysis. The St-assisted grafting mechanism of MA onto PLA was suggested based on the experimental data, *i.e.*, MA is grafted onto PLA chains via single monomers and a charge-transfer-complex (CTC) at St/MA ratios of $\leq 1/1$, while St-co-MA oligomers are the dominating grafting pendants at St/MA ratios around 2/1. Copolymerization of St and MA rather than grafting is regarded as the main reaction at St/MA ratios of around 4/1. The thermal stability of PLA was compromised to a certain extent by grafting with MA regardless of the presence of St. Consequently, the viscosity average molecular weight (M_η) and decomposition temperature ($T_{d-5\%}$) of the maleated PLA are lower than that of PLA. In addition, the crystallization and melting temperatures of the PLA were slightly reduced after the grafting of the MA or MA-St co-oligomers.

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Conflicts of Interest

The authors declare no conflict of interest.

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