

Synthesis of Styrene–Ethylene–Butylene–Styrene Triblock Copolymer-*g*-Polylactic Acid Copolymer and Its Potential Application as a Toughener for Polylactic Acid

Rongrong Qi,¹ Mengni Luo,¹ Mark Huang²

¹School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

²Institute of Microelectronics, A*STAR, Singapore 117685

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ABSTRACT: The copolymer of styrene–ethylene–butylene–styrene triblock copolymer-*g*-polylactic acid (SEBS-*g*-PLA) was successfully prepared using a novel solvothermal synthetic method, in which the graft copolymerization of PLA and SEBS was simply performed in chloroform solution at 100–150°C with benzoyl peroxide (BPO) as initiator. The effect of various factors including the reaction temperature and time and the content of BPO and PLA on the graft copolymerization was investigated in detail. It is found that the optimal reaction condition for the grafted copolymers SEBS-*g*-PLA was 120°C for 5 h, while the optimal formulation of SEBS/PLA/BPO was 5 g/2 g/0.5 g in 30 mL chloroform. The properties and microstructures of

the obtained SEBS-*g*-PLA copolymers were also studied. The tensile strength and elongation at break were higher than that of pure SEBS and improved with the increase of grafting degree. In addition, SEBS-*g*-PLA copolymer possessed two-phase structure with vague phase boundaries. The as-prepared SEBS-*g*-PLA copolymers can be used as the toughening component to improve the impact strength of PLA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2699–2706, 2011

Key words: SEBS; PLA; solve-thermal synthesis; copolymerization; SEBS-*g*-PLA copolymer

INTRODUCTION

Biodegradable polymers have played more and more important roles in environmental and biomedical applications. For example, as one of the biodegradable polymers,^{1–5} polylactic acid (PLA) has attracted much attention because of its high-mechanical properties, ease of process, and biocompatibility. Therefore, PLA has found a great variety of applications such as mulch films, controlled release matrices for fertilizers, pesticides, and herbicides.⁶ However, its inherent brittleness and low toughness limit the scope of applications.^{7–9} Recently, there are lots of research work on the modification of PLA with different focuses in a practical way, among of which is to use chemical and mechanical methods to obtain biodegradable composites such as PLA–PHBHx,¹⁰ PLA–PCL,¹¹ PLA–PBAT,^{12,13} and PLA–PBS blends.¹⁴ The other is modified by some of thermoplastic elastomers and partially biodegradable blends are prepared, such as PLA/TPO,¹⁵ PLA/LLDPE,¹⁶ PLA/EGMA,¹⁷ and PLA/PA blends.¹⁸

It is well known that most of polymer blends are thermally immiscible because of structural difference between the component polymers, which will affect the overall thermal and mechanical performance.¹⁹ To overcome the immiscibility of blends, compatibilizers (such as block or graft copolymers) are usually used to reduce the interfacial tension and improve the interface adhesion between the immiscible phases through their emulsifying properties.^{20–22} For PLA matrix blends, some compatibilizers such as polyethylene-*block*-polylacide, poly(ethylene-*alt*-propylene)-*block*-polylacide,^{23,24} and PLA/PEO/PLA triblock copolymer²⁵ were also prepared by the *in situ* reaction between the component monomers. The modification of PLA including polyolefin-*g*-MAH or polyolefin-*g*-GMA^{17,26–28} can also be made via grafting method.²⁹ Recently, a two-step reaction method has been developed to prepare TPO-*g*-PLA copolymer in the presence of 4-dimethylaminopyridine. TPO-*g*-MAH was first formed by the functionalization of TPO with maleic anhydride, and then TPO-*g*-PLA was obtained through the esterification of TPO-*g*-MAH with polylactide. The as-obtained TPO-*g*-PLA copolymer well improved the properties of TPO–PLA blends.¹⁵ However, the disadvantage of the grafting method lies in the difficulty in directly grafting one polymer to another.³⁰ Thus, it is necessary to develop a facile, economical, and effective

Correspondence to: R. Qi (rrqi@sjtu.edu.cn).

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method to prepare the compatibilizers with the component of mixed polymers through direct reaction.

Because of the increased solubility and reactivity of compounds and complexes under high temperatures and pressures, solvothermal methods can be used to synthesize the copolymers that are not available using traditional methods.^{31,32} As the toughening component is concerned, styrene–ethylene–butylene–styrene block copolymer (SEBS) exhibited balanced elasticity, good processibility and thermal stability and thus has been widely employed as the toughening agent to improve the mechanical properties in numerous polymer blending systems.^{26,33–35} In this study, a novel method was developed to prepare SEBS-*g*-poly(lactic acid) (SEBS-*g*-PLA) copolymers in solvothermal process: the directly grafting reaction between PLA and SEBS was carried out using benzoyl peroxide (BPO) as the initiator in chloroform. The effect of the various factors, including the concentration of PLA and initiator, reaction time, and temperature, on grafting copolymerization had been investigated in detail. The properties and microstructures of the obtained SEBS-*g*-PLA copolymer were also studied. Furthermore, the as-prepared SEBS-*g*-PLA copolymer can be used as a kind of toughener to improve the impact strength of PLA, and the morphologies and mechanical properties of the PLA with or without SEBS-*g*-PLA copolymer were also compared.

EXPERIMENTAL

Materials

Linear SEBS (KARTON[®] G1652) with about 30% polystyrene was purchased from North America-Kraton Polymers LLC, Houston, TX. PLA (3051D, $M_w \sim 100,000$) was obtained from Cargill Dow Polymers LLC, West Lafayette, IN. BPO (Shanghai Lingfeng Chemical Solvent Co., Shanghai, China) was purified by dissolving in chloroform at room temperature and being precipitated in cool methanol. Acetone and chloroform were supplied by Shanghai Chemical Solvent Factory (Shanghai, China).

TABLE I
Recipes for Synthesis of SEBS-*g*-PLA

Feed ratio				Reaction temperature (°C)	Reaction time (h)
SEBS (g)	PLA (g)	BPO (g)	CHCl ₃ (mL)		
3.0	2.0	1.0	30	100–150	5
3.0	2.0	1.0	30	120	1–7
3.0	2.0	0.1–1.0	30	120	5
3.0	1.0–3.0	0.5	30	120	5

Bold words emphasize the range of reactive factors changing.

TABLE II
Formulas for PLA/SEBS-*g*-PLA Blends

Samples	PLA (g)	SEBS- <i>g</i> -PLA (g)
PS0	37.5	12.5 (GD = 0)
PS 1	37.5	12.5 (GD = 8%)
PS 2	37.5	12.5 (GD = 16%)

Synthesis of SEBS-*g*-PLA copolymer

The grafting reactions in chloroform were performed in a sealed vessel (HL-0.5-20, purchased by Jinan Henghua Chemistry Company, Shanghai, China) under various conditions. In a typical process, an appropriate amount of styrene–ethylene–butylene–styrene triblock copolymer (SEBS), PLA, initiator BPO, and chloroform (as solvent) were introduced into a sealed autoclave and then was kept in an isothermal oven. After a certain duration, the products were collected from the vessel and precipitated in acetone. The solid residue was washed several times with acetone, extracted by refluxing hot acetone for 24 h to remove the PLA remnant, and then dried to a constant weight in a vacuum oven at 60°C for 24 h. The recipes for synthesis of SEBS-*g*-PLA were summarized in Table I.

Preparation of PLA/SEBS-*g*-PLA blends

PLA and styrene–ethylene–butylene–styrene triblock copolymer-*g*-poly(lactic acid) (SEBS-*g*-PLA) were simultaneously introduced into a HAAKE mixer at 180°C for 10 min the mixer to obtain the mixture of PLA/SEBS-*g*-PLA according to feed ratio in Table II.

Characterization

Fourier transform infrared

The as-obtained samples were dissolved in chloroform, and then cast into a thin film for Fourier transform infrared (FTIR) characterization. IR spectroscopy information was obtained on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer (Perkin–Elmer, Waltham, MA).

Grafting degree

Grafting degree (GD) was determined by the index of intensity ratio of absorption peak in FTIR spectra and different ratio of SEBS/PLA mixture, based on a calibration curve. First, SEBS and PLA with different proportions were dissolved in 10 mL of chloroform, held for 24 h, and then cast into the film for FTIR characterization. The relative intensity of PLA/SEBS can be calculated from the intensity ratio of

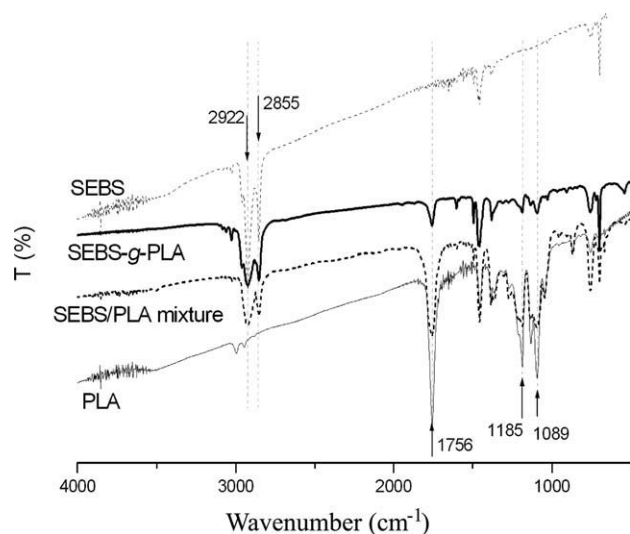


Figure 1 FTIR spectra of SEBS, PLA, SEBS-*g*-PLA, and SEBS/PLA mixture.

absorption peak in FTIR spectra (shown in Fig. 1) by the following eq. (1):

$$R = I_{1756} / (I_{2922} + I_{2855}) \quad (1)$$

The calibration curve was obtained from R values and the concentration of PLA in SEBS/PLA mixture (Fig. 2). The PLA GD of the SEBS-*g*-PLA is calculated from the linear relationship by the following eq. (2):

$$\text{GD} = 160.19R \quad (2)$$

NMR

^1H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer (Varian, Palo Alto, CA) at 400 MHz. CDCl_3 and tetramethylsilane from Shanghai Lingfeng Chemical Solvent Co., Shanghai, China, were used as solvent and the internal standard, respectively.

Morphology

Morphological analysis was carried out on frozen-fractured samples, and further examined using field emission scanning electron microscope (FESEM) (JSM-7401F, JEOL, Tokyo, Japan) and SEM (S-2150, Hitachi, Tokyo, Japan).

Mechanical testing

The tensile strength of as-synthesized blends was further measured on an Instron machine (Instron Corp, Norwood, MA) under controlled humidity and temperature according to the ASTM D882 testing method (testing rate: 50 mm/min).

The Izod notch impact strength was measured on Izod instrument (Ray-Ran). All specimens were molded in dimension of 100 mm \times 40 mm \times 2 mm according to ASTM D256. The notch was cut by a notch instrument (Ray-Ran Polytest, Nuneaton, UK).

At least five samples were tested to determine the mechanical properties.

RESULTS AND DISCUSSION

Characterization of SEBS-*g*-PLA

FTIR

The copolymer of styrene-ethylene-butylene-styrene triblock copolymer-*g*-polylactic acid (SEBS-*g*-PLA) was simply prepared using a solvothermal synthetic method and purified by refluxing in acetone for 24 h to remove the unreactive PLA. The structure of graft product was analyzed by FTIR spectra (Fig. 1). Compared to the FTIR spectrum of pure SEBS, the new absorption peaks in SEBS-*g*-PLA copolymers at 1756, 1185, and 1089 cm^{-1} representing PLA proved that PLA was successfully grafted onto SEBS through the free radical initiating reaction. The free radicals were generated from the decomposition of BPO in the solvothermal process. It should be mentioned that the sample used for FTIR test was strictly purified by refluxing in acetone for 24 h to completely remove the unreacted PLA.

FTIR analysis was also used to determine the GD based on the characteristic absorption peak at 1756 cm^{-1} (attributed to C=O group in PLA) and the absorption peaks at 2922 and 2855 cm^{-1} (due to $-\text{CH}_2-$ in SEBS). So, the PLA GD of the SEBS-*g*-PLA (GD just express their reaction ratio) is estimated from the linear relationship between R

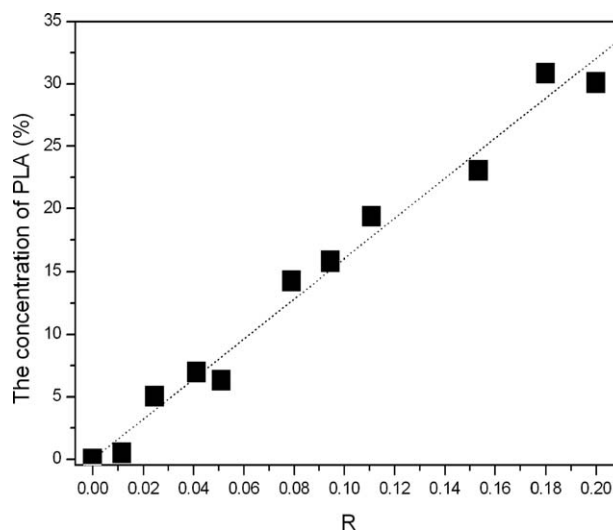


Figure 2 The calibration curve between IR intensity ratio (R) and the concentration of PLA in PLA/SEBS mixture.

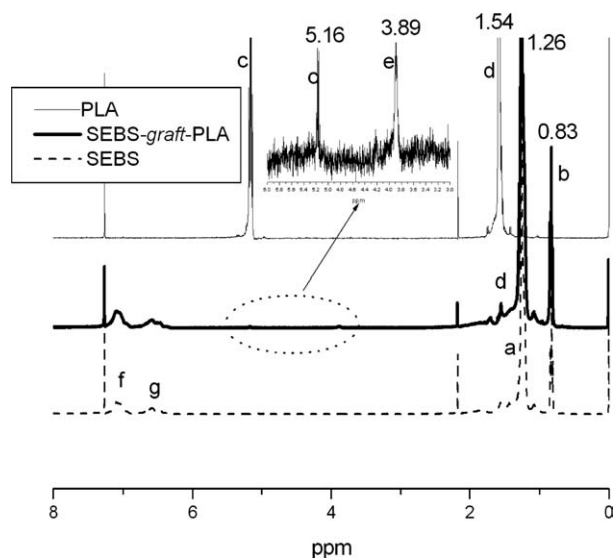


Figure 3 ^1H NMR spectra of PLA, SEBS-*g*-PLA, and SEBS in deuteriochloroform.

and the concentration of PLA in SEBS/PLA mixture (Fig. 2) by eq. (2).

NMR

The ^1H NMR spectra of PLA, SEBS-*g*-PLA, and SEBS (shown in Fig. 3) further confirmed the FTIR results. Compared to the spectra of pure PLA and SEBS, two peaks were observed at 5.16 and 3.89 ppm in the ^1H NMR spectrum of SEBS-*g*-PLA, respectively. The peak at 5.16 ppm representing methine protons (c) and the peak at 3.89 ppm representing methylene protons (e) confirmed that either PLA was successfully grafted onto the SEBS or SEBS was grafted onto the PLA.³⁶ According to the structure of SEBS^{37,38} and the results of ^1H NMR (Fig. 3), the possible reaction mechanism between SEBS and PLA was proposed in Scheme 1.

Scanning electron microscope and field emission scanning electron microscope

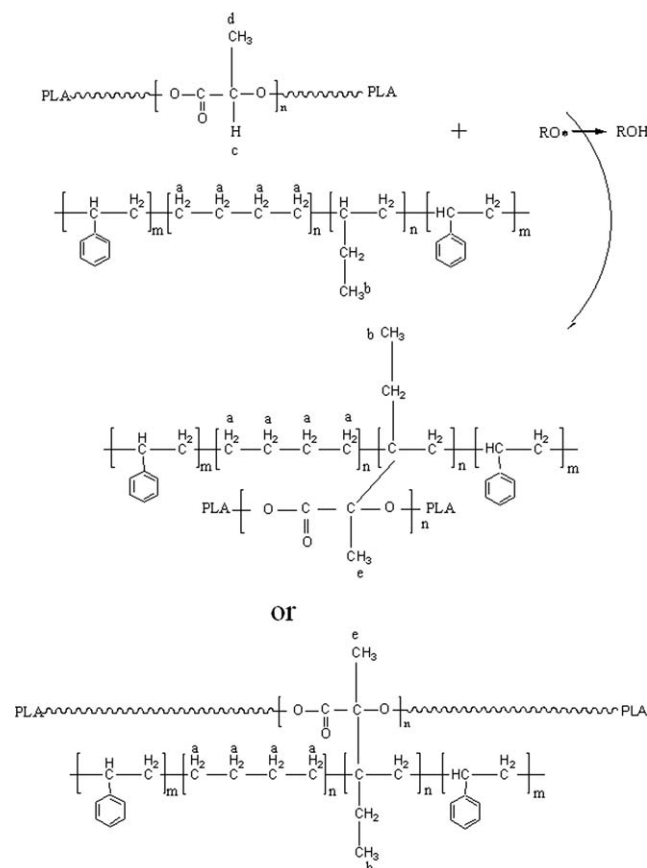
It is well known that SEBS and PLA are immiscible polymers, because SEBS is nonpolar while PLA is polar. Thus, it is indispensable to investigate their microstructure of the obtained graft copolymer and study their compatibility. To study the microstructure of SEBS-*g*-PLA copolymers, SEBS/PLA blend and SEBS-*g*-PLA copolymer were selected for scanning electron microscope (SEM) analysis (Fig. 4). It can be seen from Figure 4 that phase separation was observed in SEBS/PLA blends, confirming that the polymers were immiscible.

On the contrary, when SEBS-*g*-PLA copolymer was incorporated into SEBS/PLA system, the phase boundaries between SEBS and PLA disappeared.

This phenomenon suggested that SEBS-*g*-PLA could improve the compatibility between PLA and SEBS. To further observe the microstructure of the SEBS-*g*-PLA copolymer, field emission scanning electron microscope (FESEM) was used. From the FESEM image of the obtained SEBS-*g*-PLA copolymer (Fig. 4), microphase separation remained in SEBS-*g*-PLA copolymer, which was useful to combine the advantages of SEBS and PLA. Further detection revealed that the size of dispersed phase range from 10 to 300 nm, which was in good agreement with that of the styrene-vinylpyridine or ethylene oxide block copolymer.^{9,39} Moreover, the vague phase boundaries also imply that SEBS and PLA were chemically bonded, and PLA was well dispersed in SEBS.

Mechanical properties

The mechanical properties of SEBS-*g*-PLA of under various GD levels as shown in Figure 5 were improved compared to pure SEBS. For example, more than 200% elongation at break and about 200% of tensile strength achieved through incorporation of 16% GD of SEBS-*g*-PLA, compared to those of SEBS. For the increase of the tensile strength of SEBS-*g*-PLA, it may be due to the hard



Scheme 1 Reaction mechanism between PLA and SEBS.

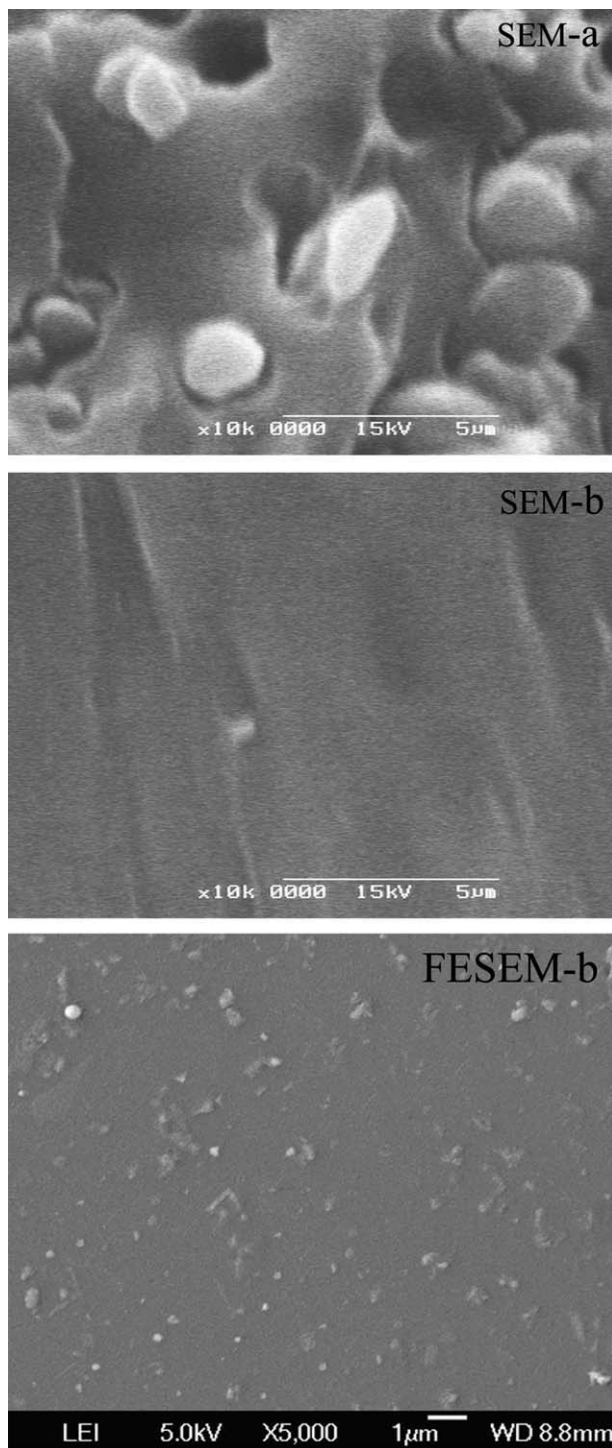


Figure 4 The SEM and FESEM photograph on the cryofracture surface of SEBS/PLA blend (a) and SEBS-g-PLA copolymer (b) (GD = 16%).

filler effect of PLA in the obtained copolymer; while the marked increase of elongation can be assigned to debonding cavitations between the interfaces when the interfacial adhesive between SEBS and PLA is not sufficient.⁴⁰ In other words, the tensile properties of SEBS can be well improved by adding thermally compatible SEBS-g-PLA.

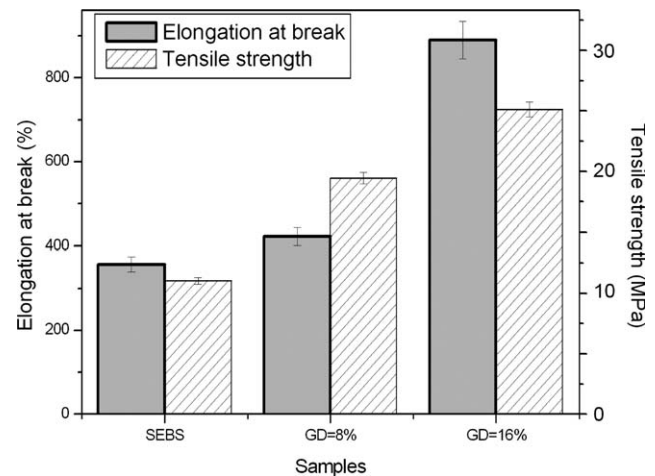


Figure 5 The tensile properties of SEBS and SEBS-g-PLA copolymer.

Affecting factors of GD

Reaction temperature

To obtain an optimal reaction temperature, the graft reactions were carried out from 100 to 150°C for 5 h (refer to Table I), and the results have been given in Figure 6. It can be seen from Figure 6 that the graft degree of copolymer increases with the increase of reaction temperature in the range of 100–120°C and reaches to maximal value at 120°C, and, after that, the graft degree decreases sharply when the reaction temperature is higher than 120°C and then reaches to a constant value when the reaction temperature is up to 140°C. The phenomenon can be attributed to the characteristic of the half-life of BPO. The previous work demonstrated that the half-life of BPO ($t_{1/2\text{BPO}}$) at 74, 92, and 130°C was corresponding to 10 h, 1 h, and 1 min,⁴¹ respectively. Thus,

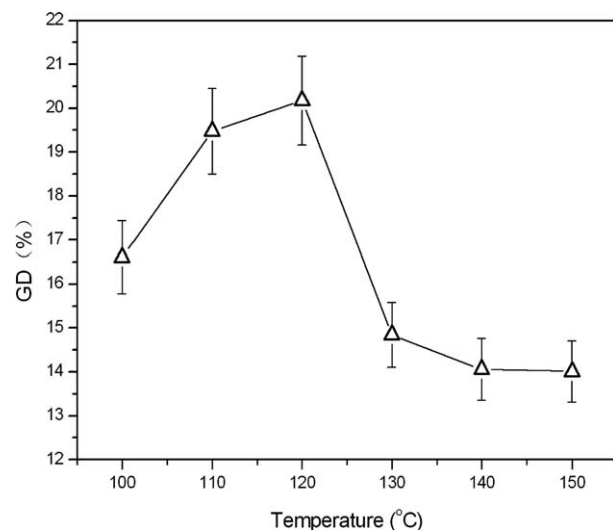


Figure 6 The effect of reaction temperature on the GD of SEBS-g-PLA.

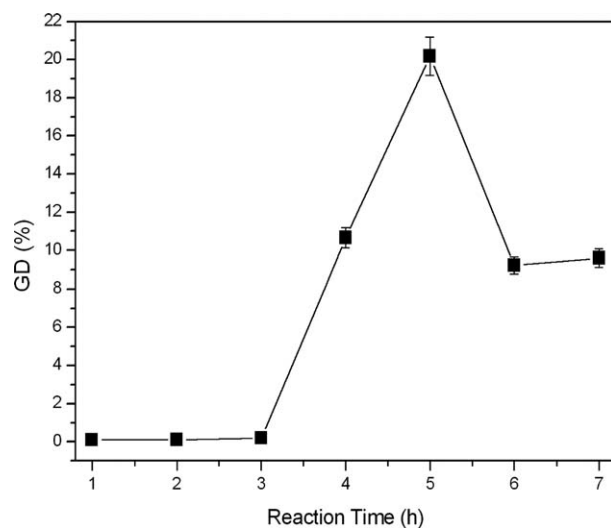


Figure 7 The effect of reaction time on the GD of SEBS-g-PLA.

reaction temperature would have great effect on the graft reaction because of the free radical reaction initiated by the temperature-dependent decomposition of BPO. In general, it is desirable that the initiator could be totally converted into free radicals within the reaction time. The previous research also demonstrated that about 97% initiator would be consumed if the reaction temperature was fivefold the half-life initiator.⁴² However, too high reaction temperature is undesirable to the graft reaction because of the decomposition of initiator in short time. Therefore, very low (<70°C) or very high temperature reaction temperature (>130°C) in the present reaction system does not match the graft reaction, because the initiation efficiency is very low. Considering other factors, such as reaction pressure, partition coefficient among initiator, the properties of SEBS substrate and PLA, and side reactions, 120°C is the optimal temperature for the SEBS-g-PLA reaction.

Reaction time

It is found that the reaction time also plays an important role in the graft reaction. Figure 7 shows the relationship between the reaction time and the GD of PLA in SEBS-g-PLA. The GD of the as-prepared SEBS-g-PLA is rather low within 3 h, and then it rapidly increases with an extended reaction time up to 5 h and then slightly decreases. Because the grafting reaction is carried out in a sealed vessel, the reaction solution containing solid polymers is cold in the beginning of reaction, and a certain time is needed for the dissolution of polymer and for the reaction system to reach reaction temperature. Thus, the grafting copolymerization is difficult to happen in the early stage, and low GD is obtained. When the reaction time is up to 5 h, the optimal reaction

conditions for the grafting reaction are obtained, and, as a result, the GD greatly increases and the highest GD is obtained. However, the further prolonged reaction time does not further increase the GD value, because all the initiator is used up. Moreover, long time heating will also cause the thermal decomposition of PLA.^{43,44}

Concentration of initiator

Because the graft reaction is initiated by BPO, the concentration of BPO would also affect the grafting polymerization of SEBS-g-PLA. At the present reaction system, the quantities of BPO are changed from 0.1 to 1.0 g (as shown in Table I). It can be seen from Figure 8 that GD increases gradually from 14.2 to 25.3% when the concentration of BPO increases correspondingly from 0.1 to 0.5 g/30 mL and then it slightly decreases. The fact can be attributed to the amount of free radical decomposed by initiator BPO, and the increase of initiator concentration will generate more free radicals; thus, higher GD is obtained in the beginning stage. However, excessive initiator will increase the chance to catch initiator radicals and get more macro radicals, which will increase the side reactions (such as the degradation of PLA and the crosslink of SEBS), and further lead to lower GD and the initiation efficiency. Based on the above results, the optimal concentration of BPO is 0.5 g/30 mL in the present work.

PLA content

The effect of PLA content on the grafting polymerization is shown in Figure 9. As shown in Figure 9, GD increases with the increase of PLA content, and the maximum value reaches to 25.2% when PLA

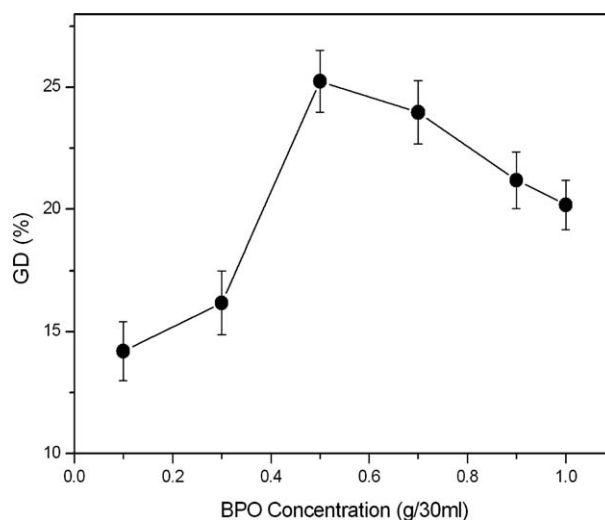


Figure 8 The effect of BPO concentration on the GD of SEBS-g-PLA.

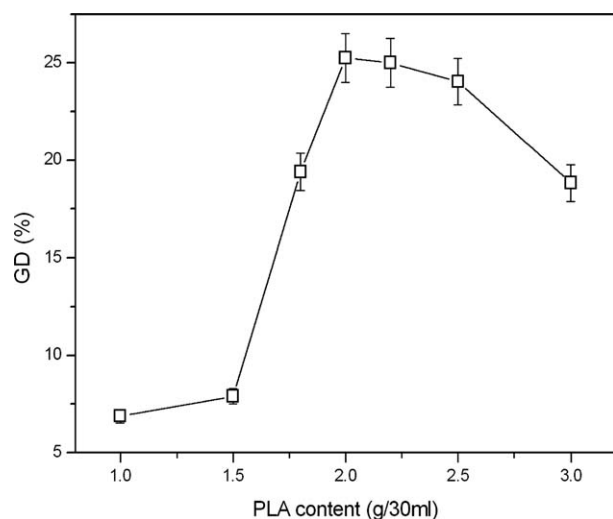


Figure 9 The effect of PLA content on the GD of SEBS-g-PLA.

content is 2.0 g/30 mL. Then, the GD decreases with the further increase of PLA content. In general, the graft reaction mainly depends on the diffusion of PLA free radicals, and a higher PLA content forms more PLA-free radicals, which are beneficial to the graft reaction and greater GD.⁴¹ However, it should also be mentioned that PLA can also act as the trap for free radicals; thus, too high content of PLA will give rise to less SEBS polymer radicals and cause more degradation of PLA, which would further restrict the grafting reaction.

Properties and morphology of PLA/SEBS-g-PLA blends

Mechanical properties of PLA/SEBS-g-PLA blend

To explore the potential application of styrene-ethylene-butylene-styrene triblock copolymer-g-poly(lactic acid) (SEBS-g-PLA) copolymer, it has been used as a toughener for PLA (refer to Table II). The effect of SEBS-g-PLA with different GD on the mechanical properties of PLA/SEBS-g-PLA blends has also been studied. Table III shows the tensile strength, elongation at break, and notched Izod impact strength of PLA/SEBS-g-PLA blends. Compared to the mechanical properties of PLA, the tensile strength of blends

TABLE III
The Mechanical Properties of PLA and PLA/SEBS-g-PLA Blends

	Notched impact strength (kJ/m ²)	Tensile strength (MPa)	Elongation at break (%)
PLA	2.3 ± 0.3	52.2 ± 7.6	4.2 ± 0.6
PS0	3.0 ± 0.4	27.0 ± 5.2	3.9 ± 0.7
PS1	3.9 ± 0.4	34.6 ± 4.7	7.6 ± 0.5
PS2	4.7 ± 0.2	41.4 ± 5.9	11.4 ± 0.4

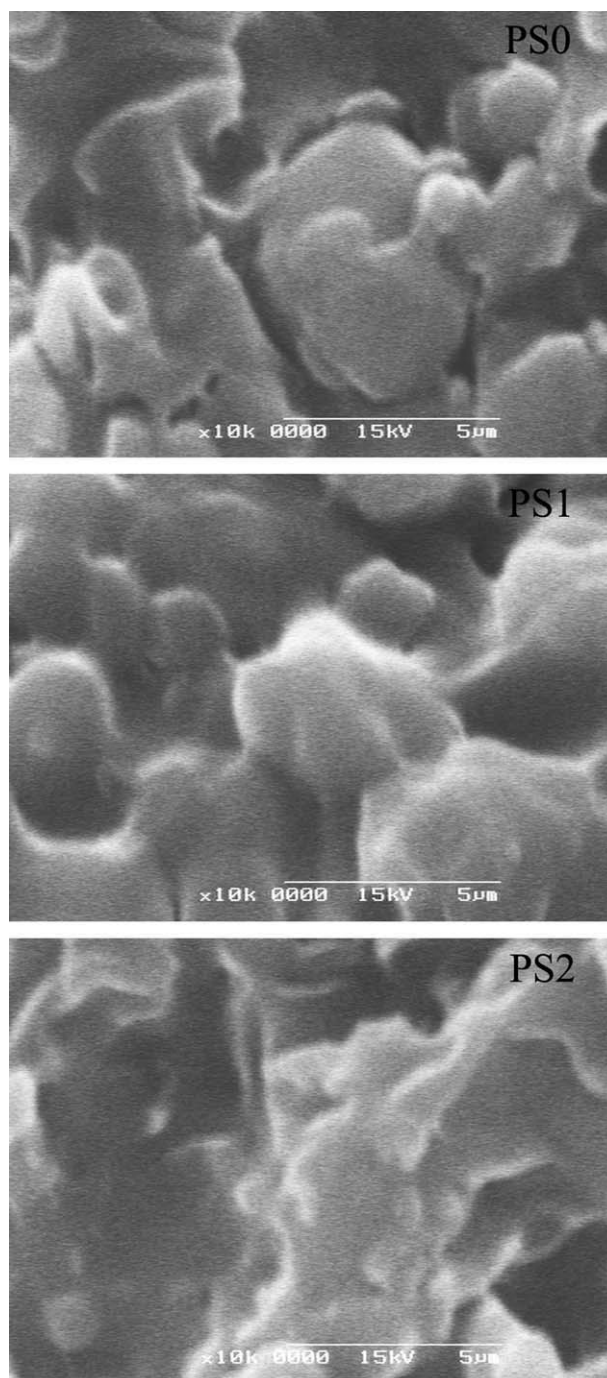


Figure 10 SEM micrographs of cyro-fracture surfaces of the blends.

decreases with the addition of SEBS-g-PLA, while the notched Izode impact strength and elongation at break of PLA/SEBS-g-PLA blends improved. The obtained high-graft degree SEBS-g-PLA copolymer would most likely yield a finer dispersion of PLA phase and stronger adhesion between PLA and SEBS phases. Moreover, the impact strength and elongation at break of the blends have also been improved with the addition of SEBS-g-PLA compared to those of pure PLA.

Morphology of PLA/SEBS-*g*-PLA blends

The volume ratio of blending components plays a predominant role in determining the dispersed phase and matrix phase of two blending components and further affects their properties. The morphology of PLA/styrene-ethylene-butylene-styrene triblock copolymer-*g*-polylactic acid (SEBS-*g*-PLA) blends was studied using SEM. PLA occurs as the continuous phase for over 75 wt % content (as shown in Fig. 10), while SEBS-*g*-PLA serves as the dispersed phase.¹⁵ Further observation reveals that a clear interface blurred with the increase of grafting yield in the PLA/SEBS-*g*-PLA blend, and the domain size decreases with the increase of GD. The above facts further indicate that high-graft degree SEBS-*g*-PLA can improve the compatibility of PLA and SEBS-*g*-PLA blends through modifying their morphologies.

CONCLUSION

SEBS-*g*-PLA copolymer was successfully synthesized by the solvothermal method, and the influence of the reaction parameters on GD was systematically investigated. Furthermore, the properties, microstructure, and application of SEBS-*g*-PLA copolymer were also discussed. The important results are summarized as follows:

1. The graft copolymerization between SEBS and PLA can be achieved via the solvothermal method.
2. The obtained SEBS-*g*-PLA copolymer possesses two-phase structure with vague phase boundaries, and the size of dispersed phase ranges from 10 to 300 nm. Its tensile strength and elongation at break are higher than that of pure SEBS and increase with the increase of GD.
3. The optimal reaction condition for the grafted copolymers SEBS-*g*-PLA is 120°C for 5 h, and the optimal formulation of SEBS/PLA/BPO is 5 g/2 g/0.5 g in 30 mL chloroform.
4. SEBS-*g*-PLA can be served as a toughener to improve the impact strength and elongation at break of PLA.

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