Fabrication of high-viscosity biodegradable poly(butylene succinate) (PBS)/solid epoxy (SE)/carboxyl-ended polyester (CP) blends

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ABSTRACT: Expanding the applications of poly(butylene succinate) (PBS) in processing fields requiring high melt strength, PBS/solid epoxy (SE)/carboxyl-ended polyester (CP) blends with high melt viscosity were fabricated by the *in-situ* crosslinking reaction using SE and CP. The influence of SE/CP had been studied in terms of the rheological property, crystallization behavior, and mechanical property of PBS. The results showed that the melt viscosity of PBS could be enhanced significantly by three orders of magnitude, when the loading ratio of SE to CP was over 15/15. Furthermore, it had also been found that SE/CP component had positive impact on the mechanical properties of PBS, inclusive of reduction of brittleness. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42193.

INTRODUCTION

With the wide spread and huge consumption in the last few decades, engineering plastics have brought great convenience to our daily life. However, owing to the difficulty in degradation of plastics after disposal, using of plastics has given rise to a more serious problem of white pollution, threatening the environment.[1] Thus, there are a growing number of researches focusing on biodegradable polymer resins. Among them, the aliphatic polyesters have received more attention and shown a brighter future according to their excellent biodegradability, biocompatibility, and processibility.[2,3] Poly(butylene succinate) (PBS), as one kind of the aliphatic polyesters, possesses various advantages, including relatively higher melting point, good mechanical properties, and favorable nature for processing, over the other common biodegradable aliphatic polyesters such as poly(ethylene succinate), poly(ethylene adipate), and poly(butylene adipate) (PBA).[4,5] Besides, when exposed to the proper enzymes produced by various micro-organisms, plants, and animals in nature, PBS can be readily decomposed into carbon dioxide and water. Moreover, PBS only degrades under the attack by micro-organisms but preserves its stability during usual storage and utilization.[4]

With the continuous demanding for high-performance polymer materials, polymer modification has been a hotspot in polymer materials and engineering fields. For PBS, the low melt strength and melt viscosity resulting from the highly linear chain structure and weak intermolecular interaction limit its application, especially in those areas that high melt viscosity is required for polymer melt, such as film blowing, foaming, and spinning.[2,5,6] The mechanical properties of pristine PBS are also not good enough. Thus, many efforts have been paid to improve PBS melt viscosity and to reinforce PBS. In general, the enhancement of PBS melt strength and melt viscosity can be realized by many methods. For example, chain extension using chain-extending agents to couple two polymer chains thus improving the PBS molecular weight;[7–9] crosslinking of PBS via peroxide[10,11] or irradiation by electron-beam,[12,13] γ-ray,[14,15] or ultraviolet;[16] copolymerization with a small amount of tri-functional monomer (e.g., triols) to introduce long-chain branches to increase the entanglement among polymer chains in melt resulting in the improvement of melt viscosity;[5,6,17,18] stretched blown bottle, foamed films and fibrillated materials, and highly expanded foamed articles based on PBS have been successfully prepared after improving the melt strength of PBS.[6,19] As for the modification of PBS mechanical properties, natural cellulose filler (e.g., wood flour, white straw and sisal-fiber[20,21]) and inorganic nanoparticles, including organoclay,[22] carbon nanotubes,[23] and polysilsesquioxane (POSS)[24] have been found effectively to reinforce pristine PBS.

In our previous study, we found that carboxyl-ended polyester (CP) and solid epoxy (SE) could effectively enhance the melt

Table I. Formulations for PBS/SE/CP Blends

Samples	PBS (phr)	SE (phr)	CP (phr)	1010 (phr)	168 (phr)
PBS	100	0	0	0.5	0.5
100/5/5	100	5	5	0.5	0.5
100/10/10	100	10	10	0.5	0.5
100/15/15	100	15	15	0.5	0.5
100/20/20	100	20	20	0.5	0.5
100/25/25	100	25	25	0.5	0.5

strength and melt viscosity of PLA through the *in-situ* crosslinking reaction investigated by rheological properties.[25] In light of the aliphatic polyesters of PBS and PLA, a similar viscosity improvement effect of SE/CP on PBS may be expected because of their similar chemical structure. Thus, SE and CP are used to improve the melt viscosity of PBS and fabricate PBS/SE/CP blends. The properties of PBS/SE/CP blends were carefully characterized, including rheological, thermal, mechanical property, and microscopic morphology. Furthermore, PBS foams were also successfully prepared by the PBS/SE/CP blends through a common compressing molding method.

EXPERIMENTAL

Materials

PBS with a melt flow index of 30 g/10 min (190°C/2.16 kg) and a density of 1.26 g/mL, was purchased from Anqing Hexing Chemicals, Anhui Province, China. CP (P5980; weight-average molecular weight = 3000 determined by gel permeation chromatography) and SE (E903, epoxy equivalent = 700 g/mol obtained from the technical data sheet) were kindly supplied by DSM, Heerlen, Holland. Antioxidant 1010 and 168 were purchased from Ciba Specialty Chemicals, Shanghai, China.

Preparation of PBS/SE/CP Blends

The preparation of PBS/SE/CP blends is following our previous work.[26] PBS pellets were fed first on a two-roll mill at a temperature of ~100°C for 4 min, then the other ingredients were uniformly mixed with PBS according to the formulations in Table I for 10 min at the same temperature. After this blending process, the as-obtained resins were compressed into flat sheet with a thickness of 1 or 3 mm on a compressing-molding machine at a temperature of 160°C and pressure 10 MPa for 20 min, and subsequently cooled at room temperature for 5 min.

Characterization

Gel Content Measurement. The PBS/SE/CP blends were kept at 160°C for 20 min first, then the weight of the original sample was recorded as W_1 and the vacuum drying (60°C for 24 h) sample as W_2 after Soxhlet extraction by hot chloroform at a temperature of 100°C for 48 h. Gel content was calculated by the following equation:

$$\text{Gel content} = \frac{W_2}{W_1} \times 100\%$$

Rheological Properties. For the rheological behavior investigation, samples were pressed into plates with thickness in 1 mm on the compressing-molding machine at 160°C under a pressure

of 10 MPa for about 20 min and subsequently cooled at room temperature for 5 min. The rheological measurement was carried out on a Gemini 200 Rheometer instrument (Malvern Instruments, Worcestershire, UK). Frequency sweep for the samples was performed under nitrogen atmosphere at 160°C through a parallel plate of 25 mm in diameter and 1 mm in plate spacing. A strain sweep test was initially conducted to determine the linear viscoelastic region of samples. Afterward, testing was operated under the condition of strain at 5% and angular frequency in the range of 0.01–100 rad/s. Finally, Gemini 200 software was used to analyze the data.

Differential Scanning Calorimeter (DSC). DSC analysis was performed on a DSC-7 (PerkinElmer, Waltham, MA). A total of 5–10 mg of blends were weighed and sealed in an aluminum crucible. Then, under the atmosphere of N_2, a sample was heated up from 20 to 160°C at a rate of 20°C/min and held for 3 min to eliminate the thermal history. And then, the sample was cooled to 20°C at a cooling rate of 10°C/min (first scan) and finally reheated to 160°C from 20°C at a rate of 10°C/min (second scan).

The crystallization temperature (T_c) and enthalpy of fusion (ΔH_c) were determined from the DSC exotherm curves in first scan, whereas the melting temperature (T_m) from endotherm curves in second scan. The degree of crystallinity of PBS (X_c) was approximately calculated by below equation:

$$X_c = \frac{\Delta H_c}{\chi \Delta H_m^0} \times 100\%$$

ΔH_c: the experimental crystallization enthalpy of PBS crystals;

χ: the weight fraction of PBS in PBS/SE/CP blends; and

ΔH_m^0: $\Delta H_m^0 = 110$ J/g, the melting enthalpy of fusion for completely crystalline PBS.[6,27]

Polarized Optical Microscope (POM). Crystallization morphology of the specimens was studied by the POM (LEICA DM LP; Leica Microsystems GmbH, Wetzlar, Germany). All samples were first heated to 180°C and kept for 3 min, and then cooled from melt to the selected crystallization temperature of ~40°C at a rapid cooling rate. The PBS spherulites were observed after isothermal crystallization for 30 min.

Scanning Electron Microscope (SEM). To study the morphology of blends, SEM S-2150 (Hitach, Tokyo, Janpan) was used to characterize the freezing fracture surface of PBS, and PBS/SE/

Table II. The Extraction Experiment Results of PBS/SE/CP Blends

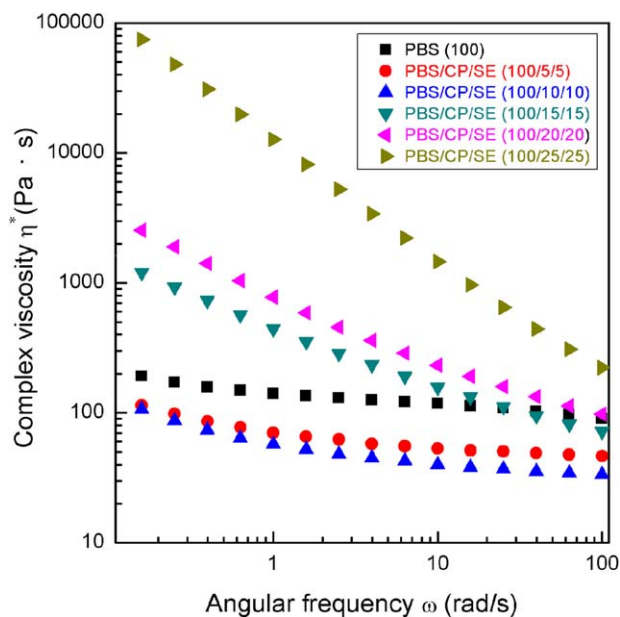| Samples	Composition	Content of SE/CP (%)	Gel content (%)
PBS	100	0	0.5
PBS/SE/CP	100/5/5	9.0	6.7
PBS/SE/CP	100/10/10	16.7	14.5
PBS/SE/CP	100/15/15	23.1	23.8
PBS/SE/CP	100/20/20	28.6	30.1
PBS/SE/CP	100/25/25	33.3	35.9

Figure 1. Complex viscosity η^* as a function of angular frequency$\omega$of PBS and PBS/SE/CP blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CP blends after being corrosive by chloroform to remove PBS component.

Mechanical Properties. Tensile tests were performed on Instron 4465 (Instron Corp, Norwood, MA) machine with a crosshead speed of 50 mm/min according to the ASTM D638 standard. The test values were the average values of at least five specimens for each sample.

As to the notched Izod impact strength tests, the measurement were carried out on Universal Pendulum Impact Tester (RAY-RAY Test Equipment Ltd., Warwickshire, UK) in accordance with GB/T 1843-2008 standard.

RESULTS AND DISCUSSIONS

Reaction Between PBS, SE, and CP

PBS are usually synthesized via the polycondensation of succinic acid and 1, 4-butanediol, and some residual groups, such as hydroxyl, carboxyl groups may exist in the end of PBS chain segments as terminal groups which may facilitate PBS to react with other compounds containing hydroxyl, carboxyl or epoxy groups.[7,8] In our PBS/SE/CP system, three main types of reactions were likely to happen, namely crosslinking reaction between SE and CP, transesterification of PBS and CP, and condensation reaction between PBS and SE.[25] We intended to investigate the probable reaction types in PBS/SE/CP system through FTIR. However, the overlapping of absorption band and complexity of spectrum made it too difficult to figure out what kind of reactions happened during processing. Thus, the Soxhlet extraction was performed to qualitatively state that reactions did exist between PBS, SE, and CP.

Table II presents the extraction experiment results of PBS/SE/CP blends. With the increase of SE/CP content, the gel content rises all the time, even though it is not beyond the original con-

tent of SE/CP until the content of SE/CP is more than 15/15. The result may be because the reaction extent between PBS, SE, and CP is affected by the content of SE/CP. When SE/CP content is below 15/15, curing reaction is only partially finished because of the segregation of PBS chains hindering the crosslinking reaction. After more and more SE/CP is incorporated into PBS/SE/CP, degree of curing reaction is improved gradually, which means more complete reaction between SE and CP, and even PBS taking into the curing reaction. From the discussion above, we believe that the crosslinking reaction carries out between multifunctional groups in PBS, SE, and CP. And the influence of SE/CP incorporation on PBS properties would be discussed in detail later.

Rheological Properties

As mentioned above, the low melt strength and melt viscosity of pristine PBS imped its applications in processing fields in which high melt viscosity is usually necessary. In our previous research, the SE/CP was found to greatly improve the melt viscosity of PLA.[25] Similar to that study, we attempted to increase the melt strength of PBS by introducing SE/CP into PBS and the rheological property characterization was made to study the effect of SE/CP on the melt viscosity of PBS.

Figure 1 gives the curves of complex viscosity, η^*, as a function of angular frequency, ω. From Figure 1, one can clearly see that the complex viscosity of PBS/SE/CP blends has a significant increase (1–3 orders of magnitude) compared with that of pristine PBS when the loading of SE/CP is only over 15/15. The fact is a little different from our results in PLA/SE/CP system before, in which the melt viscosity of PLA/SE/CP composites had been improved for all samples, even when the loading of SE/CP was rather low.[25] In PLA/SE/CP system, the curing reaction temperature of PLA, SE and CP was 180°C, 20°C higher than that of PBS/SE/CP system. As discussed before,[25] the crosslinking reaction degree of SE/CP mainly depended on reaction temperature. On the contrary, the dispersion of CP and SE in PBS matrix is good, and this may weaken the interaction between CP and SE. The partially cured reaction for PBS/SE/CP in lower temperature could only be compensated by increasing the SE/CP content if the same melt viscosity is expected.

Moreover, with the increase of angular frequency and SE/CP amount, the gradually obvious downward trend of complex viscosity η^* over the entire testing frequency range in Figure 1 reflected the improved sensitivity to frequency, which was an indication of pseudoplastic characteristics and non-Newtonian behaviors.[5] And the shear thinning behavior is similar to the influence of long chain branching on polypropylene (PP) complex viscosity reported by Su and Huang.[28,29] Together with the extraction experiment results, we could found that the melt viscosity of PBS/SE/CP blends was closely related to the gel content of blends, which was determined by the SE/CP content. When the loading of SE/CP was below 15/15, the lower viscosity of PBS/SE/CP blends could be due to the plasticization of PBS by one of the uncured, low molecular weight components, CP or SE.[25] However, when the loading of SE/CP was above 15/15, the melt strength of PBS could be significantly enhanced because of the formation of complete cured network. This may
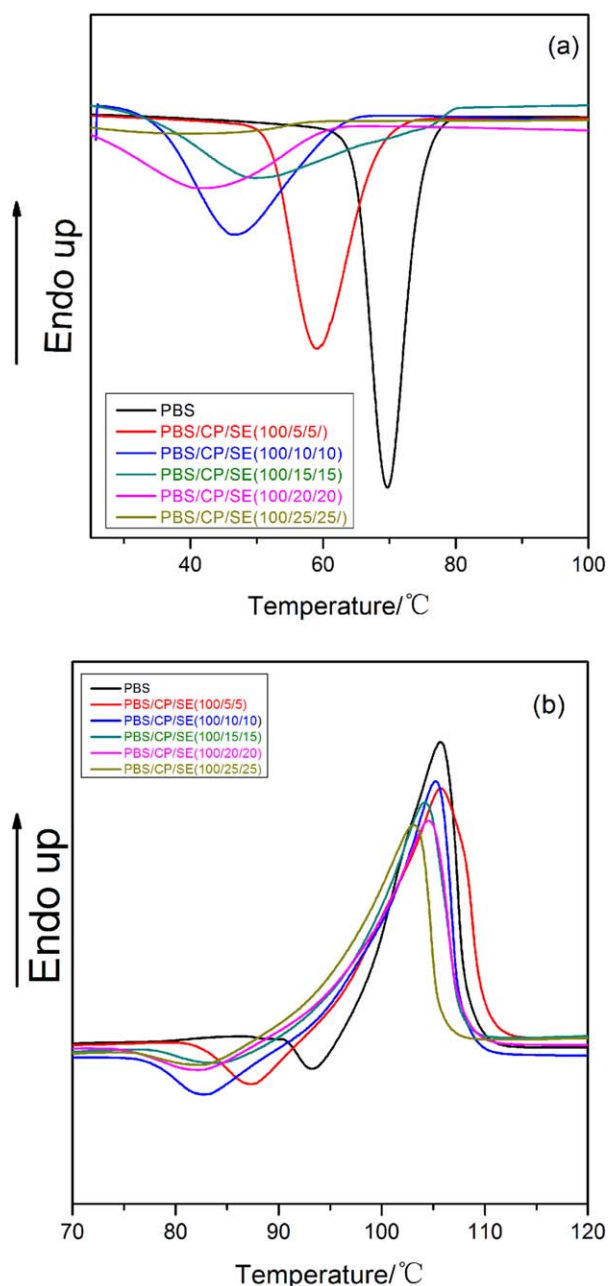
Figure 2. DSC curves of PBS and PBS/SE/CP blends (a) the first cooling curves, (b) the second heating curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The DSC Results of PBS and PBS/SE/CP Blends

PBS/SE/CP blends	T_c (°C)	$\triangle H_c$ (J·g^{-1})	T_m (°C)	χ_c (%)
100/0/0	69.75	55.86	105.67	50.78
100/5/5	59.22	50.83	105.74	50.83
100/10/10	46.36	45.52	105.18	49.66
100/15/15	48.92	36.72	104.16	43.40
100/20/20	41.27	27.93	104.59	35.55
100/25/25	38.93	3.44	103.07	4.69

From Figure 2(b) and Table III, it could be seen that the melting temperature (T_m) was almost independent of the incorporation of SE/CP and remained constant at a temperature around of 105°C, in good agreement with the work of Wang et al.[5] However, the sluggish exothermal peaks in Figure 2(a) and change in crystallinity listed in Table III suggested that the crystallization behavior of PBS was definitely affected by the addition of SE/CP. And the increasing of SE/CP content leads to a downtrend of the crystallinity of PBS. When the loading of SE/CP was over 15/15, a sharp drop of PBS crystallinity appeared. This inhibition effect of SE/CP on PBS crystallinity should be attributed to the gradually increasing curing reaction between SE, CP, and PBS (Table II), thus hindering the crystallization process of PBS.

The effect of SE/CP on the crystallization behavior of PBS could be further and directly reflected by polarized optical micrographs under crossed polarizer, as shown in Figure 3. For pure PBS, abundant spherulites with a typical Maltese Cross could be noticed, though they stacked with each other. The typical Maltese Cross was still obvious when the loading of SE/CP was below 15/15. However, once SE/CP content was above 15/15, the sharply weakened Maltese Cross and decreased spherulite numbers were much noticeable, as shown in Figure 3(c,d). When content of SE/CP was lower than 15/15, the incomplete reaction and partially cured particles of SE/CP failed to affect PBS crystallization process, thus the Maltese Cross in polarized optical micrographs almost unchanged. However, the crosslinking network as a consequence of the complete reaction between SE, CP, and PBS would block the formation of crystal nucleus and growing process of PBS, which would lead to weaken Maltese Cross and decrease spherulite numbers in Figure 3(d).[5,25,30]

Morphology

To further investigate the influence of SE/CP on the melt viscosity and crystallization property of PBS, the freezing fracture surfaces of PBS and PBS/SE/CP blends after being corrosive by chloroform to remove PBS were used to study the internal morphology change by SEM images (shown in Figure 4). In general, PBS should be removed and SE/CP particles were preserved after the corrosion of chloroform. However, Figure 4(a–c) shows that PBS appears as the continuous phase with cured SE/CP particles dispersed in PBS. With increasing the content of SE/CP to over 15/15, the phase structure firstly became a co-continuous structure [Figure 4(d–e)] from the sea-island phase
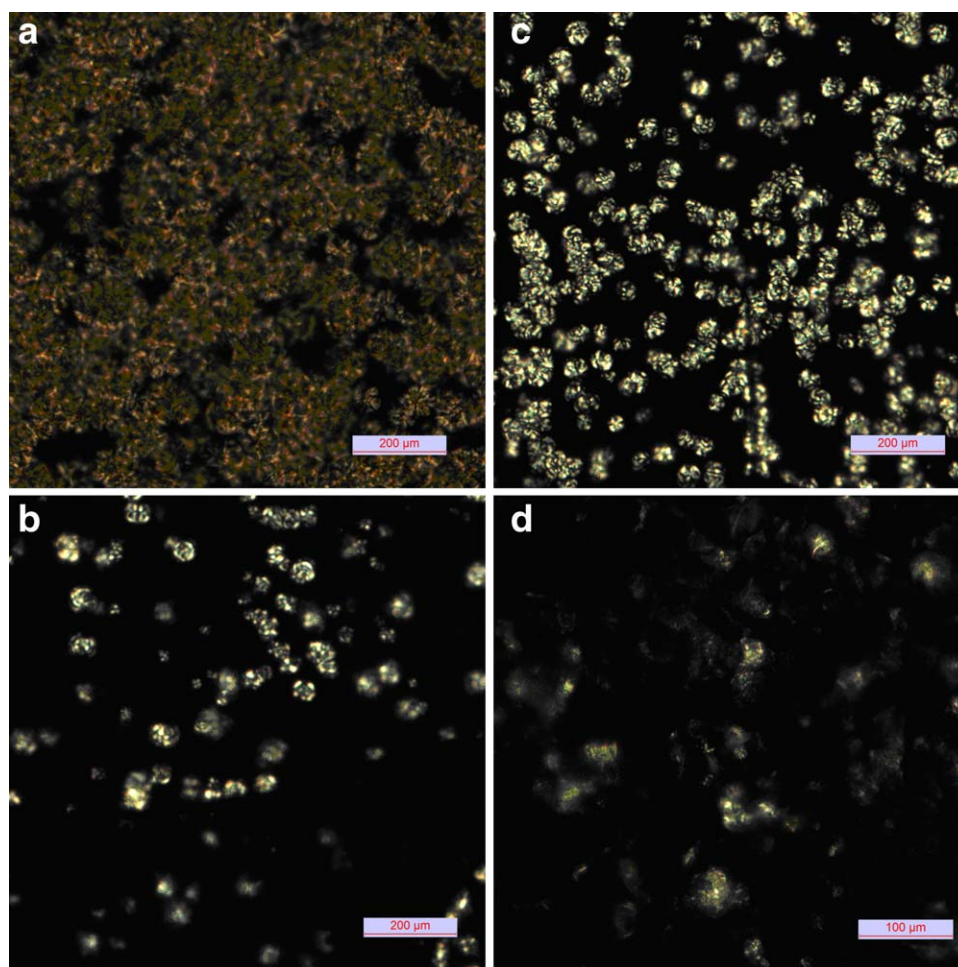
be due to increased with the content of CP and SE, CP, and SE collision probability increases, which makes crosslinking reaction easily to be completed. Based on the above results and discussion, we believe the existed curing reaction between PBS, SE, and CP could be beneficial to improve the melt viscosity of PBS.

Crystallization Behaviors of PBS and PBS/SE/CP Blends

PBS is a kind of semi-crystalline polymers, and the crystallization property affects its performances. Thus, DSC was first used to evaluate the influence of SE/CP on PBS crystallization property (Figure 2), and the results were summarized in Table III.

Figure 3. Polarized optical microscopy images of pristine PBS(a) and PBS/SE/CP blends of 100/5/5(b), 100/15/15(c) and 100/25/25(d) after isothermal crystallization at 40°C for 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure [Figure 4(a–c)], and finally turned into a sea-island phase structure (the cured SE/CP became the continuous phase) again in Figure 4(f). This micro-phase structure transformation was the result of the increasing of SE/CP content and curing reaction degree, in which the curing reaction between SE/CP got more and more thoroughly after the content of SE/CP was over 15/15. Meanwhile, PBS was still etched by chloroform and relative content of PBS in PBS/SE/CP blends dropped with the increasing of SE/CP content. Thus, a co-continuous phase structure appeared for PBS/SE/CP blends with higher SE/CP content. And when SE/CP content reached to 25/25, phase inversion occurred and cured SE/CP dominated the continuous phase with etched PBS holes dispersed in SE/CP, as shown in Figure 4(f).

In fact, the micro-phase structure transformation of the blends from sea-island structure to co-continuous structure and then to sea-island structure finally was also related to the viscosity change of system, determined by reaction degree between SE, CP, and PBS. According to Vanoene's model of dispersion in two components system,[31] the migration and stratification would happen to reduce the overall viscosity of blends. In our system, with the increasing content of SE/CP and degree of cur-

ing reaction, the viscosity of SE/CP should go up all the time, as shown in Figure 1, thus a viscosity difference between SE/CP and PBS of which the viscosity kept constantly, and a phase separation behavior happened finally.

Besides, the micro-phase structure transformation of the blends was in good agreement with the rheological property and DSC characterization. The increasing of melt viscosity and decreasing of degree of crystallinity were the results of complete curing reaction forming the network structure of blends at high loading of SE/CP. When content of SE/CP was below 15/15, the partially reacted SE/CP particles were well dispersed in PBS matrix and worked as "plasticizers" to decline the melt strength.

Mechanical Properties

In our previous wok of high-viscosity PLA preparation, SE/CP was successfully used to improve the melt viscosity of PLA. However, the PLA/SE/CP was too brittle, of which the elongation at break was only below 4%.[25] Similar to PLA, PBS is also a kind of fragile material and the modification for PBS with good strength and better toughness is in urgent need. Although graphene oxide (GO) was used to reinforce PBS in past years, and the tensile strength was improved to approximately 46 MPa
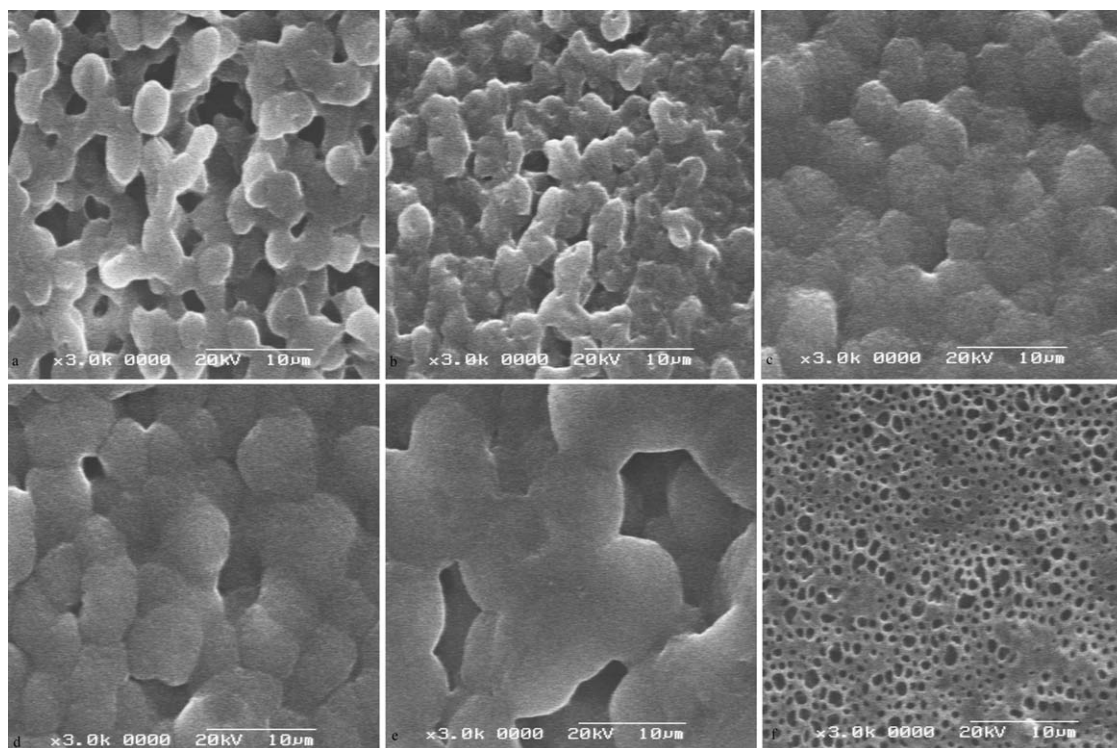
Figure 4. SEM micrographs of freezing fracture surfaces of etched PBS(a) and PBS/SE/CP blends after corrosion: (b)100/5/5, (c)100/10/10, (d)100/15/15, (e)100/20/20, ands (f)100/25/25.

from 30 MPa.[32] The PBS/GO composite was still too brittle for application because the elongation at break was below 20%. In this study, PBS was significantly toughed with a maximum elongation at break of 420.1% and its stress was relatively maintained with a little drop, as shown in Figure 5 and Table IV.
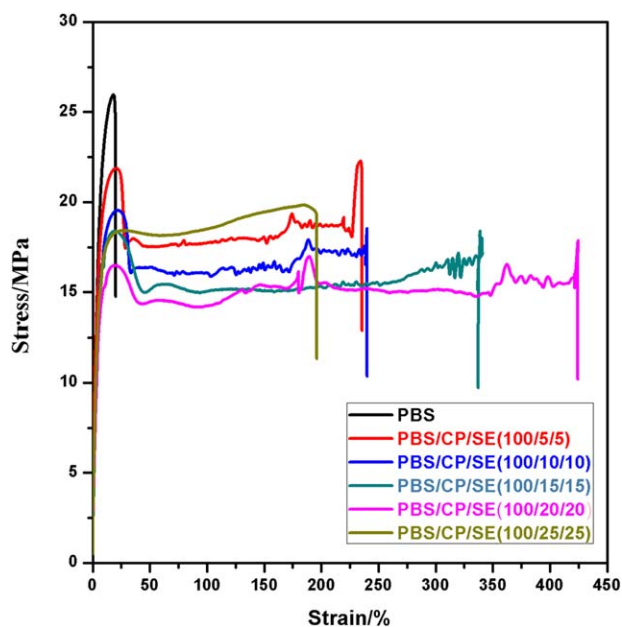

Figure 5. Tensile stress–strain curves of PBS and PBS/SE/CP blends with various SE/CP content.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The toughness effect of SE/CP on PBS could be ascribed to the plasticization and energy absorbing of partially cured SE/CP particles dispersed in PBS matrix in the case of low loading of SE/CP content. As discussed before, when the SE/CP loading was below 15/15, the partially reacted and well dispersed SE/CP particles in blends, as shown in Figure 4(a–c), could work as "plasticizers" to absorb the external energy. Meanwhile, the relative high degree of PBS crystallinity, as presented in Table III, could compensate the yield strength drop for SE/CP "plasticization effect," so the yield strength was not decreased too much.

When the incorporation of SE/CP was over 15/15, the cured network hindered the crystallization process of PBS, and then enabled chain segment fixed in the crystalline before to respond the stress through the chain segment motion and conformation adjustment. Actually, the elongation at break and impact strength of PBS/SE/CP blends went up all the time with increasing SE/CP content and decreasing PBS crystallinity. However, the over crosslinking, just as in the case of 100/25/25 PBS/SE/CP, would increase the rigidity of chain segment and disable the motion of chain segment, thus a decline in elongation at break and impact strength. Moreover, for 100/15/15, 100/20/20 PBS/SE/CP systems, the elongation at break had been improved much dramatically compared with other PBS/SE/CP system. This might be attributed to the well developed co-continuous phase structure in these two systems, as shown in Figure 4(d,e). A synergistic effect might exist for the well dispersed and interpenetrated cured SE/CP particles and PBS to better absorb external energy and improve the toughness of PBS/SE/CP blends.

Table IV. Mechanical Properties of PBS and PBS/SE/CP blends

PBS/SE/CP blends	Yield strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)
100/0/0	25.6	11.4	8.5
100/5/5	21.2	227.2	11.4
100/10/10	19.7	232.2	12.4
100/15/15	18.6	329.7	14.8
100/20/20	16.5	420.1	18.7
100/25/25	19.4	187.3	12.1

CONCLUSIONS AND OUTLOOK

In this article, we reported the fabrication of PBS/SE/CP blends by a simple compressing molding method. The effects of SE/CP on the properties of PBS were studied by Rheometer, DSC, POM, SEM, and tensile test machine. All results implied that the *in-situ* reaction between SE, CP, and PBS did exist, and the reaction degree determined by the SE/CP content had a remarkable influence on the PBS property. At a SE/CP loading of over 15/15, the complete reacted SE/CP would enhance the viscosity of PBS dramatically (three orders of magnitude) and modify the brittleness of PBS.

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