

Biocompatibility and characterization of polylactic acid/styrene-ethylene-butylene-styrene composites

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Abstract. Polylactic acid (PLA)/styrene-ethylene-butylene-styrene (SEBS) composites were prepared by melt blending. Differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WXRd) were used to characterize PLA and PLA/SEBS composites in terms of their melting behavior and crystallization. Curves from thermal gravimetric analysis (TGA) illustrated that thermostability increased with SEBS content. Further morphological analysis of PLA/SEBS composites revealed that SEBS molecules were not miscible with PLA molecules in PLA/SEBS composites. The tensile testing for PLA and PLA/SEBS composites showed that the elongation at the break was enhanced, but tensile strength decreased with increasing SEBS content. L929 fibroblast cells were chosen to assess the cytocompatibility; the cell growth of PLA was found to decrease with increasing SEBS content. This study proposes possible reasons for these properties of PLA/SEBS composites.

Keywords: Polylactic acid (PLA), styrene-ethylene-butylene-styrene (SEBS), tensile property, biocompatibility

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1. Introduction

Tissue engineering incorporates many fields that relate to the principles of chemical, biological, and materials engineering applied to tissue regeneration. Biomaterials have been studied for various applications in tissue engineering such as various drug delivery systems, as well as scaffolds [1], or biodegradable composites designed for bone tissue [2-4]. Polylactic acid (PLA) is a well-known biodegradable thermoplastic which can be produced from renewable resources [5, 6]. PLA is a biomedical material with high biocompatibility and good mechanical properties [7, 8]. However, its brittleness and slow crystallization limit its usage in many applications. Blending PLA with other polymers [9-21], fillers [22, 23], or plasticizers [24] has been proven a feasible way to improve the processability of PLA in products or for extrusion. SEBS polymers successfully combine elastomeric properties with low processing costs. The great aging resistance of SEBS is attributed to the carbon double bond. SEBS is commercially available and possesses excellent thermostability [25] making it a prime candidate as a toughener for improving the processability and toughness of PLA. Yoo, et al. [26] proposed maleated styrene-ethylene/butylene-styrene (SEBS-g-MAH) to improve the impact strength of PP/PLA. Chow, et al. [27] also posited the blending of PLA with nano-precipitated calcium carbonate composites, which was then toughened with SEBS-g-MAH. Both studies used modified SEBS to enhance the toughness of PLA. However, the biotoxicity showed a tendency to increase after modification of SEBS. To date, the biocompatibility of pure SEBS blended with PLA has not been reported.

2. Experimental

The melt flow index (MFI) of poly (L-lactide) (Nature Works 2002D), with an average molecular weight of ~200000, was 4-8 g/10 min (190°C/2.16 kg, ASTM D1238). The MFI of styrene-ethylene-butylene-styrene (SEBS) (6152H), supplied by TSRC Co. Ltd., Taiwan, was 4-8 g/10 min (190°C/2.16 kg, ASTM D1238). Various ratios of PLA/SEBS blends were prepared by melt mixing using a Brabender Plasticorder PLE 331 (Brabender, Germany) at 60 rpm and 190°C for 5 minutes. Thermal gravimetric analysis (TGA), WXR, and DSC methods were employed to characterize PLA and its blends with SEBS. TGA was processed at a rate of 20°C/min. For DSC, the temperature increased at the rate of 20°C/min to observe cold crystallization. The specimen morphology was observed by Hitachi scanning electron microscope (SEM) (model SU1510). Specimens were fixed on a sample holder with a conductive double-sided adhesive tape and were then coated with a thin layer of gold to improve the image resolution. The samples were photographed at 2.0 K magnification. The tensile property was measured by universal testing machine (model QTest 5). Testing was conducted with ASTM D638. Specimen film dimensions were 45 mm × 8 mm × 0.2 mm (L × W × T). For WXR, CuK α radiation was utilized at an operating voltage of 35 KV, a current of 30 mA, and a scan rate of 1°/min in the range of 10-30°C. The cell culture reactions of PLA, PLA/SEBS, and SEBS were evaluated by in vitro cell culture test, with mouse L929 fibroblast cells were used as a test model.

3. Results and discussion

3.1. Thermal gravimetric analysis (TGA)

Figure 1 displays the TGA curves for PLA, PLA/SEBS-10, PLA/SEBS-30, and SEBS. It illustrates a thermostability increase with the addition of SEBS as the additive thermostability is higher. It is because the thermostability of SEBS is better than that of PLA. It is reasonable that the thermodegrada-

tion temperature of pure SEBS is significantly higher than that of PLA and PLA/SEBS composites. Table 1 lists the characteristic TGA values, indicating that the temperature of the composites at 5% and 10% weight losses and the char residue at 400 °C significantly increase with the amount of SEBS.

3.2. Differential scanning calorimetry (DSC)

Figure 2 demonstrates that the T_g of PLA decreases slightly with the addition of SEBS. It might be that the lower T_g of SEBS weakens the T_g of PLA. Furthermore, PLA/SEBS composites appear to exhibit smaller exothermic cold crystallization when the SEBS content is high, as shown in Table 2, because SEBS inhibits the crystal growth of PLA. In addition, there are two peaks for T_m , which have been reported using the melt-recrystallization model [27-29]. The reason for the two T_m peaks might be the small and imperfect crystals that change continually into more stable crystals according to the melt-recrystallization mechanism. With an increasing amount of SEBS, it is possible to inhibit the integrity of crystallization. Therefore, the T_m peak area decreases at higher temperatures.

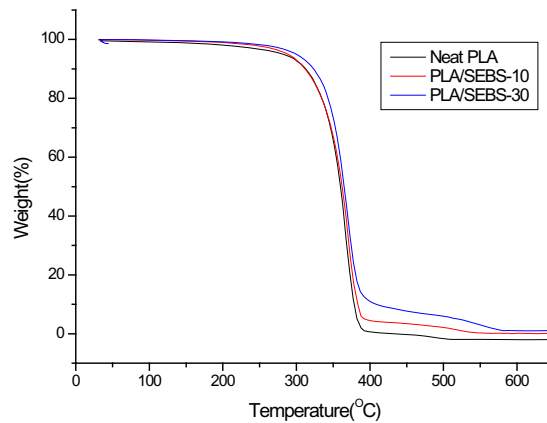


Fig. 1. TGA curves for PLA, PLA/SEBS-10, PLA/SEBS-30, and SEBS.

Table 1
TGA for PLA, PLA/SEBS-10, PLA/SEBS-30, and SEBS

Sample	Td 5 wt% (°C)	Td 10 wt% (°C)	Char residue at 400 °C
PLA	281.6	311.7	0.58%
PLA-SEBS-10	292.0	312.0	4.45%
PLA-SEBS-30	306.8	324.1	10.94%
SEBS	324.1	338.7	0.58%

Table 2
Characteristic values of the DSC curves for PLA and PLA/SEBS composites

	T_g (°C)	T_{cc} (°C)	ΔH_c	T_m (°C)	
PLA	60.2	99.8	23.49	143.8	153.7
PLA/SEBS-10	59.8	102.8	22.68	145.1	154.8
PLA/SEBS-30	59.7	111.9	21.29	145.8	154.3

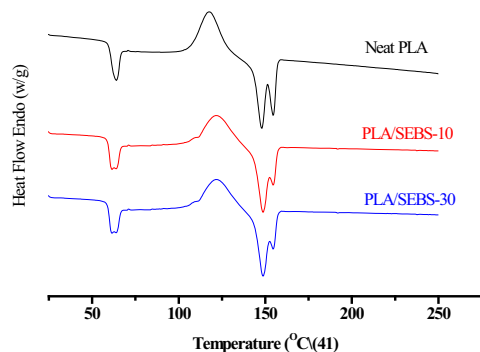


Fig. 2. DSC for PLA, PLA/SEBS-10, and PLA/SEBS-30.

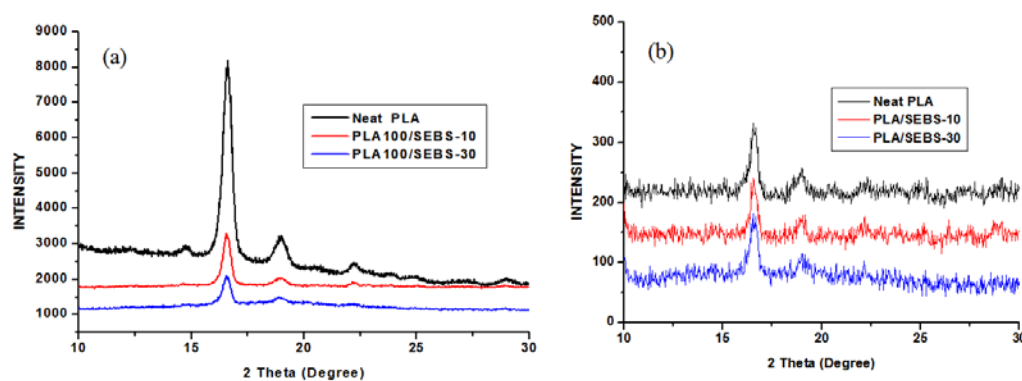


Fig. 3. (a) Cold crystallization and (b) melt crystallization of WAXRD patterns for PLA and PLA/SEBS composites.

3.3. Wide-angle X-ray diffraction (WAXRD)

As demonstrated in Figure 3, the WAXRD pattern for PLA displays two peaks 16.6° and 19.1°, which correspond to the α crystal form of PLA. Pure PLA and different PLA/SEBS composites still exhibit two important peaks at the same 2θ positions, indicating that the addition of SEBS does not alter the PLA crystal form [22]. Figure 3(a) indicates that the peak height of PLA decreases with increasing SEBS during cold crystallization, because SEBS hinders PLA crystallization. However, Figure 3(b) shows that the melt crystallization of PLA/SEBS-10 and PLA/SEBS-30 is similar to that of pure PLA.

3.4. Morphology

SEM images of the fracture surfaces of PLA and PLA/SEBS composites are shown in Figure 4. As shown in Figure 4(a), the fracture surface morphology of PLA is relatively brittle and smooth. In contrast, relatively ductile withdrawn debris was found on the fracture surface of SEBS, as shown in Figure 4(d). After blending SEBS with PLA, some SEBS droplets were found dispersed in the PLA matrix, with the SEBS content at 10 phr, as shown in Figure 4(b). These interesting morphological results further support the concept that SEBS molecules are not miscible with PLA molecules. When the

amount of SBS is 30 Phr, as shown in Figure 4(c), more phase-separated SEBS can be observed in the PLA, possibly due to incompatibility between PLA and SEBS.

3.5. Tensile property

The tensile strength and elongation at break of PLA and PLA/SEBS composites are plotted in Figure 5. The tensile strength and elongation at break of PLA are 53.9 MPa and 4.3%, respectively. After blending SEBS with PLA, PLA/SEBS composites are formed which exhibit a slight increase in elongation at break. Because SEBS is an elastic polymer, SEBS improves the toughness of PLA. In contrast, the tensile strengths of PLA/SEBS composites are decreased significantly with increasing amounts of SEBS. Their blend incompatibility results in poor tensile property, which is consistent with the result in Figures 4(a), 4(b), and 4(c).

3.6. Biocompatibility

Cell culture experiments with mouse L929 fibroblasts were used to determine the cell compatibility of PLA, PLA/SEBS-10, PLA/SEBS-30, and pure SEBS. The cells on the surface of the specimens were cultured for three days, when the actin filaments of fibroblasts on each surface were stained for cell growth assay. As shown in Figure 6, results of the cytocompatibility show that cell growth in PLA decreases slightly with an increasing amount of SEBS. The cell growths in both specimens are better than those in the SEBS specimen.

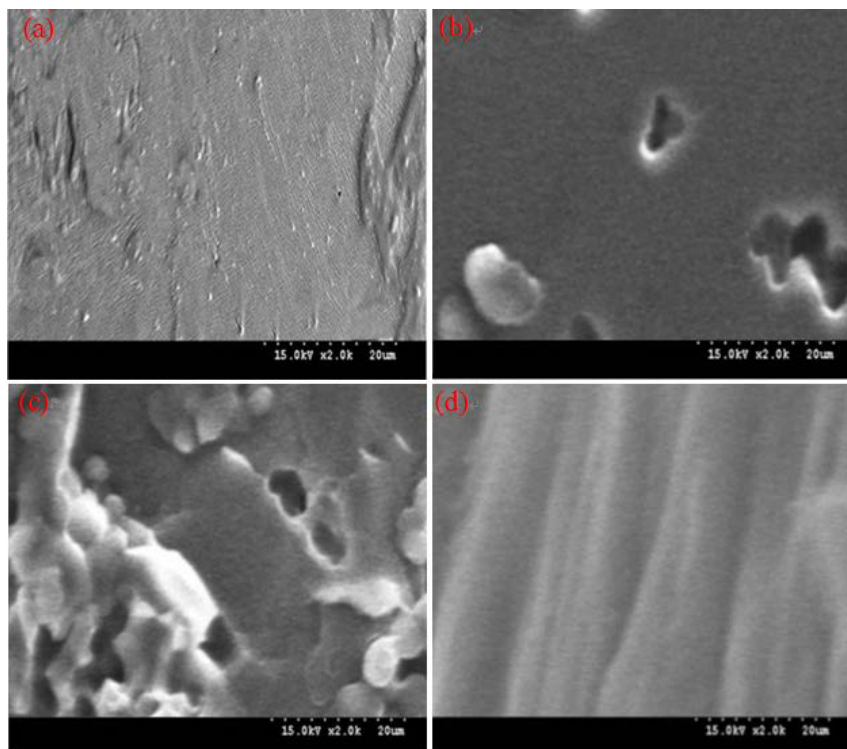


Fig. 4. SEM images of (a) PLA; (b) PLA/SEBS-10; (c) PLA/SEBS-30; and (d) SEBS.

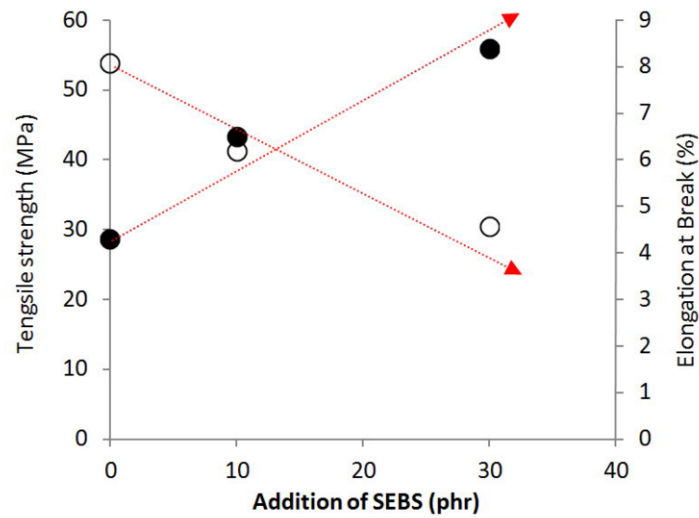


Fig. 5. Tensile properties of PLA and PLA/SEBS composites.

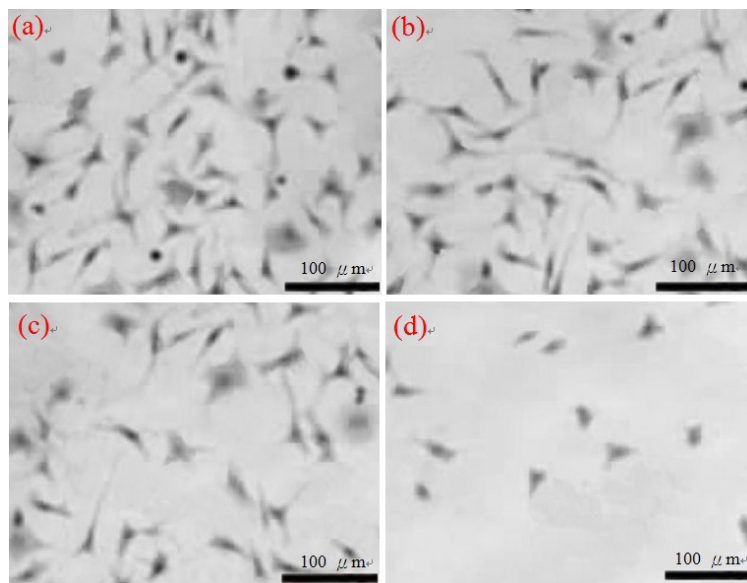


Fig. 6. Staining of fibroblast cells cultured for three days on (a) PLA; (b) PLA/SEBS-10; (c) PLA/SEBS-30; and (d) SEBS.

4. Conclusion

The melt-blending method was adopted to mix various ratios of PLA and SEBS using a Brabender Plasticorder. TGA values demonstrated that the thermostability of PLA/SEBS composites increased with the addition of SEBS, as the thermodegradation temperature of pure SEBS is higher than that of pure PLA. WXRd results indicated that adding SEBS to PLA did not change the characteristic peaks and crystal form of PLA; the intensity of the characteristic peaks was reduced with the addition of SEBS for cold crystallization, but the intensity of all specimens was similar for melt crystallization.

The elongation at break was improved while the tensile strength was reduced with an increasing amount of SEBS. The cytocompatibility of pure PLA and PLA/SEBS composites was determined to be better than that of SEBS specimen alone.

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