Synthesis of Poly(L-lactide)-*b*-poly(ethylene glycol)-*b*-poly(L-lactide) Bioplastic with Bio-based Isosorbide Diester

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In situ chain-extended poly(L-lactide)-*b*-poly(ethylene glycol)-*b*-poly(L-lactide) (PLLA-PEG-PLLA) block copolymers synthesized by ring-opening polymerization of L-lactide in the presence of chain extender were more flexible than PLLA. However, flexibility of PLLA-PEG-PLLA requires further improvement to broaden its applications. Herein, plasticization of PLLA-PEG-PLLA with an isosorbide diester bio-based plasticizer (5-20 %wt) is described. PLLA/isosorbide diester blends were also prepared for comparison. The blends prepared *via* melt blending revealed that isosorbide diester showed good phase compatibility with both the PLLA and PLLA-PEG-PLLA. The addition of isosorbide diester significantly enhanced plastic deformation of cryo-fracture surfaces for PLLA-PEG-PLLA-based blends whereas the plastic deformation was started at 20 %wt isosorbide diester for PLLA-based blends. Crystallization properties and thermal stability of PLLA-PEG-PLLA greatly improved after the addition of isosorbide diester but did not increase the thermal stability for PLLA-based blends. The strains at break of the PLLA-PEG-PLLA-based blends containing 5 %wt, 10 %wt and 20 %wt isosorbide diester were 89.9%, 145.3% and 110.5%, respectively: these were higher than the pure PLLA-PEG-PLLA (59.8%). The plastic deformation, thermal stability and strain at break of the PLLA-PEG-PLLA-based blends increased greatly with content of isosorbide diester, reaching a maximum at 10 %wt isosorbide diester. Therefore, isosorbide diester is promising as a bio-based plasticizer for PLLA-PEG-PLLA to produce highly flexible PLLA-based bioplastics.

Keywords: Poly(lactic acid), Block copolymer, Plasticization, Crystallization properties, Mechanical properties.

INTRODUCTION

Poly(L-lactide)-*b*-poly(ethylene glycol)-*b*-poly(L-lactide) (PLLA-PEG-PLLA) block copolymers are PLLA-based bioplastics that are more flexible and susceptible to faster biodegradation than PLLA due to flexible and hydrophilic PEG middle-blocks [1-3]. Melt strength of PLLA-PEG-PLLA was adjusted for conventional melt processing by post reactive blending with chain extender [4] and by *in situ* polymerization in the presence of chain extender [1]. The advantages of the latter method are that it is more energy- and time-efficient as well as more convenient because the chain extender is added during the polymerization process. However, the flexibility of *in situ* chain-extended PLLA-PEG-PLLA was less than the post reactive chain-extended PLLA-PEG-PLLA because some cross-linking structures were formed [1]. Therefore, improvement

of PLLA-PEG-PLLA flexibility is an important factor required to broaden its applications.

Many environmental friendly plasticizers such as PEG [5-8], epoxidized soybean oil [7], epoxidized palm oil [9] and isosorbide diester (Polysorb™ ID) [10,11] have been used to improve flexibility of PLLA. Polysorb™ plasticizers are phthalate-free bio-based plasticizers that are blends of diesters obtained from esterification of isosorbide with plant-based fatty acids [12], which are non-toxic and fully biodegradable plasticizers [12,13]. Their properties can be tailored by adjusting alkanoic acid types. Polysorb™ plasticizers also showed good compatibility with PLA [10,11]. However, the use of Polysorb™ plasticizers for PLLA-PEG-PLLA has not been reported.

In this work, the effect of Polysorb™ plasticizer on the thermal and mechanical properties of PLLA-PEG-PLLA is investigated by differential scanning calorimetry (DSC) and

tensile testing, respectively. The thermal decomposition behaviours and phase morphology of the blends were also determined by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), respectively. The PLLA/Polysorb blends were also prepared for comparison.

EXPERIMENTAL

A chain-extended PLLA-PEG-PLLA block copolymer was synthesized through ring-opening polymerization of L-lactide monomer at 165 °C for 6 h [14]. PEG with molecular weight of 20,000 (Carlo Erba) was used as an initiator. Stannous octoate (95%, Sigma) was used as a catalyst and Joncryl ADR 4368 (BASF) was used as a chain extender. Number-average molecular weight (M_n) and dispersity (Đ) of the obtained PLLA-PEG-PLLA were 108,500 and 2.2, respectively [14]. Isosorbide diesters (Polysorb™ ID46, Roquette) and PLLA with M_n of 93,200 and Đ of 1.7 (3251D, NatureWorks) [15] were used without further purification.

Preparation of blends: The PLLA-PEG-PLLA was dried in a vacuum oven at 80 °C overnight to remove moisture before melt blending with a Polysorb plasticizer (0, 5, 10 and 20 wt.%) at 190 °C in an internal mixer (HAAKE Polylab OS Rheomix batch mixer) for 5 min. Rotor speed was 100 rpm. Compression molding of PLLA-PEG-PLLA-based blends was carried out using a hot-press machine (Auto CH Carver) by heating at 180 °C without compression force for 4 min. The blends were then hot pressed at 180 °C under 10 MPa compression force for 1 min. The blends were then cooled using a water-cooled press under 10 MPa compression force for 1 min. The size of blend films was 100 mm × 100 mm × 0.2 mm. PLLA/Polysorb blends were also prepared by the same method for comparison.

Characterization of blends: The thermal transition properties of the blends were evaluated using a Pyris Diamond differential scanning calorimeter (DSC, Perkin-Elmer) under nitrogen gas flow. For DSC heating scans, the blend was first melted at 200 °C for 2 min to destroy the prior thermal history before quenching to 0 °C. Subsequently, the blend was scanned from 0 to 200 °C at a heating rate of 10 °C/min under a nitrogen gas flow. The degree of crystallinity (X_c) of blend was calculated using eqn. 1:

$$X_c\ (\%) = \frac{\Delta H_m - \Delta H_{cc}}{93 \times W_{PLLA}} \times 100 \qquad (1)$$
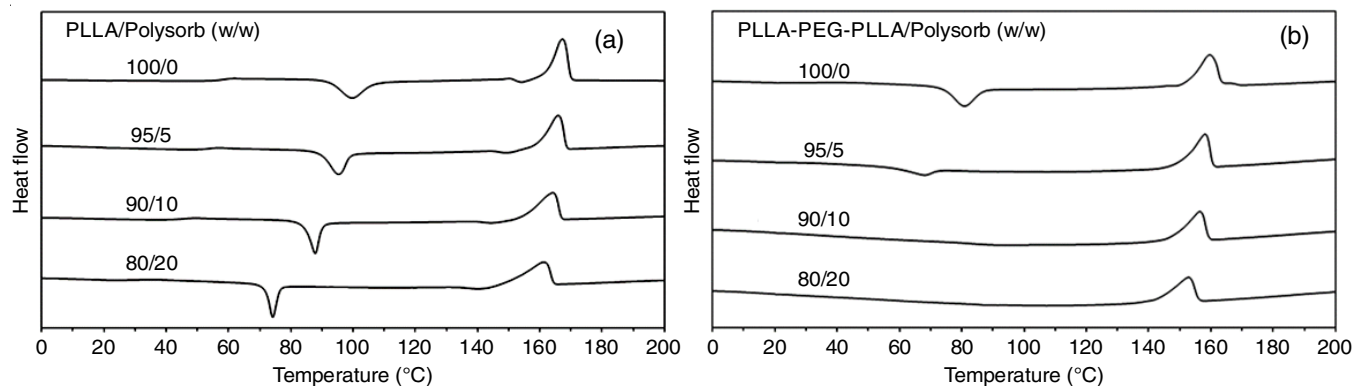
where ΔH_m and ΔH_{cc} are the melting and cold-crystallization enthalpies, respectively. The ΔH_m of 100% X_c PLLA is 93 J/g [16] and W_{PLLA} is the weight fraction of PLLA phase.

For DSC cooling scans, the blend was melted at 200 °C for 2 min to erase the prior thermal history. The blends were then scanned from 200 to 0 °C at a cooling rate of 10 °C/min under a nitrogen gas flow.

The thermal decomposition behaviours of the blends were investigated using a SDT Q600 thermogravimetric analyzer (TGA, TA-Instrument). TGA was carried out from 50 to 1000 °C at a heating rate of 20 °C/min under a nitrogen gas flow.

The tensile properties of the blend films with a size of 100 mm × 10 mm were tested at 25 °C using a LY-1066B universal mechanical tester (Dongguan Liyi Environmental Technology Co., Ltd.) according to ASTM D882. The gauge length of the sample was 50 mm, the crosshead speed was 50 mm/min and the load cell was 100 kg. The tensile results were obtained as the average value of five samples.

RESULTS AND DISCUSSION

Thermal transition properties: The DSC heating thermograms of the blends are shown in Fig. 1 to investigate the thermal transition properties of the blends. The results of DSC heating scans comprising glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m) and degree of crystallinity (X_c) are summarized in Table-1. The T_g and T_{cc} of the PLLA-based blends significantly shifted to lower temperatures compared with that of pure PLLA as increasing Polysorb content. This indicates that the addition of Polysorb enhanced chain mobility for PLLA crystallization by plasticizing effect [6,17-19]. The X_c values of the PLLA-based blends containing 5 wt.%, 10 wt.% and 20 wt.% Polysorb increase to 118%, 170% and 335%, respectively. It has been reported that the plasticizing effect also increased the crystallinity content of PLLA matrix [20].

The T_g and T_{cc} of pure PLLA-PEG-PLLA were at lower temperatures than for pure PLLA because the PEG middle-blocks acted as plasticizing sites to chain mobility of the PLLA end-blocks [21,22]. However, the T_g and T_{cc} of PLLA-PEG-PLLA-based blends could not be detected when the Polysorb contents were 5 wt.% and 10 wt.%, respectively. Since, it is well-known that higher X_c polymers have larger crystalline fractions, which suppress their chain mobility for glassy-to-

Fig. 1. DSC heating thermograms of (a) PLLA/Polysorb and (b) PLLA-PEG-PLLA/Polysorb blends with various Polysorb contents

TABLE-1
THERMAL TRANSITION PROPERTIES FROM DSC HEATING THERMOGRAMS OF
PLLA-BASED AND PLLA-PEG-PLLA-BASED BLENDS

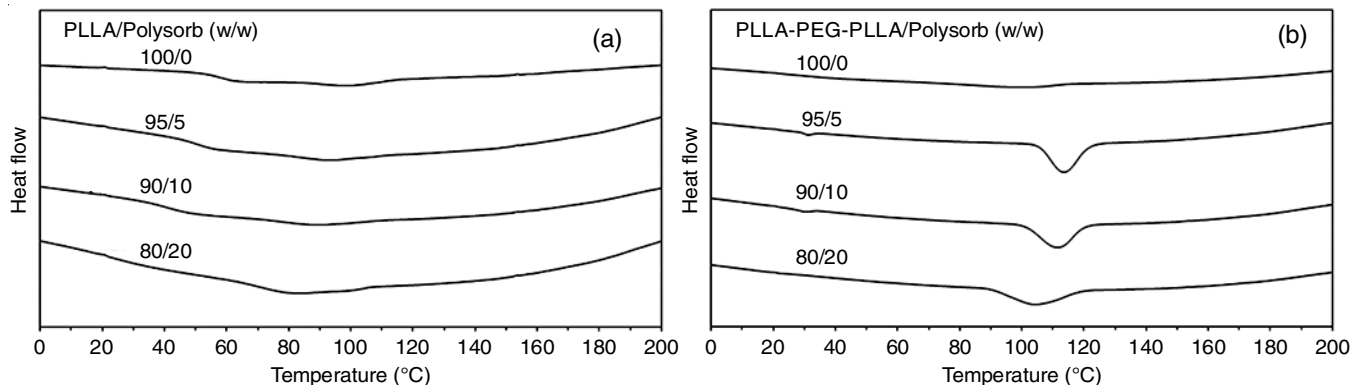| Polysorb content (%wt)	PLLA-based blends				PLLA-PEG-PLLA-based blends			
	T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)	T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)
–	58	100	167	6.0	34	81	159	12.0
5	52	95	166	13.1	–	68	158	29.7
10	43	88	164	16.2	–	–	156	40.2
20	30	74	161	26.1	–	–	153	50.4

Fig. 2. DSC cooling thermograms of (a) PLLA/Polysorb and (b) PLLA-PEG-PLLA/Polysorb blends with various Polysorb contents

rubbery transition and cold crystallization. The X_c values of the PLLA-PEG-PLLA-based blends containing 5 wt.%, 10 wt.% and 20 wt.% Polysorb increase to 147.5%, 235% and 320%, respectively. It was concluded from the X_c results that the PEG middle-blocks and added Polysorb exhibited a synergic effect for PLLA crystallization of PLLA-PEG-PLLA-based blends. The T_m peaks of both the PLLA-based and PLLA-PEG-PLLA-based blends slightly shifted to lower temperatures when the content of Polysorb increased. This was due to the blending with plasticizers causing depression of the T_m by inducing the smaller crystals of PLLA, which melt more easily [17,20,23].

The DSC cooling thermograms of the blends are illustrated in Fig. 2 to determine the crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) and the results of DSC cooling scans are summarized in Table-2. With increasing Polysorb content, the ΔH_c values of the PLLA-based blends slightly increased, demonstrating that the crystallization ability of PLLA was slightly improved. For the PLLA-PEG-PLLA-based blend containing 5 wt.% Polysorb, the T_c peak shifted to a higher temperature and value of ΔH_c dramatically increased compared to pure PLLA-PEG-PLLA, indicating that addition of Polysorb greatly enhanced PLLA chain mobility for crystallization as indicated by the cooling scan [17,24-26]. The PLLA-PEG-PLLA based blend containing 10 wt.% Polysorb had the T_c and ΔH_c values similar to 5 wt.% Polysorb addition. However, when the Polysorb content was increased up to 20 wt.%, the T_c peak shifted to a lower temperature and the ΔH_c value decreased compared with the 10 wt.% Polysorb addition. This may be due to the high Polysorb content leading to agglomeration of excessive Polysorb and to decreased plasticizing effect, which is unfavourable for PLLA crystallization during the cooling scan.

Thermal decomposition behaviours: Thermogravimetric analysis (TGA) was used to investigate the thermal decompo-

TABLE-2
THERMAL TRANSITION PROPERTIES FROM DSC
COOLING THERMOGRAMS OF PLLA-BASED
AND PLLA-PEG-PLLA-BASED BLENDS

Polysorb content (%wt)	PLLA-based blends		PLLA-PEG-PLLA-based blends	
	T_c (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_c (J/g)
–	99	5.0	99	11.5
5	92	7.7	114	31.5
10	90	8.2	113	30.9
20	82	10.7	104	28.5

sition behaviours of the blends. The thermogravimetric (TG) and differential TG (DTG) thermograms of Polysorb are shown in Fig. 3. The weight loss of Polysorb as indicated by the TG thermogram was in the range 150-400 ºC. Decomposition temperature at maximum rate ($T_{d, max}$) of Polysorb was 367 ºC as shown by the DTG thermogram.
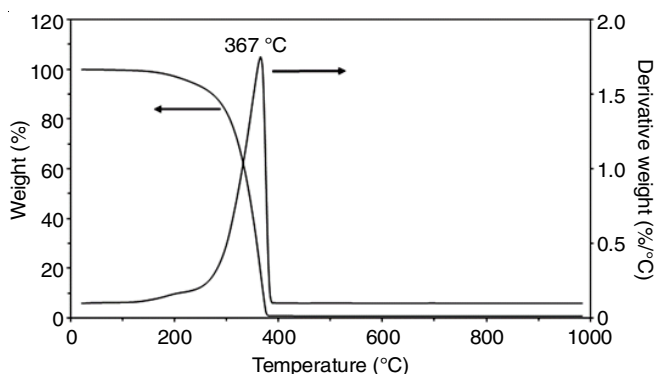

Fig. 3. TG and DTG thermograms of Polysorb ID46

Figs. 4 and 5 show the TG and DTG thermograms of the blends, respectively and Table-3 summarizes the thermal
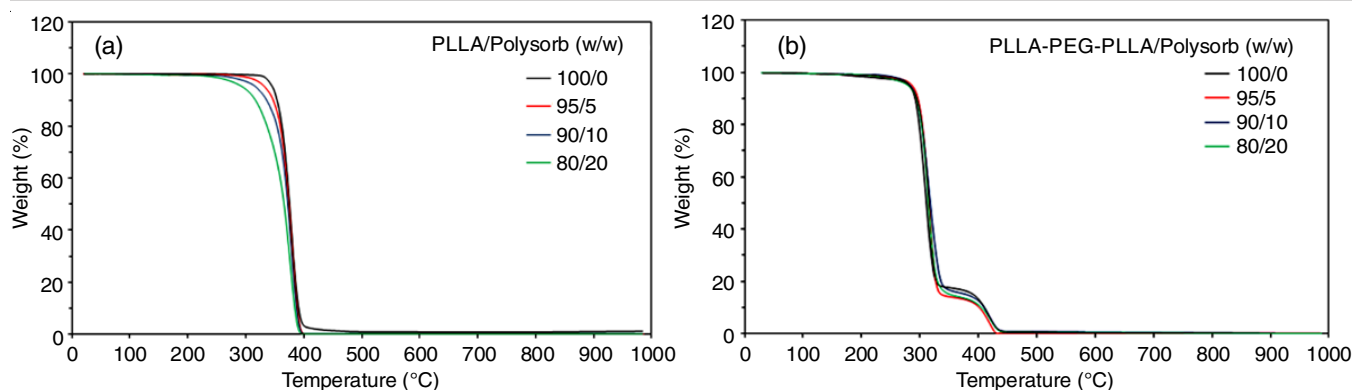
Fig. 4. Thermogravimetric curves of (a) PLLA/Polysorb and (b) PLLA-PEG-PLLA/Polysorb blends with various Polysorb contents
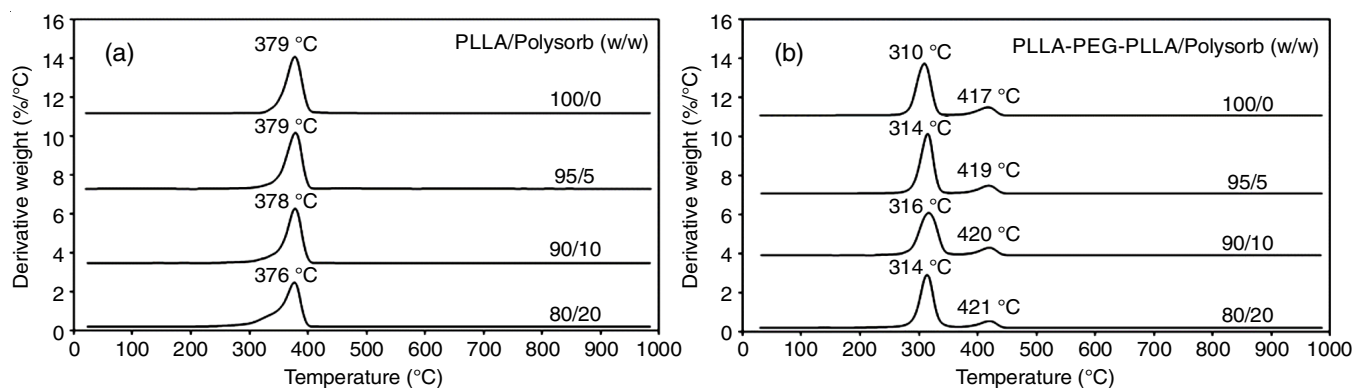

Fig. 5. DTG thermograms of (a) PLLA/Polysorb and (b) PLLA-PEG-PLLA/Polysorb blends with various Polysorb contents

TABLE-3
THERMAL DECOMPOSITION BEHAVIOURS OF PLLA-BASED AND PLLA-PEG-PLLA-BASED BLENDS

Polysorb content (%wt)	PLLA-based blends			PLLA-PEG-PLLA-based blends		
	5%-T_d (°C)[a]	PLLA-$T_{d, max}$ (°C)[b]	PEG-$T_{d, max}$ (°C)[b]	5%-T_d (°C)[a]	PLLA-$T_{d, max}$ (°C)[b]	PEG-$T_{d, max}$ (°C)[b]
–	345	379	–	282	310	417
5	333	379	–	285	314	419
10	318	378	–	286	316	420
20	294	376	–	280	314	421

[a]Obtained from TG thermograms; [b]Obtained from DTG thermograms.

decomposition results. Pure PLLA showed a single-step weight loss in the temperature range 350-450 °C due to unzipping of the PLLA chain-ends [8,27]. The thermal decomposition temperatures at 5% weight loss (5%-T_d) dramatically shifted to lower temperatures with increasing Polysorb content because of faster thermal decomposition of Polysorb (Fig. 3). The $T_{d, max}$ peaks of PLLA fraction (PLLA-$T_{d, max}$) slightly shifted to lower temperatures as the Polysorb content increased. This may be explained by the interactions on PLLA chains were inhibited by plasticizing effect from added Polysorb to reduce the thermal stability of PLLA matrices [7,28,29].

The pure PLLA-PEG-PLLA exhibited two-step weight losses in the ranges 250-350 °C and 350-450 °C, which were attributed to thermal decompositions of PLLA and PEG blocks, respectively [27,30]. The 5%-T_d, PLLA-$T_{d, max}$ and PEG-$T_{d, max}$ of PLLA-PEG-PLLA shifted to higher temperatures as 5 wt.% and 10 wt.% Polysorb were incorporated. This may be explained by the interactions between PLLA-PEG-PLLA and Polysorb having occurred. The shielding effect from added Polysorb

then improved thermal stability of PLLA-PEG-PLLA matrices [8,31-33]. However, according to the above DSC results, the 5%-T_d of PLLA-PEG-PLLA blend containing 20 wt.% Polysorb shifted to a lower temperature because of agglomeration of excessive Polysorb.

Phase morphology: The SEM images of cryo-fractured surfaces were used to reveal the phase separation and fracture characteristics of the blends as shown in Figs. 6 and 7 for PLLA-based and PLLA-PEG-PLLA-based blends, respectively. Phase separation between film matrices and Polysorb was not detected for all the blends indicating that Polysorb had good phase compatibility with both the PLLA and PLLA-PEG-PLLA matrices [34].

The pure PLLA had a smooth fracture surface (Fig. 6a), which indicated its brittle characteristic [35,36]. The fracture surfaces of PLLA-based blends with 5 wt.% and 10 wt.% Polysorb in Figs. 6b-c, respectively, were similar to those of pure PLLA. Rough surfaces were observed for the PLLA-based blend containing 20 wt.% Polysorb in Fig. 6d and this was
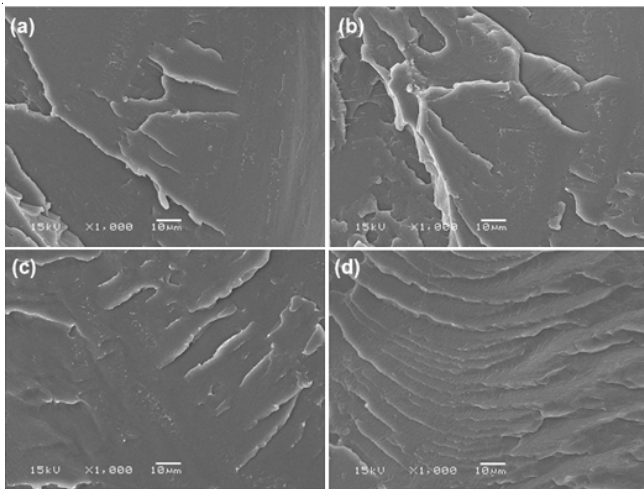
Fig. 6. SEM images of (a) pure PLLA and PLLA-based blends with Polysorb contents of (b) 5 %wt, (c) 10 %wt and (d) 20 %wt (All bar scales = 10 μm)
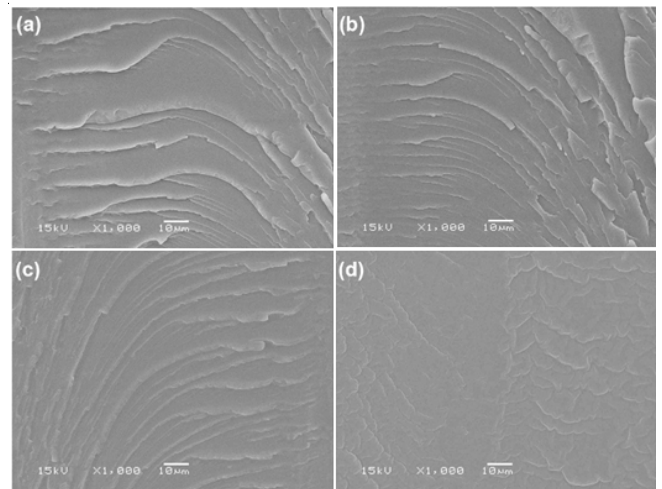

Fig. 7. SEM images of (a) pure PLLA-PEG-PLLA and PLLA-PEG-PLLA-based blends with Polysorb contents of (b) 5 %wt, (c) 10 %wt and (d) 20 %wt (All bar scales = 10 μm)

related to plastic deformation [6,9,22]. A rough surface was observed for pure PLLA-PEG-PLLA as shown in Fig. 7a indicative of a typical ductile fracture. The fracture surfaces become rougher as 5 wt.% and 10 wt.% Polysorb were incorporated as shown in Fig. 7b-c, respectively, thereby indicating that the plastic deformation areas had increased due to the addition of Polysorb. However, the roughness of fracture surfaces diminished when the Polysorb content increased up to 20 wt.% (Fig. 7d). This may be due to excessive Polysorb becoming agglomerated according to the above DSC and TG results, resulting in decreased plasticizing effect. However, phase separation was not clearly observed for all the PLLA-based and PLLA-PEG-PLLA-based blends.

Mechanical properties: The mechanical properties of the blends were investigated from tensile curves as displayed in

Fig. 8. The tensile results are summarized in Table-4. Pure PLLA with a strain at break of 2.9% was hard and brittle. The addition of Polysorb decreased both the stress at break and Young's modulus of the PLLA films because the plasticizing effect suppressed the intermolecular forces of PLLA chains [37,38]. The addition of 5 wt.% and 10 wt.% Polysorb showed no effect regarding the strain at break of PLLA whereas the strain at break increased to 60.6% when the 20 wt.% Polysorb was incorporated according to the above SEM results.

Pure PLLA-PEG-PLLA films had a strain at break of 59.8%. The addition of Polysorb significantly decreased both the stress at break and Young's modulus of the PLLA-PEG-PLLA films as well as increasing the strain at break. The results indicated that the Polysorb acted as a plasticizer for both the PLLA and PLLA-PEG-PLLA. It should be noted that 5 wt.%
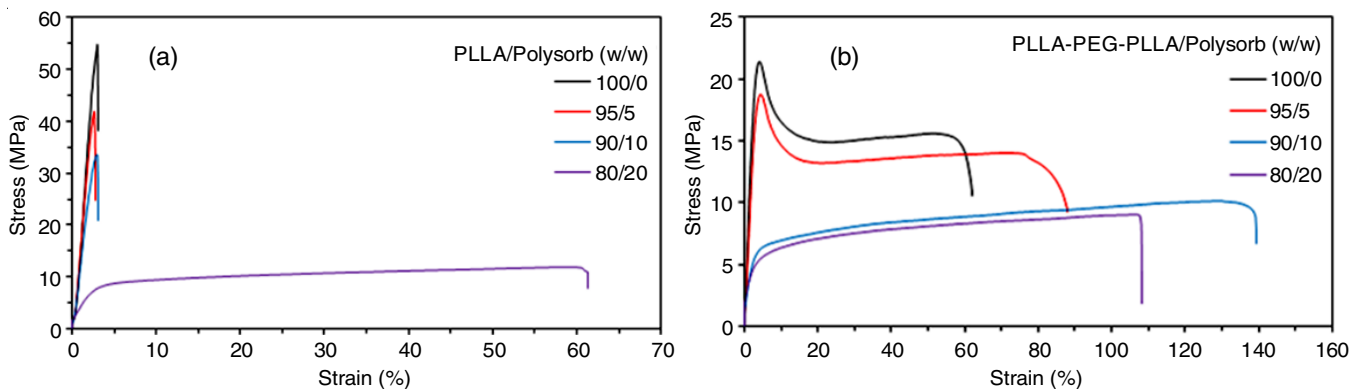

Fig. 8. Tensile curves of (a) PLLA/Polysorb and (b) PLLA-PEG-PLLA/Polysorb blends with various Polysorb contents

TABLE-4
MECHANICAL PROPERTIES OF PLLA-BASED AND PLLA-PEG-PLLA-BASED BLENDS

Polysorb content (%wt)	PLLA-based blends			PLLA-PEG-PLLA-based blends		
	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)
–	52.8 ± 5.2	2.9 ± 1.1	837 ± 21	17.4 ± 2.5	59.8 ± 15.6	311 ± 32
5	46.2 ± 4.8	3.1 ± 1.2	680 ± 17	16.1 ± 1.6	89.9 ± 17.4	315 ± 21
10	34.5 ± 4.5	2.8 ± 1.1	534 ± 24	11.2 ± 1.2	145.3 ± 21.2	79 ± 13
20	12.7 ± 3.6	60.6 ± 3.8	123 ± 12	9.1 ± 1.7	110.5 ± 18.3	57 ± 14

and 10 wt.% Polysorb can increase the strain at break for PLLA-PEG-PLLA but did not increase for PLLA. However, the strain at break of PLLA-PEG-PLLA blend films decreased from 145.3% to 110.5% when the Polysorb content increased from 10 wt.% to 20 wt.% because of agglomeration of excessive Polysorb leading to films fracturing easily, according to the above SEM results. It can be concluded from the tensile results that the Polysorb more effectively enhanced plasticization to increase film extensibility for PLLA-PEG-PLLA than for PLLA.

Conclusion

In this work, the plasticization properties of PLLA-PEG-PLLA/Polysorb blends were compared with those of PLLA/Polysorb blends. The blends containing Polysorb plasticizer (5-20 wt.%) were prepared by melt blending using an internal mixer. The DSC results showed that the crystallizability and crystallinity content of PLLA-PEG-PLLA matrix were greatly improved by the incorporation of Polysorb. The addition of Polysorb significantly improved the thermal stability of the PLLA-PEG-PLLA but did not improve for PLLA, as investigated by TGA technique. The SEM images showed that Polysorb exhibited good phase compatibility with both PLLA and PLLA-PEG-PLLA matrices. A rough fracture surface of PLLA-based blend related to plastic deformation was observed as 20 wt.% Polysorb was added. The plastic deformation of PLLA-PEG-PLLA-based blends increased with the Polysorb content until 20 wt.% Polyosrb was blended. Compared with the pure PLLA-PEG-PLLA (59.8%), the strain at break of blends were 89.9% and 145.3% when the Polysorb contents were 5 wt.% and 10 wt.%, respectively, as determined by tensile tests. The strain at break of PLLA (2.9%) was not insignificantly changed when 5 wt.% and 10 wt.% Polysorb were added. These results suggest that Polysorb may be a promising effective bio-based plasticizer for the PLLA-PEG-PLLA blends in highly flexible bioplastic applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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