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Effect of poly(ethylene glycol) end groups on properties of plasticized poly(L-lactide) bioplastic films

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ABSTRACT

Poly(L-lactide) (PLLA) film has received much attention in food packaging because of its biodegradability and that it is produced from renewable resources. The rigid PLLA films need to be plasticized for use as soft films. In this paper, polyethylene glycol (PEG) with hydroxyl (PEG-OH) and carboxyl (PEG-COOH) end groups for blend ratios of 5%, 10%, 15% and 20%wt. were used for plasticizing the PLLA films. The influence of PEG end groups on morphology, thermal properties and mechanical properties of the PLLA blend films were investigated. The phase separation occurred as pore structures for both PLLA/PEG-OH and PLLA/PEG-COOH blend films. The glass transition temperature and thermal stability of PLLA blend films significantly decreased as the PEG-OH blend ratio increased but did not for the PEG-COOH blending higher than 5%, which indicated a greater degree of interaction between PLLA and PEG-COOH. The elongation at break of PLLA blend films were largely and slightly increased with the PEG-OH and PEG-COOH blend ratios, respectively.

Keywords: Biodegradable polymers; poly(L-lactide); poly(ethylene glycol); plasticization, morphology; thermal properties; mechanical properties.

1. Introduction

Poly(L-lactide) (PLLA) has received much attention for use as a substitute for commodity plastics due to its biodegradability, renewability, good processing ability and good mechanical properties [1–3]. However PLLA has a high glass transition temperature ($T_g \approx 55$ °C) that leads to brittleness in PLLA products [4], which limits its practical applications. The flexibility of PLLA can be enhanced either by copolymerization [5] or by blending PLLA with other substances and polymers [6–9]. The blending method is an easy method, which is less expensive and fast for plasticization of PLLA.

Polyethylene glycol (PEG) has been widely used as a plasticizer for PLLA due to its biodegradability and food contactable applications [10, 11]. The PLLA/PEG blends have a lower glass transition temperature, higher elongation and lower tensile strength [10]. Influences of PEG molecular weight and blend ratio have been extensively investigated. However, the effects of the end groups of PEG, such as hydroxyl and carboxyl, have not been reported.

In the present work, the PLLA and PEG were blended in various blend ratios via solution blending before film casting. The objective of this paper was to study the effect of PEG end groups (hydroxyl and carboxyl) on the morphological, thermal and mechanical properties of the PLLA films.

2. Experimental

2.1 Materials

The poly(L-lactide) (PLLA) was synthesized by ring-opening polymerization of a L-lactide monomer in bulk at 165 °C for 2.5 h under a nitrogen atmosphere using 0.01 mol% stannous octoate (95%, Sigma) and 0.14 mol% 1-dodecanol (98%, Fluka) as the initiating system. The obtained PLLA was purified by being dissolving in chloroform before precipitation in cool n-hexane and drying in a vacuum oven at room temperature for a week. The intrinsic viscosity ($[\eta]$) and viscosity-average molecular weight (M_v) of the PLLA were determined in chloroform at 25 °C, and were 2.53 dL/g and 104,700 g/mol, respectively. All reagents used were analytical grade. Poly(ethylene glycol) with hydroxyl end groups (PEG-OH, molecular weight of 600, Sigma-Aldrich) and carboxyl end groups (PEG-COOH, molecular weight of 600, Fluka) were used as plasticizers.

2.2 Preparation of plasticized PLLA films

The PLLA/PEG blend films were obtained via solution blending before film casting. The PLLA and PEG were completely dissolved in 50 mL of chloroform at a concentration of 1 g/dL at room temperature under magnetic stirring for 30 min. The blend solution was then cast onto a Petri dish followed by solvent evaporation at 40 °C in an air oven for 24 h. The blend film was then dried in a vacuum oven at 70 °C for 48 h to remove any residue solvent. The blend films with PEG contents of 5%, 10%, 15% and 20% wt. were investigated. The neat PLLA film was also prepared by the same method for comparison.

2.3 Characterization of plasticized PLLA films

The phase morphology of the PLLA films was determined using a JEOL JSM-6460LV scanning electron microscope (SEM). For the SEM observation, samples were prepared by cryofracture under liquid nitrogen. The sample was then sputter coated with gold to enhance the conductivity before scanning.

The thermal transition properties of the PLLA films were determined with a Perkin-Elmer Pyris Diamond differential scanning calorimeter (DSC) under a nitrogen flow. For DSC, samples of 3 – 5 mg in weight were heated at 10 ^{o}C/min to 200 °C before quenching to 0 °C. The second heating was then scanned from 0 – 200 °C at 10 ^{o}C/min to detect their glass transition temperature (T_g), crystallizing temperature (T_c), heat of crystallization (ΔH_c), melting temperature (T_m) and heat of melting (ΔH_m).

The thermal stability of the PLLA films was determined with a TA-Instrument SDT Q600 thermogravimetric analyzer (TGA) in a non-isothermal mode. For TGA analysis, samples of 5 – 10 mg in weight were heated at 20 °C/min under a nitrogen atmosphere over the temperature range 50 to 800 °C to assess their temperature of maximum decomposition rate ($T_{d,\ max}$).

Mechanical properties, including stress at break, elongation at break and initial Young’s modulus, of the PLLA films were determined at 25 °C and 65% relative humidity with a Lloyds LRX+ Universal Mechanical Testing Machine. The film samples (80 × 10 mm) were tested with a gauge length of 25 mm and a crosshead speed of 10 mm/min. The mechanical properties were determined from the average of five measurements for each sample.

3. Results and discussion

3.1 Phase morphology of blend films

The phase morphology of the blend films was determined from SEM images of the cryogenic fractured surfaces of the blend films as shown in Figs. 1 and 2 for the PLLA/PEG-OH and PLLA/PEG-COOH blend films, respectively. The neat PLLA film showed a smooth fractured surface. All the blend film matrices contained pore structures in the PLLA continuous phase. This may be due to the polarities of the hydrophobic PLLA and hydrophilic PEG phases being different. The pore sizes increased as the PEG blend ratio increased indicated that more phase separation occurred.

In addition, the pore sizes of PLLA/PEG-OH blend films being smaller than those of the PLLA/PEG-COOH blend films for the same blend ratio suggested that the carboxyl end groups of PEG-COOH induced more phase separation.

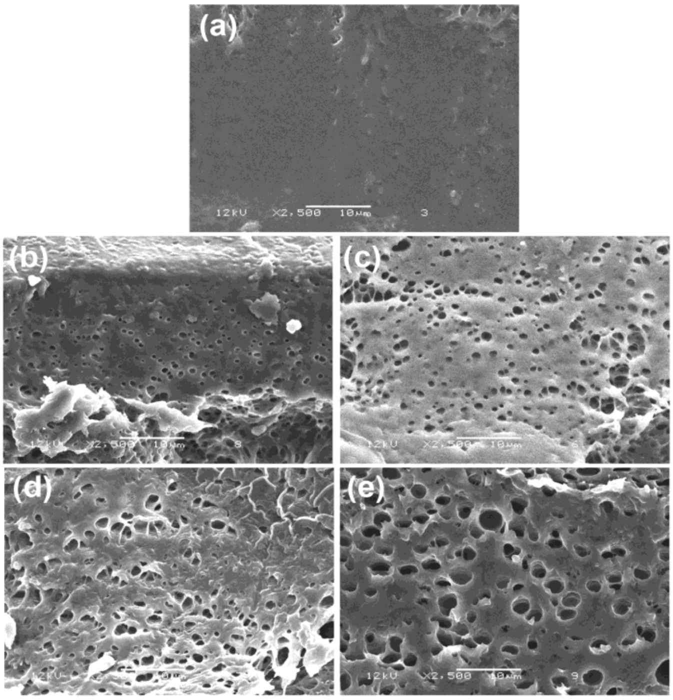

Fig. 1 SEM images of film fractures of (a) neat PLLA and PLLA blended with PEG-OH ratios of (b) 5%, (c) 10%, (d) 15% and (e) 20% wt. All bars = 10 µm.

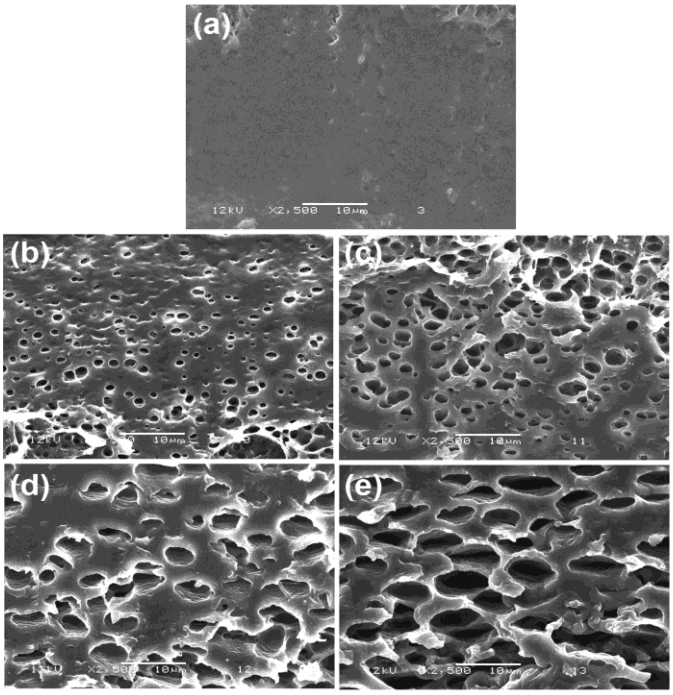

Fig. 2 SEM images of film fractures of (a) neat PLLA and PLLA blended with PEG-COOH ratios of (b) 5%, (c) 10%, (d) 15% and (e) 20% wt. All bars = 10 µm.

3.2 Thermal properties of blend films

The thermal transition properties of the blend films were investigated from DSC thermograms as illustrated in Fig. 3. They exhibited T_g, T_c and T_m peaks of the PLLA film matrix. The DSC results are summarized in Table 1. The T_g, T_c and ΔH_c of the neat PLLA film were 53 °C, 99 °C and 32.2 J/g, respectively. The T_g, T_c and ΔH_c of the PLLA film matrix decreased steadily as the PEG-OH blend ratio increased. The PEG molecules penetrated between the PLLA molecules and increased the free volume of the PLLA film matrix. The T_g of PLLA then decreased that indicated the plasticization action had occurred [12, 13]. The PLLA plasticized with PEG easily rearranged for crystallization. The T_c and ΔH_c of PLLA were also decreased. The T_g, T_c and ΔH_c of the PLLA film matrix also decreased after blending with 5%wt. PEG-COOH. However, the T_g and T_c did not change when the PEG-COOH blend ratio was higher than 5% wt. This may be explained by the carboxyl end groups of PEG-COOH interacting with PLLA. The T_m and ΔH_m of the PLLA matrix did not show significant changes after PEG-OH and PEG-COOH blending.

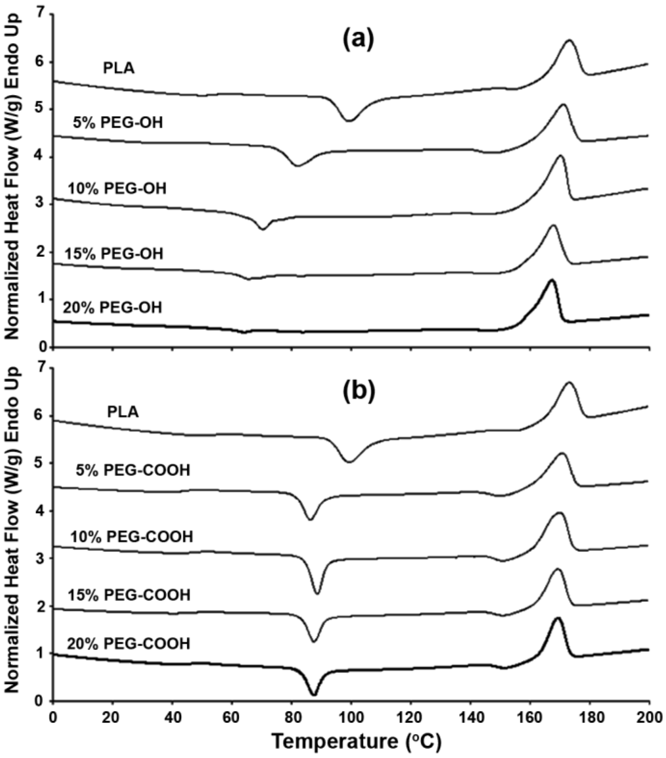

Fig. 3 Second heating scan DSC thermograms of PLLA films blended with (a) PEG-OH and (b) PEG-COOH for various blend ratios.

Table 1 Thermal transition properties of plasticized PLLA from DSC thermograms.

Plasticizer content (%wt.)	Tg (°C)	Tc (°C)	ΔHc (J/g)	Tm (°C)	ΔHm (J/g)
0	53	99	32.2	173	45.8
PEG-OH					
5	41	82	24.2	171	47.4
10	32	70	14.4	170	46.8
15	30	65	5.6	168	46.3
20	27	64	2.0	168	45.8
PEG-COOH					
5	44	88	24.8	171	45.2
10	44	88	24.2	169	43.4
15	44	88	18.1	169	41.5
20	44	88	18.6	169	42.9

Thermal decomposition behaviors of the blend films and PEG were determined from derivative thermogravimetry (DTG) thermograms as shown in Fig. 4. They have a single peak of $T_{d,\ max}$. The $T_{d,\ max}$ values of PLLA, PEG-OH and PEG-COOH were 360 °C, 404 °C and 407 °C, respectively as summarized in Table 2. The $T_{d,\ max}$ values of the blend films were lower than the neat PLLA film, and they decreased as the PEG-OH blend ratio increased. This may be explained by the PEG-OH molecules inhibiting the intermolecular forces of PLLA molecules. Thus, the PEG-OH blending decreased the thermal stability of the PLLA blend films. It should be noted that the thermal decomposition of PEG-OH was also observed as shoulder peaks at 372 °C and 376 °C for the 15% and 20% PEG-OH blend ratios, respectively.

Table 2 $T_{d,\ max}$ values of plasticized PLLA from DTG thermograms.

Sample	$T_{d,\ max}$ of PLLA (°C)	$T_{d,\ max}$ of PEG (°C)
PLLA	360	-
5% PEG-OH/PLLA	321	-
10% PEG-OH/PLLA	299	-
15% PEG-OH/PLLA	294	372
20% PEG-OH/PLLA	238	376
PEG-OH	-	404
5% PEG-COOH/PLLA	350	-
10% PEG-COOH/PLLA	353	-
15% PEG-COOH/PLLA	350	374
20% PEG-COOH/PLLA	351	381
PEG-COOH	-	407

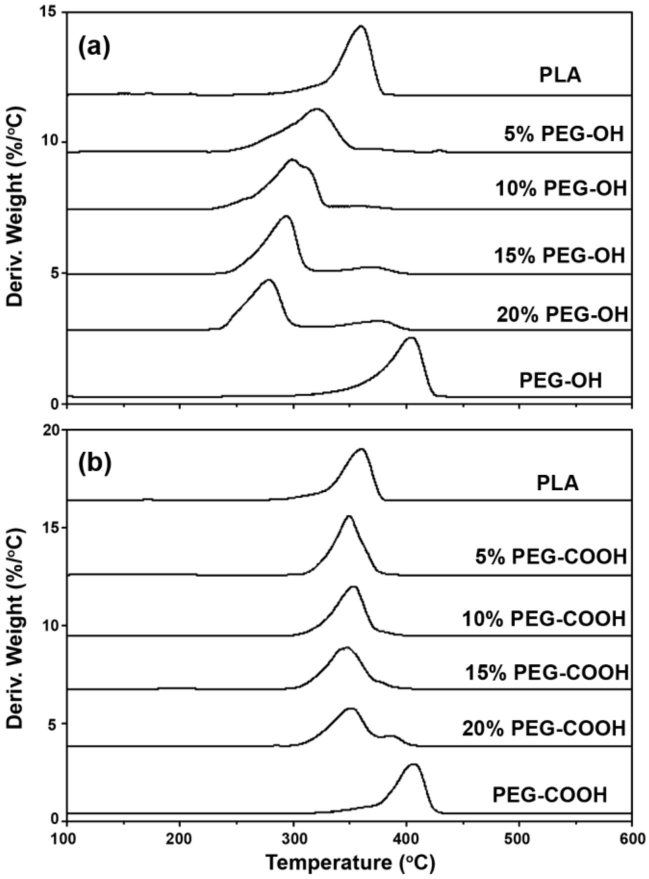

Fig. 4 DTG thermograms of PLLA films blended with (a) PEG-OH and (b) PEG-COOH for various blend ratios.

The $T_{d,\ max}$ of the PLLA film decreased from 360 °C to 350 °C after blending with 5% PEG-COOH (see Table 2). However, the $T_{d,\ max}$ of the blend film did not significantly change when the PEG-COOH blend ratio was higher than 5%. This may be due to interactions between the PEG-COOH and PLLA molecules being formed. Then the thermal stability of the PLLA matrix did not decrease.

3.3 Mechanical properties of blend films

Fig. 5 presents the tensile properties of the blend films compared to the neat PLLA film. It is clearly seen that the tensile strength at break and Young's modulus of the blend films decreased and elongation at break increased as the PEG blend ratio increased. The results of the mechanical properties are attributed to the plasticizing effect of PEG-OH and PEG-COOH [14]. However, the mechanical property changes of the PLLA/PEG-COOH blend films were less than the PLLA/PEG-OH blend films. This may be due to the interactions of the PLLA/PEG-OH and PLLA/PEG-COOH blends being different.

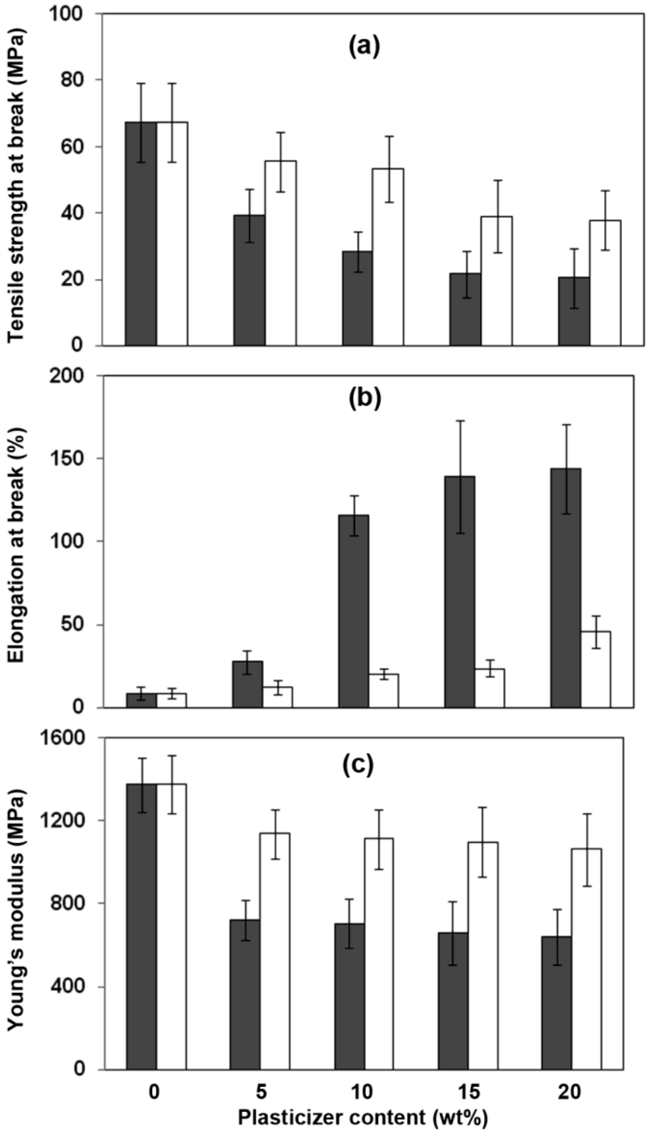

Fig. 5 (a) Tensile strength at break, (b) elongation at break and (c) Young's modulus of PLLA films blended with (■) PEG-OH and (□)PEG-COOH for various blend ratios.

4. Conclusions

Both PEG-OH and PEG-COOH can be used as plasticizers for PLLA film. The thermal and mechanical properties of the PLLA/PEG blend films strongly depended upon the end groups of PEG. The T_g of the PLLA film largely decreased and elongation at break dramatically increased when the PEG-OH was blended. However, the thermal stability of the PLLA/PEG-COOH blend films was higher than the PLLA/PEG-OH blend films for the same blend ratio. The thermal and mechanical properties of plasticized PLLA could be adjusted by varying the blend ratio and end group of the PEG plasticizer. The effect of the ageing time on the thermal and mechanical properties of the PLLA/PEG blend films is under investigation.

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