Plasticization of poly (L-lactide) bioplastic films with poly (propylene glycol)-*b*-oligo (ε-caprolactone)

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Abstract

Liquid ε-caprolactone (CL) oligomers were synthesized by a ring-opening reaction of CL using a propylene glycol (PPG) as the initiator for use as new plasticizers of poly (L-lactide) (PLA) films. PPG-CL oligomers containing two (PPG-2CL) and four (PPG-4CL) units of CL at both PPG end-chains were prepared. The PLA/oligomer blend films were prepared by solution blending before film casting. The tiny pools of the liquid plasticizer droplets were observed throughout the PLA film matrices, which indicated that a phase separation had occurred. The sizes of the plasticizer droplets increased as did the plasticizer blend ratio. The phase separations were in the order of PPG>PPG-4CL>PPG-2CL. The plasticizer blending slightly decreased the glass transition and crystallization temperatures of the PLA films. The crystallinities of the PLA films increased with the PPG-CL blend ratio but did not increase with the PPG. The PPG-CL blending improved the flexibility of the PLA films more than the PPG blending. The PPG-CL oligomers could be used as novel plasticizers for PLA films.

Keywords: poly (L-lactide); poly (propylene glycol); ε-caprolactone; oligomer; plasticizer.

1. INTRODUCTION

Poly (L-lactide) (PLA), one of the most important bioplastics, has received much attention for use as a substitute for commodity plastics because of its renewability, biodegradability, biocompatibility, good processability and good mechanical properties [1-3]. However, the high glass transition temperature ($T_g \approx 55$ °C) and the low flexibility of the PLA films have limited their applications in packaging situations

[4]. The flexibility of PLA can be enhanced by copolymerization [5] and by blending PLA with other substances and polymers [6-10]. The plasticizer blending is more convenient, more efficient, lower cost and faster compared to copolymerization.

Citrate esters are low molecular weight plasticizers that significantly reduce the T_g and improve the flexibility of the PLA films [11, 12]. However, the migration of these plasticizers from the PLA film matrix to the film surface due to their high mobility increases the T_g and reduces the film flexibility with aging, which is the main problem [13, 14]. To decrease the migration of the plasticizers on aging, high molecular weight plasticizers, such as poly (ethylene glycol) (PEG) and poly (propylene glycol) (PPG), were investigated for plasticizing PLA films [15-18]. However, phase separation occurred between the high molecular weight plasticizers and the PLA film matrices. It has been reported that tiny pools of liquid plasticizers, such as PPGs, are dispersed in the PLA film matrices and may locally plasticize PLA during plastic flow and have better effects on drawability than the crystallizable plasticizers such as PEGs [17, 18]. The PPGs have also been shown to give efficient plasticization to improve the flexibility of the PLA.

Semi-crystalline poly (ε-caprolactone) (PCL) is a flexible biodegradable polyester due to its very low T_g (around-60 °C). The five methylene units of the CL units induce high chain mobility and a low T_g. PCL and CL oligomers have been investigated as biodegradable plasticizers [19, 20]. However, to the best of our knowledge, the influence of the liquid PPG-*b*-oligo (CL) blending on the flexibility of a PLA film has not been reported so far.

In the present work, the CL oligomers were synthesized using PPG as an initiator for plasticization of the PLA film. The influences of the CL chain length (two and four units) on each PPG chain and CL oligomer blend ratio (5-20 wt%) on the phase separation, thermal properties and mechanical properties of the PLA blend films were investigated. The PLA films blended with PPG were also prepared for comparison.

2. MATERIALS AND METHODS
2.1 Materials
The PLA was synthesized in our research unit at Mahasarakham University by a 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 PLA was granulated before drying in a vacuum at 110 °C for 2 h to remove any un-reacted lactide. The intrinsic viscosity ($[\eta]$) and viscosity-average molecular weight (M_v) of the PLA were determined in chloroform at 25 °C, and they were 2.53 dL/g and 104, 700 g/mol, respectively. The ε-caprolactone (CL, 99%, Acros Organics) monomer was purified by distillation under reduced pressure before use. The PPG with a molecular weight of 4, 000 g/mol (Acros Organics) was used without further purification. All reagents used were analytical grade.

2.2 Synthesis of CL oligomers

The CL oligomers were synthesized by ring-opening polymerization of the CL monomer in bulk at 145 °C for 24 h under a nitrogen atmosphere using 0.04 mol% stannous octoate and PPG as the initiating system. The resulting oligomers were purified by heating at 110 °C under a vacuum for 6 h to remove un-reacted CL monomer. The CL monomers with two and four units were reacted at each hydroxyl end-group of the PPG, giving PPG-2CL and PPG-4CL, respectively. The chemical reaction of the PPG-CL oligomers is illustrated in Scheme 1.

2.3 Characterization of CL oligomers

The molecular weight characteristics, including number-average molecular weight (M_n) and molecular weight distribution (MWD), of the CL oligomers were determined by Gel Permeation Chromatography (GPC) using a Waters e2695 separation module equipped with PLgel 10 μm mixed B 2 columns operating at 40 °C at a flow rate of 1.0 mL/min and employing a refractive index detector. Tetrahydrofuran was used as the solvent.

The chemical structures of the CL oligomers were investigated by ^{1}H-NMR spectrometry using a Varian Mercury Plus 400 MHz ^{1}H-NMR spectrometer at 25 °C with $CDCl_3$ as the solvent. Tetrametylsilane was used as the internal reference.

The thermal transition properties of the CL oligomers were determined by Differential Scanning Calorimetry (DSC) under a nitrogen flow using a Perkin-Elmer Pyris Diamond DSC to detect the glass transition temperature (T_g) and melting temperature (T_m). For the DSC, samples (3-5 mg) were heated at 10 °C/min over a temperature range of 0 to 200 °C for the 1st heating scan. Then, the samples were quenched to 0 °C according to the DSC instrument's own default cooling mode before heating from 0 to 200 °C for the 2nd heating scan. The T_g was taken as the midpoint of the heat capacity increment associated with the glass-to-rubber transition. The T_m was measured as the peak value of the endothermal phenomena in the DSC curve.

2.4 Preparation of PLA/oligomer blend films

The PLA/oligomer blend films were prepared by solution blending before film casting. Chloroform was used as a blending solvent. The blend solution (0.4 g/20 ml) was poured on to a glass petri dish and evaporated at 40 °C for 24 h before drying in a vacuum at 70 °C for 24 h. The PLA blend films with PLA/oligomer blend ratios of 95/5, 90/10 and 80/20 %wt were investigated. The neat PLA and PLA/PPG blend films were also prepared by the same method for comparison.

2.5 Characterization of PLA/oligomer blend films

The morphology of the blend films was determined by scanning electron microscopy (SEM) using a JEOL JSM-6460LV SEM. The film samples were coated with gold to enhance their conductivity before scanning.

The thermal transition properties of the blend films were investigated using the DSC method as described above to observe the T_g, T_m, crystallizing temperature (T_c), heat of crystallization (ΔH_c) and heat of melting (ΔH_m). The T_c was measured as the peak value of the exothermal phenomena in the DSC curve. The ΔH_c and ΔH_m were

calculated from the total areas of the T_c and T_m peaks, respectively. The degree of crystallinity (X_c) of the PLA phase was calculated from equation (1).

$$X_c\,(\%) = [\,(\Delta H_m - \Delta H_c)/\,(\Delta H_{m,\,100\%} \times w_{PLA})]\times 100\% \tag{1}$$

where w_{PLA} is the weight fraction of the PLA in the blend films. ΔH_m and ΔH_c are the heat of melting and heat of crystallization, respectively, which were obtained using the DSC method. The heat of melting for 100% crystallinity ($\Delta H_{m,\,100\%}$) of PLA is 93.7 J/g [14].

The mechanical properties, including stress at break, elongation at break and initial Young's modulus, of the blend 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 averaged from five measurements for each sample.

3. RESULTS AND DISCUSSION

3.1 Characterization of CL oligomers

The yields of the CL oligomers measured by the evaporation of the un-reacted CL were higher than 95%. Both the PPG-2CL and the PPG-4CL were liquid at room temperature, which was similar to the PPG initiator. The M_n and MWD of the PPG obtained from the GPC curve were 3, 400 g/mol and 1.7, respectively. The GPC curves of both the PPG-2CL and the PPG-4CL were of the unimodal type with the MWDs being 1.6 and 1.4, respectively. The M_ns of the CL oligomers from the GPC method were higher than the PPG and increased with the CL units. The M_ns of the PPG-2CL and the PPG-4CL were 3, 700 and 4, 800 g/mol, respectively. The GPC results indicated that the CL monomers were ring-opened at the two hydroxyl end-groups of the PPG to connect with the PPG molecules. Thus, PPG-CL oligomers with different CL chain lengths can be prepared.

The chemical structures of the CL oligomers were determined from ^{1}H-NMR. Figure 1 shows the ^{1}H-NMR spectra of the CL oligomers, including the peak assignments. The peaks of a and b were assigned to the methylene (-CH$_2$-) with the methine (-CH-) protons and the methyl (-CH$_3$-) of the propylene glycol (PG) units, respectively [21]. The ^{1}H-NMR results suggest that the PPG-CL oligomers consisted of both the PPG and the CL characters. It should be noted that the peak area ratio of the CL/PG units, such as the area ratio of peak c/peak a, increased as the CL units increased from two to four on each arm. The ^{1}H-NMR results support that the CL chain length increased with the initial CL feed ratio according to the GPC results.

From the DSC analysis (DSC thermograms not shown), both the 1st and the 2nd heating scans did not exhibit the T_m of the CL crystalline. The CL sequences with two and four units of the PPG-2CL and the PPG-4CL, respectively, could not be crystallized. They are liquid at room temperature.
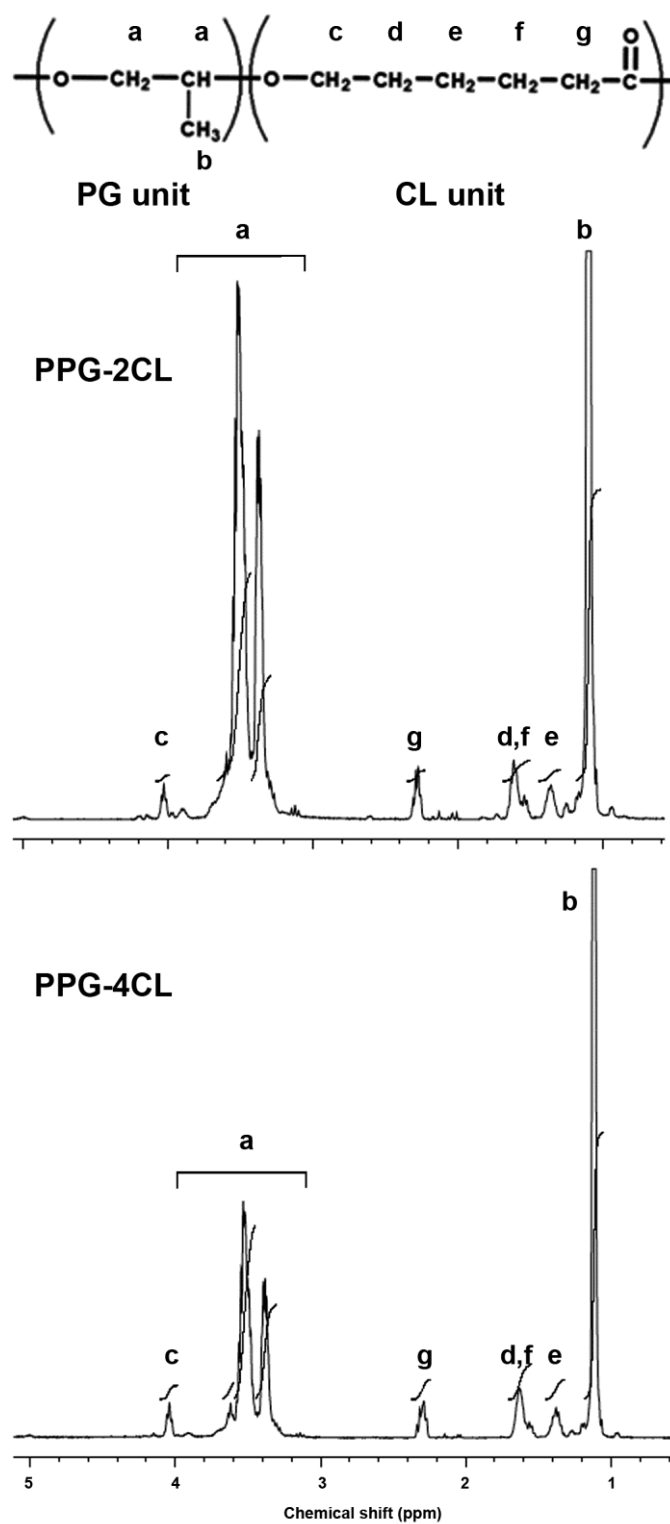
Figure 1: ^{1}H-NMR spectra of (above) PPG-2CL and (below) PPG-4CL in CDCl3 (peak assigments as shown).

3.2 Characterization of PLA blend films

The film morphology was determined from SEM images. The film surfaces were smooth for all the PLA blend films (SEM images not shown). Figures 2 (a)-4 (d) show the fractured surfaces of the neat PLA and the PLA/PPG blend films. The fractured surface of the neat PLA film was continuous. However, the PLA/PPG blend films revealed empty voids in the fractured surfaces where the liquid PPG may have accumulated during film drying [17, 18]. This suggests that phase separation between the continuous PLA matrix and the dispersed liquid PPG had occurred. The void sizes increased significantly as the PPG ratio increased [see Figures 2 (b)-4 (d)]. Similar features were found on the fractured surfaces of the PLA/PPG-2CL and the PLA/PPG-4CL blend films. Empty voids dispersed throughout the PLA/PPG-CL film matrices were also observed.

However, the empty void sizes of the PLA/PPG-2CL blend films were smaller than those in the PLA/PPG blend films, and examples of these are shown in Figure 2 (e) for the 20 wt% PPG-2CL. This suggests that the hydrophobic 2 CL sequences of the oligomers reduced the phase separation. The empty void sizes seemed to increase when the PPG-4CL was blended with the PLA instead of the PPG-2CL [see Figure 2 (f)]. This may be due to the longer CL unit length that induced greater hydrophobicity in the PGG-CL oligomer.

The thermal transition properties of the PLA blend films were determined from the DSC thermograms, examples of which are shown in Figure 3 for the PLA/PPG-4CL blend films. The T_m of the PLA was only detected on the 1st heating scan DSC thermograms. The T_m and ΔH_m of the PLA obtained from the 1st heating scan DSC thermograms, including the X_c values, are summarized in Table 1. The T_ms of the PLA blend films were similar in the range of 170-175 °C. The X_c values of the PLA/PPG blend films were similar in the range of 29.8-32.4%, which were lower than that of the neat PLA film (45.7%). This suggests that the PPG blending inhibited the PLA crystallization during film drying. However, the X_c values of the PLA/PPG-CL blend films were higher than that of the neat PLA film and increased with the PPG-CL blend ratio. The results suggest that the PPG-CL oligomers enhanced the segmental mobility of the PLA in an amorphous phase to improve the PLA crystallization.

The T_g, T_c and T_m of the PLA phase were detected on the 2nd heating scan DSC thermograms as reported in Table 2. The T_g of the PLA film matrices was clearly measured from the expanded DSC curves in the temperature range of 20-80 °C. The T_g and T_c of the PLA blend films were lower than for the neat PLA film. This indicates that the PPG and the PPG-CL oligomers acted as plasticizers to decrease the T_g and T_c of the PLA by enhancing the segmental mobility of the PLA in the amorphous phase. The T_g and T_c slightly decreased as the PPG and the PPG-CL oligomer ratios increased. The changes in the X_c values of the PLA blend films obtained from the 2nd heating scan DSC thermograms were similar to the 1st heating scan as summarized in Table 2.

The mechanical properties, including stress at break, Young's modulus and elongation at break, of the film samples were investigated by tensile testing. Figure 4 illustrates the tensile curves of the films as a function of the plasticizer type and the blend ratio.

It can be observed that the PPG and the PPG-CL oligomer blending can improve the film extension at break of the PLA films. It should be noted that the PLA/PPG and the PLA/PPG-CL blend films showed the yield or plasticizing effects for all the blend ratios. This indicates the suitability of both the PPG and the PPG-CL for PLA plasticization. The results of the mechanical properties are clearly compared in Figure 5. It can be seen that the stress at break and the Young's modulus decreased and the elongation at break increased as the PPG and the PPG-CL blend ratio increased, except for the 20 wt% PPG-4CL blending. The results of the mechanical properties suggest that the flexibility of the PLA films was improved by blending with the PPG and the PPG-CL oligomers.

The PPG, PPG-2CL and PPG-4CL were in a liquid state at room temperature. The tiny liquid pools of these plasticizers dispersed throughout the PLA film matrices exhibited a plasticization effect on the PLA films during plastic flow, and this enhanced the film drawability [17]. Although phase separation occurred with the PLA/PPG-CL blend films and induced a further slight decrease in the T_g, there was an enhancement of the drawability of the PLA films compared to the PLA/PPG blend films. This may be explained by the CL chains that were connected to the PPG end-chains enhancing the mobility of the PLA chain in an amorphous phase. The film drawability increased with the CL chain length. However, the elongation at break of the PLA film did not improve when the 20 wt% PPG-4CL was blended. This may be due to the higher blend ratio of the more hydrophobic PPG-4CL inducing more phase separation as described in the SEM results.

Table 1: Thermal transition properties of neat PLA and blend films from 1st heating scan DSC thermograms.

PLA/plasticizer ratio (w/w)	T_m (°C)	ΔH_m (J/g)	X_c (%)
Neat PLA film	174	42.8	45.7
PLA/PPG blend films			
95/5	175	27.1	30.4
90/10	174	25.1	29.8
80/20	174	24.3	32.4
PLA/PPG-2CL blend films			
95/5	174	43.3	48.6
90/10	172	42.2	50.0
80/20	170	40.8	54.4
PLA/PPG-4CL blend films			
95/5	171	51.4	57.8
90/10	170	49.7	58.9
80/20	170	45.1	60.2

Table 2: Thermal transition properties of neat PLA and blend films from 2nd heating scan DSC thermograms.

PLA/plasticizer ratio (w/w)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
Neat PLA film	58	101	18.3	175	42.9	26.2
PLA/PPG blend films						
95/5	56	97	18.4	175	32.6	16.0
90/10	53	94	15.9	175	28.2	14.6
80/20	49	89	13.4	173	25.1	15.6
PLA/PPG-2CL blend films						
95/5	56	86	26.3	171	59.1	36.8
90/10	52	82	18.0	171	50.2	38.2
80/20	50	80	16.9	170	50.0	44.2
PLA/PPG-4CL blend films						
95/5	53	88	28.6	169	58.2	33.2
90/10	53	86	25.9	168	55.5	35.1
80/20	52	85	25.6	168	54.4	38.4
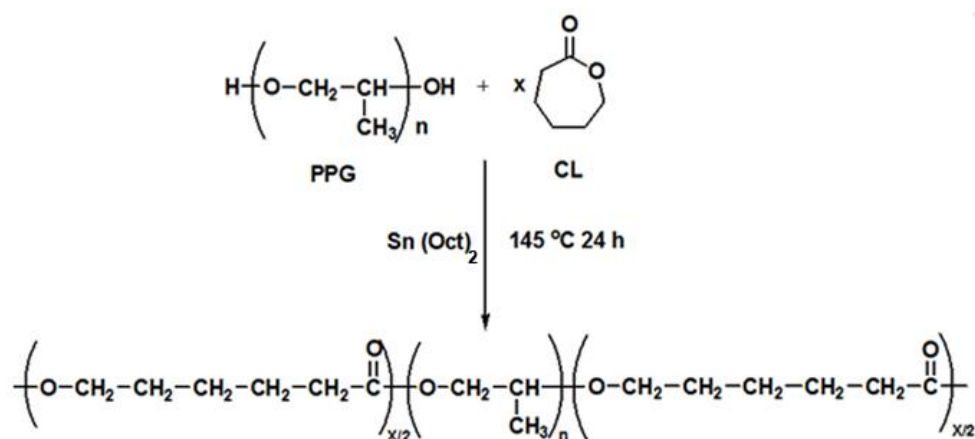
Scheme 1: Synthesis of PPG-CL oligomers (x = 4 and 8 mole for PPG-2CL and PPG-4CL, respectively).
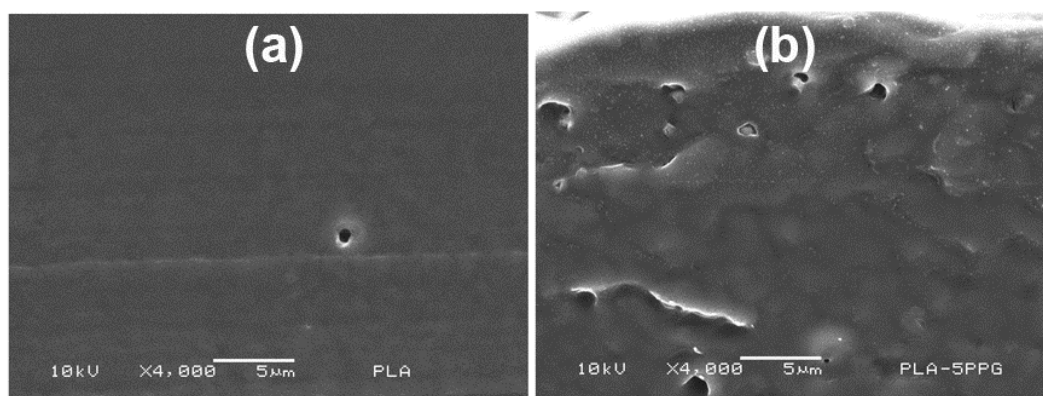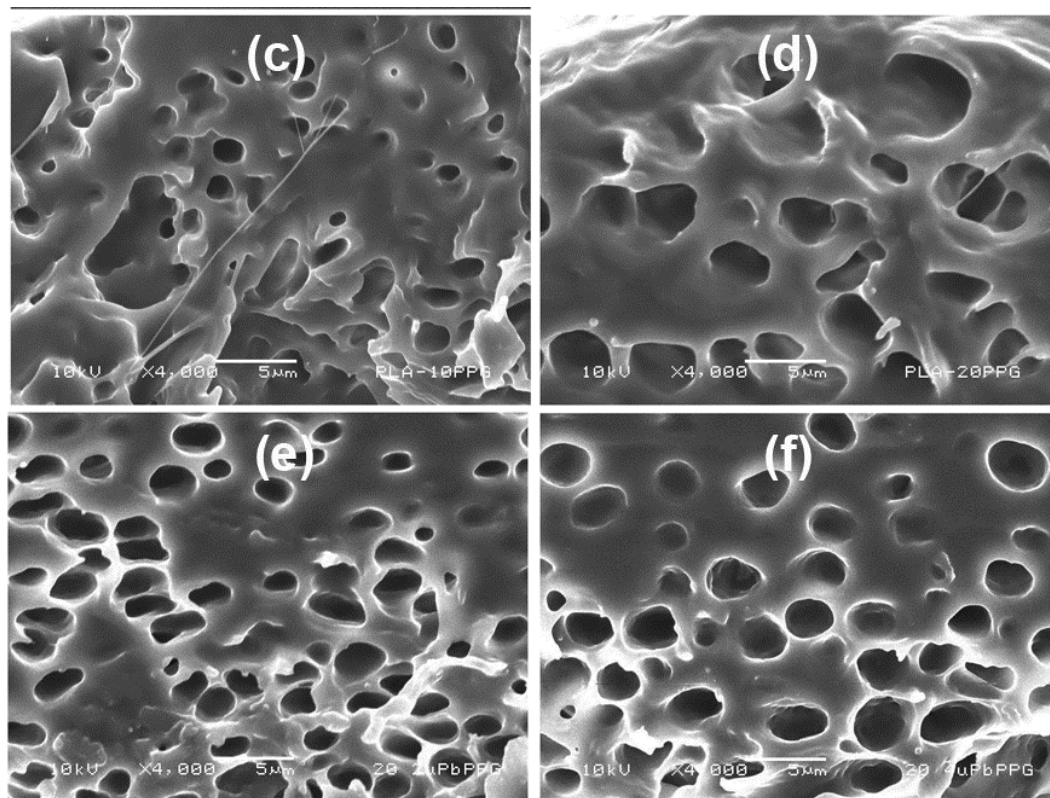
Figure 2: SEM images of fractured surfaces of (a) neat PLA, (b) 95/5 PLA/PPG, (c) 90/10 PLA/PPG, (d) 80/20 PLA/PPG, (e) 80/20 PLA/PPG-2CL and (f) 80/20 PLA/PPG-4CL blend films (all scale bars = 5 μm).
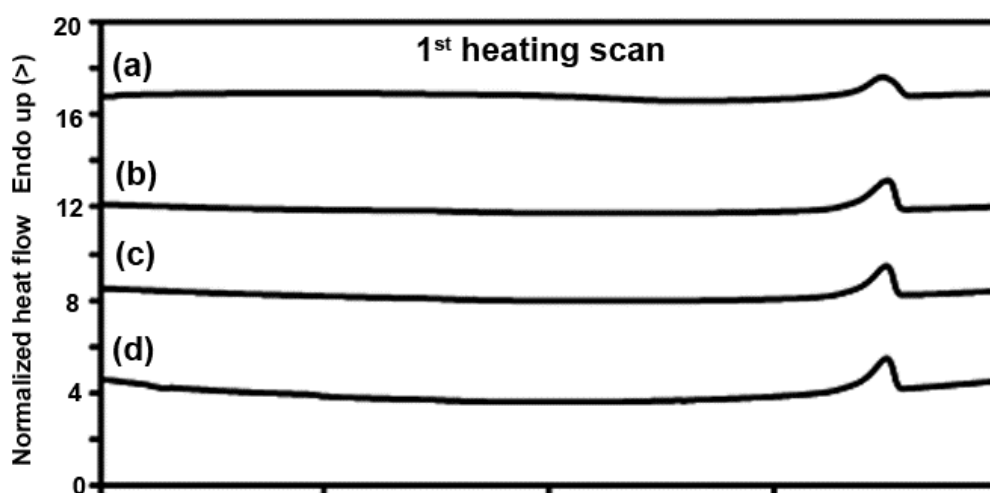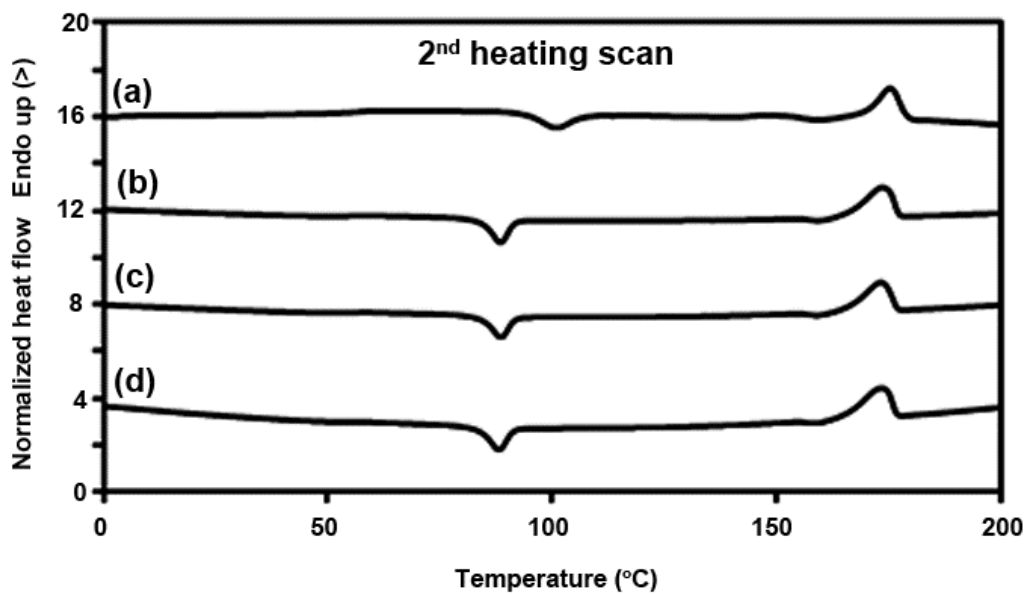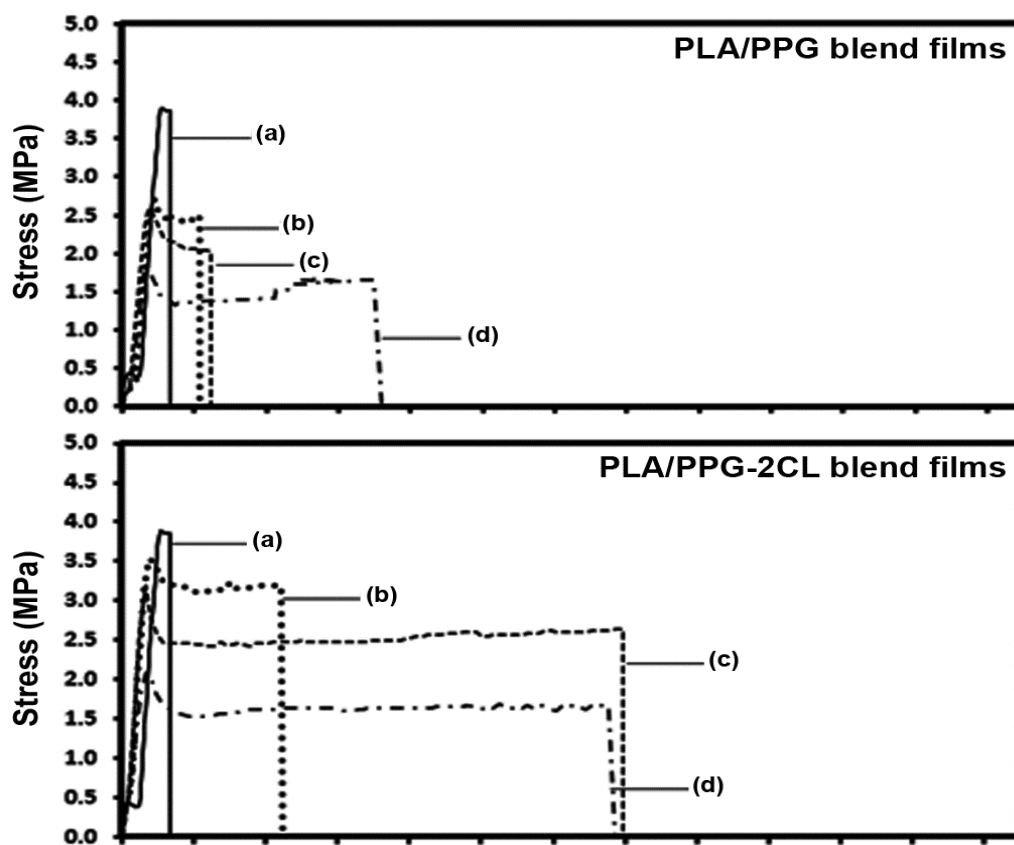
Figure 3 1st (above) and 2nd (below) heating scan DSC thermograms of (a) neat PLA, (b) 95/5 PLA/PPG-4CL, (c) 90/10 PLA/PPG-4CL and (d) 80/20 PLA/PPG-4CL blend films.
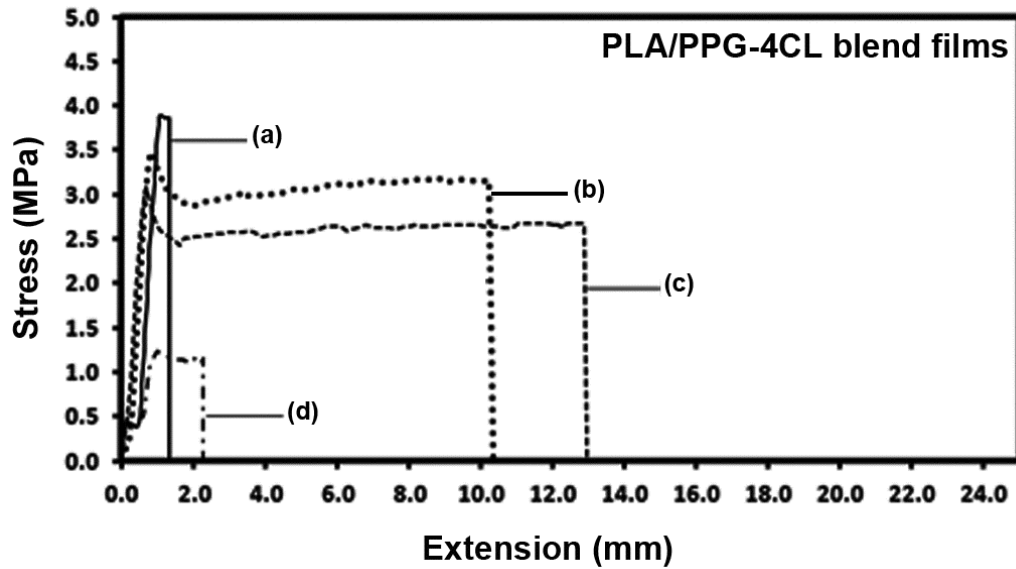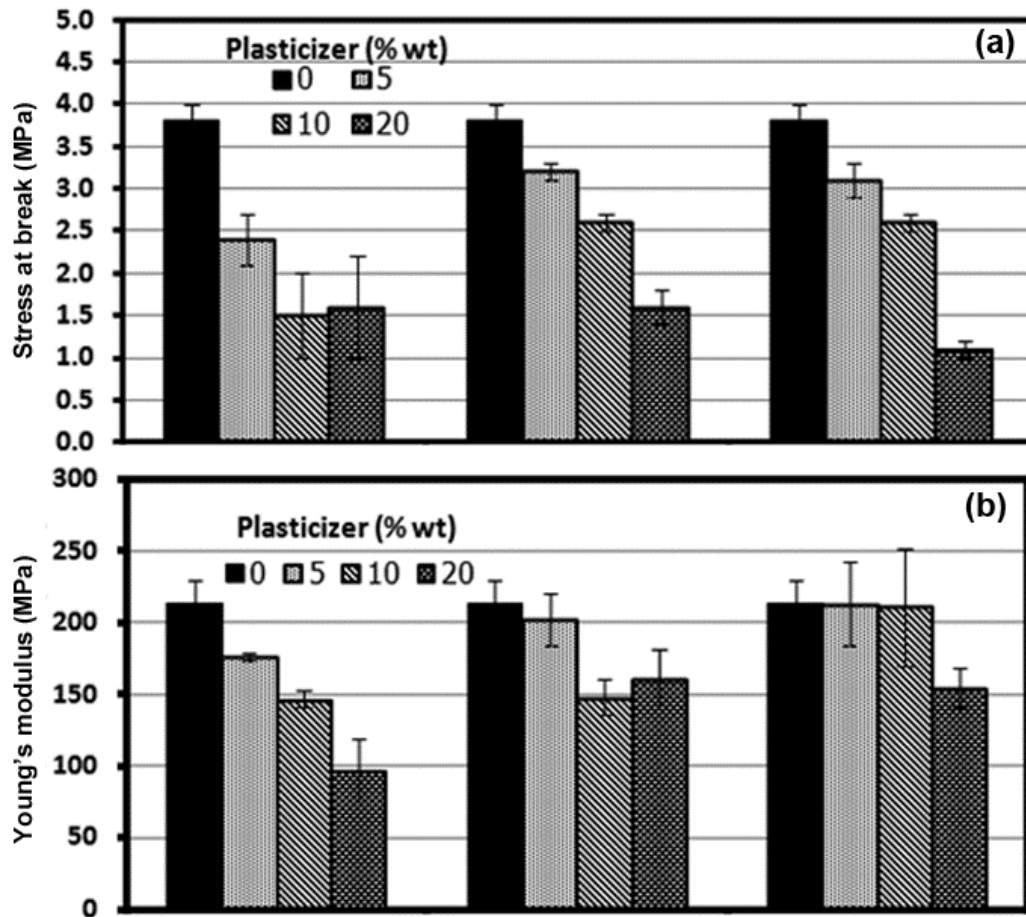
Figure 4 Tensile curves of (a) neat PLA and PLA blend films prepared with PLA/plasticizer ratios of (b) 95/5, (c) 90/10 and (d) 80/20 wt%.
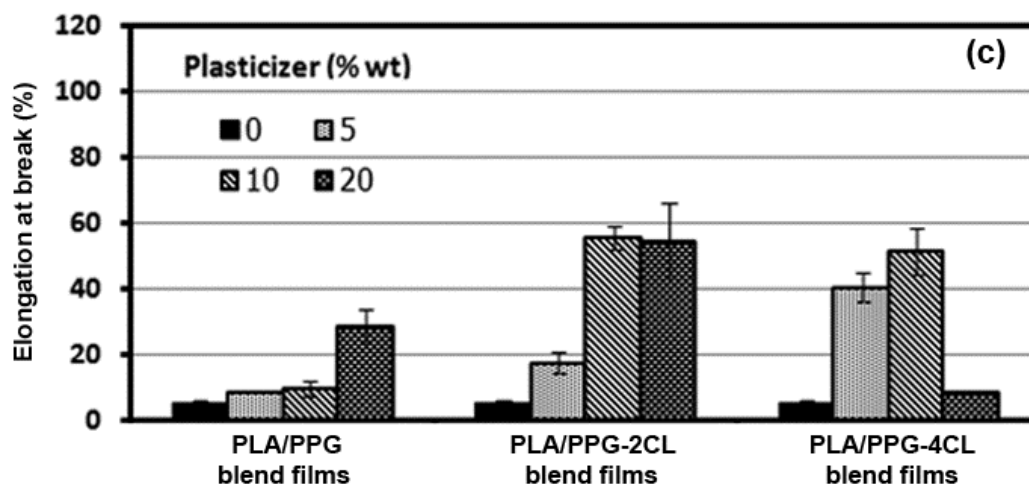
Figure 5 Tensile properties of PLA/plasticizer blend films: (a) stress at break, (b) Young's modulus and (c) elongation at break.

4. CONCLUSIONS

Two liquid PPG-CL oligomeric plasticizers were prepared by a ring-opening reaction of the CL monomer using liquid PPG containing two hydroxyl end-groups as the initiator. The different CL units of oligomers (two and four units on each end for the PPG-2CL and the PPG-4CL, respectively) were supported by GPC and ^{1}H-NMR analyses.

The phase separation between the PLA and plasticizer phases can be clearly detected as the formation of emptied voids in the SEM images of their fractured surfaces. These emptied voids were the tiny pools of liquid plasticizer. The phase separation increased (sizes of tiny pools increased) with the plasticizer blend ratio. However, both the PLA/PPG-CL blend films showed less phase separation than the PLA/PPG blend film. The PPG and the PPG-CL blending slightly depressed the T_g of the PLA. The tiny pools of the liquid PPG-CL oligomers obviously enhanced the plastic deformation to improve the drawability of the PLA films. In conclusion, the plasticization efficiency of the PPG can be improved by connection with the CL chains. The flexibility of the PLA blend films can be adjusted by varying the PPG-CL blend ratio and the CL chain length for potential use in packaging applications. A migration study of these plasticizers from the PLA film matrices is *in progress*.

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