

## SYNTHESIS OF STAR-SHAPED $\epsilon$ -CAPROLACTONE OLIGOMERS AND THERE CHARACTERIZATION

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### ABSTRACT

The phase separation increased (sizes of tiny pools increased) with the plasticizer blend ratio. However, both the PLA/Boltorn-CL blend films showed less phase separation than the PLA/Boltorn<sup>®</sup> H2004 blend film. The Boltorn<sup>®</sup> H2004 and the Boltorn-CL blending slightly depressed the  $T_g$  of the PLA. The tiny pools of the liquid Boltorn-CL oligomers obviously enhanced the plastic deformation to improve the drawability of the PLA film.

**KEYWORDS:** The phase separation Boltorn-CL drawability of the PLA film.

### INTRODUCTION

Semi-crystalline poly( $\epsilon$ -caprolactone) (PCL) is a flexible biodegradable polyester due to its very low  $T_g$  (around  $-60^\circ\text{C}$ ).<sup>[1-5]</sup> The five methylene units of the CL units induce high chain mobility and low  $T_g$ . PCL and CL oligomers have been investigated as biodegradable plasticizers.<sup>[6-7]</sup> However, to the best of our knowledge, the plasticization effect of star-shaped CL oligomers on PLA films has not been reported so far. Thus, this paper describes the synthesis of liquid CL oligomers with 6-arm star-shaped structures for plasticizing PLA film. Effects of the CL chain length (two and four units) on each arm and plasticizer blend ratios (5 – 20 wt%) on the phase separation, thermal properties and mechanical properties of the PLA blend films were evaluated. The PLA films blended with the 6-arm initiator, Boltorn<sup>®</sup> H2004, were also prepared for comparison. The flexibility of PLA films can be improved either by copolymerization<sup>[8-9]</sup> or by plasticizer blending.<sup>[7]</sup> The plasticizer blending is more convenient, more efficient, lower cost and faster compared to copolymerization. Low molecular weight plasticizers, such as citrate esters, significantly reduce the  $T_g$  and obviously improve the elongation at break of the PLA films.<sup>[10]</sup> 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 drawability with aging, which is the main problem.<sup>[11]</sup>

## MATERIALS AND METHODS

The poly(L-lactic acid) (PLA) was synthesized in our research unit at Mahasarakham University 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 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  $\epsilon$ -caprolactone (CL, 99%, Acros Organics) monomer was purified by distillation under reduced pressure before use. A liquid fatty acid modified dendritic polyol with six terminal hydroxyl groups, trade name Boltorn<sup>®</sup> H2004, with a molecular weight of 3,100 g/mol (Perstrop) was used without further purification. All reagents used were analytical grade.

### 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/Boltorn<sup>®</sup> H2004 blend films were also prepared by the same method for comparison. The film thicknesses were approximate 50  $\mu\text{m}$ .

### 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 conductivity before scanning.

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

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

where  $w_{PLA}$  is the weight fraction of PLA in the blend films.  $\Delta H_m$  and  $\Delta H_c$  are the heat of melting and heat of crystallization, respectively, which were obtained from the DSC method. The heat of melting for 100% crystallinity ( $\Delta H_{m,100\%}$ ) of PLA is 93.7 J/g.<sup>[18-20]</sup>

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.

#### 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 4(a) – 4(d) illustrate the fractured surfaces of the neat PLA and the PLA/Boltorn<sup>®</sup> H2004 blend films. The fractured surface of the neat PLA film was continuous. Meanwhile, the PLA/Boltorn<sup>®</sup> H2004 blend films revealed emptied voids on the fractured surfaces where the liquid Boltorn<sup>®</sup> H2004 may have been accumulated during film drying similar to the PLA/PPG blend films.<sup>[12-14]</sup> This suggests that phase separation between the continuous PLA and the dispersed Boltorn<sup>®</sup> H2004 phases had occurred. This may be due to the hydrophilicity of the six hydroxyl end-groups of the Boltorn<sup>®</sup> H2004 that induced the phase separation. The void sizes increased significantly as the Boltorn<sup>®</sup> H2004 ratio increased. Similar features were found on the fractured surfaces of the PLA/Boltorn-2CL and the PLA/Boltorn-4CL blend films. Emptied voids dispersed throughout the PLA/Boltorn-CL film matrices were also detected.

However, the void sizes of the PLA/Boltorn-CL blend films were smaller than those in the PLA/Boltorn<sup>®</sup> H2004 blend films for the same blend ratio and examples of these are shown in Figures 4(e) and 4(f) for the 20 wt% Boltorn-2CL and the 20 wt% Boltorn-4CL, respectively. This suggests that the hydrophobic CL chains of the oligomers enhanced the phase compatibility by decreasing the hydrophilicity of the Boltorn<sup>®</sup> H2004 cores.

The thermal transition properties of the PLA blend films were investigated from the 2<sup>nd</sup> heating scan DSC thermograms, an example of which is shown in Figure 1 showing NMR of polymer. for the PLA/ Boltorn<sup>®</sup> H2004 blend films. The  $T_g$ ,  $T_c$  and  $T_m$  of the PLA phase were detected. The DSC results are summarized in Table 1, including the  $X_c$  values. The  $T_g$ ,  $T_c$  and  $T_m$  of the PLA blend films were a little lower than for the neat PLA film. This indicates that the Boltorn<sup>®</sup> H2004 and the Boltorn-CL acted as plasticizers to decrease the  $T_g$ ,  $T_c$  and  $T_m$  of the PLA by enhancing the segmental mobility of the PLA in an amorphous phase. The  $T_g$  slightly decreased as the plasticizer ratio increased.

The  $X_c$  of the PLA are also summarized in Table 1 and they decreased slightly when the PLA was blended with the Boltorn<sup>®</sup> H2004 and the blend ratio was increased. The  $X_c$  of the PLA also decreased when the Boltorn-2CL and the Boltorn-4CL were blended for the 5 wt% blend ratio. However, the  $X_c$  of the PLA increased as the Boltorn-CL blend ratio increased from 5 wt% to 10 and 20 wt%. This demonstrates that the Boltorn<sup>®</sup> H2004 inhibited crystallization of the PLA, although the Boltorn<sup>®</sup> H2004 and the Boltorn-CL had practically the same effect on the  $T_g$ . This result is similar to the plasticizing and nucleating effects on PLA films of poly(propylene glycol) (PPG) and poly(ethylene glycol) (PEG).<sup>[15-17]</sup> The  $T_g$  of the PLA films was depressed by blending with both the PPG and the PEG. However, the PPG affected the  $X_c$  of the PLA less.

The thermal stabilities of the PLA blend films were determined from the TG thermograms, as shown in Figure 5. It can be seen that the thermal stabilities of all the plasticizers was better than those of the neat PLA and the PLA blend films. The neat PLA and the 95/5 wt% PLA/plasticizer blend films showed similar single decomposition profiles in the temperature range of 300 – 400°C, with the initial decomposition temperature about 300°C. The weight losses of the 10 wt% and the 20 wt% plasticizer blend ratios were faster than the neat PLA film. The weight loss changes of the PLA films blended with Boltorn, Boltorn-2CL and Boltorn-4CL, were similar for the same blend ratios.

Figure 6 shows the DTG thermograms of the PLA blend films compared with their plasticizers. The PLA blend films exhibited single  $T_{d, \max}$  peaks. Table 2 reports the  $T_{d, \max}$  of the PLA blend films. The  $T_{d, \max}$  of the 95/5 wt% PLA/plasticizer blend films were higher than the neat PLA films for all the plasticizers. However, increasing the plasticizer ratios from 5% to 10% and 20% significantly depressed the  $T_{d, \max}$ .

The mechanical properties, including stress at break, elongation at break and initial Young's modulus, of the film samples were determined by tensile testing. Table 1,2 shows the tensile properties of the films as a function of the plasticizer type and the blend ratio. It can be seen that the elongation at break of the PLA films was not changed by the Boltorn<sup>®</sup> H2004 blending. While the Boltorn-2CL and the Boltorn-4CL blending can improve the elongation at break of the PLA films. In addition, the PLA/Boltorn-2CL and the PLA/Boltorn-4CL blend films exhibited the yield or plasticizing effects for all the blend ratios, but the PLA/ Boltorn<sup>®</sup> H2004 blend films did not. The results of the mechanical properties are summarized in Table 3. It was found that the stress at break and the initial Young's modulus decreased and the elongation at break increased as the Boltorn-2CL and the Boltorn-4CL were blended and the blend ratio increased, except for the Boltorn<sup>®</sup> H2004 blending. The results of the mechanical properties indicate that the Boltorn-2CL and the Boltorn-4CL improved the flexibility of the PLA films.

Kulinski *et al.* reported the plasticization of PLA films by tiny liquid pools of PPG during plastic flow and this had positive effects on the film drawability. Thus, in this work, the tiny liquid pools of the Boltorn-CL enhanced the film drawability. The phase separation occurred on the PLA/Boltorn-CL blend films and induced a further slight decrease of the  $T_g$  but largely enhanced the drawability of the PLA films, while the PLA/ Boltorn<sup>®</sup> H2004 blend films did not have this for all the blend ratios. This may be explained by the hydrophilicity between the continuous PLA and the dispersed Boltorn<sup>®</sup> H2004 phases being very different.<sup>[18-19]</sup>

Two liquid Boltorn-CL oligomeric plasticizers were prepared by a ring-opening reaction of the CL monomer using the liquid star-shaped Boltorn<sup>®</sup> H2004 containing six hydroxyl end-groups as the initiator. The different CL units of oligomers (two and four units on each arm for the Boltorn-2CL and the Boltorn-4CL, respectively) were supported by <sup>1</sup>H-NMR and TGA analyses.

### Supplimentary Date

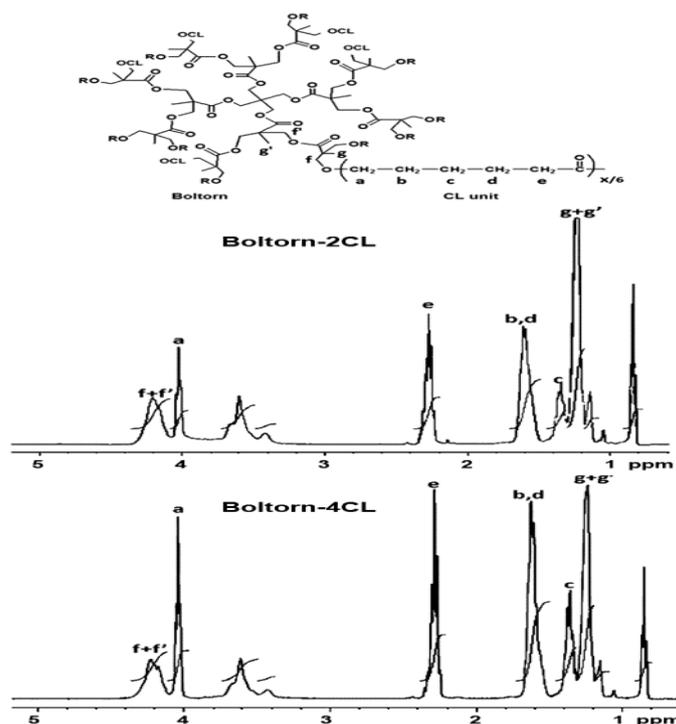
**Table 1.  $T_{d, max}$  values of neat PLA and PLA blend films from DTG thermograms.**

PLA/plasticizer blend ratio (w/w)	$T_{d, max}$ (°C)
Neat PLA blend film	360
PLA/Boltorn blend films	
95/5	366
90/10	352
80/20	334

PLA/Boltorn-2CL blend films	
95/5	365
90/10	358
80/20	336
PLA/Boltorn-4CL blend films	
95/5	367
90/10	360
80/20	358

Table 3. Mechanical properties of PLA blend films.

PLA/plasticizer blend ratio (w/w)	Stress at break (MPa)	Young's modulus (MPa)	Elongation at break (%)
Neat PLA film			
PLA/Boltorn blend films	3.8 ± 0.2	213.0 ± 17.0	5.4 ± 0.8
95/5			
90/10	2.6 ± 0.2	158.6 ± 20.9	4.4 ± 0.7
80/20	2.2 ± 0.4	147.6 ± 17.0	4.2 ± 0.2
PLA/Boltorn-2CL blend films	1.6 ± 0.4	87.6 ± 8.8	4.8 ± 0.5
95/5	3.9 ± 0.4	193.5 ± 24.6	28.5 ± 2.1
90/10	3.3 ± 0.2	167.2 ± 27.9	73.3 ± 7.8
80/20	2.8 ± 0.4	155.1 ± 38.6	91.8 ± 8.7
PLA/Boltorn-4CL blend films	3.8 ± 0.4	204.5 ± 10.7	26.6 ± 4.2
95/5	2.8 ± 0.5	182.8 ± 27.8	38.4 ± 5.9
90/10	2.4 ± 0.2	148.8 ± 13.1	69.9 ± 10.8
80/20			



NMR Study of polymer film

## CONCLUSIONS

The phase separation between the PLA and plasticizer phases can be clearly observed 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/Boltorn-CL blend films showed less phase separation than the PLA/Boltorn<sup>®</sup> H2004 blend film. The Boltorn<sup>®</sup> H2004 and the Boltorn-CL blending slightly depressed the  $T_g$  of the PLA. The tiny pools of the liquid Boltorn-CL oligomers obviously enhanced the plastic deformation to improve the drawability of the PLA films, but the liquid Boltorn<sup>®</sup> H2004 did not. In conclusion, the flexibility of the PLA blend films can be tailored by controlling the Boltorn-CL blend ratio and the CL chain length for potential use as flexible bioplastic films in packaging applications.

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