

## Effect of Tween 80 on the Mechanical and Thermal Properties of Solution-Cast Blends of Poly(lactic acid) and Cellulose Acetate Butyrate Films

Sutinee Girdthep<sup>1</sup>, Winita Punyodom<sup>1,+</sup>, Robert Molloy<sup>1</sup> and Wasinee Channuan<sup>2</sup>

<sup>1</sup> Polymer Research Group, Department of Chemistry, Faculty of Science,  
Chiang Mai University, Chiang Mai, 50200, Thailand

<sup>2</sup> Faculty of Agriculture Product Innovation and Technology, Srinakharinwirot University,  
Bangkok, 10110, Thailand

**Abstract.** There is growing pressure in the fresh fruits and vegetables packaging sector to replace petrochemical-based packaging films with more environmentally friendly biodegradable materials. Poly(lactic acid), PLA, and cellulose acetate butyrate, CAB, are interesting candidates which are derived from renewable resources. However, both PLA and CAB films are brittle. Thus, the aim of this work has been to investigate the effect of a plasticizer on the properties of PLA, CAB and PLA/CAB blend films. The films were plasticized with different amounts of polysorbate 80 (Tween 80). The influence of Tween 80 on the mechanical properties of the plasticized polymer films was determined by tensile testing. It was found that the polymer blend films were more flexible than the pure polymer films. In addition, the elongation at break and tensile strength of all film types containing 10% wt. of Tween 80 were the highest. Furthermore, the thermal properties were investigated by differential scanning calorimetry (DSC). The DSC results suggest that blends of PLA and CAB are partially compatible in the amorphous phase. It was confirmed by scanning electron microscopy (SEM) that phase separation occurred in the polymer blend without Tween 80. Moreover, the SEM results suggest that Tween 80 acts as a compatibilizer in PLA/CAB blend films.

**Keywords:** poly(lactic acid), cellulose acetate butyrate, Tween 80, polymer blends, biodegradable polymers

### 1. Introduction

The use of biodegradable packaging is a growing trend due to the need to minimize the deposition of nondegradable solid residues in the environment [1] and the realization that our petroleum resources are finite [1-2]. One of the most studied biodegradable polymers is poly(lactic acid), PLA, an aliphatic polyester derived from renewable resources such as corn, cassava and sugar beet and is completely degradable under composting conditions. Its mechanical properties make it useful for packaging and other applications traditionally dominated by petroleum-based resins. It also has a significantly lower non-renewable energy content compared to various other common polymers, partly due to the elimination of fossil fuels for its monomer source. PLA has a number of useful properties including biodegradability, good mechanical properties, and processability. For these reasons, PLA is an interesting candidate for producing biodegradable packaging materials [3]. However, considerable improvements are still required to overcome the following disadvantages: (1) slow crystallization, (2) poor heat resistance, (3) brittleness and (4) relatively high cost [4]. Thus, it would be useful to find versatile methodologies to manipulate the mechanical behavior and minimize these problems.

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Corresponding author. Tel.: 053-943341-5 ext. 312; fax: 053-892277  
E-mail address: winita@chiangmai.ac.th

Blending is a commonly used technique in polymer technology [5] which aims to improve the overall properties of PLA. Polymer blends are mixtures of two or more polymers that may or may not be compatible [6]. In previous work, materials such as starch and cellulose derivatives have been extensively studied as blend components for PLA because of their lower cost compared to other materials.

Scandola *et al.* [7-8] have investigated the miscibility, thermal and viscoelastic properties of blends of polyhydroxybutyrate (PHB) with either cellulose acetate butyrate (CAB) or cellulose acetate propionate (CAP). It has been reported [9] that when the CAB or CAP content in the blends is more than 50% by weight, the blends are stable homogeneous amorphous glasses characterized by a single composition-dependent glass transition temperature,  $T_g$ . When the CAB or CAP component is less than 50% by weight, PHB crystallizes upon room temperature storage and the blends become partially crystalline.

Plasticizers are widely used to improve the processability, flexibility and ductility of polymers. In the case of a semi-crystalline polymer like PLA, an efficient plasticizer has to not only reduce the  $T_g$  but also depress the melting point ( $T_m$ ) and the crystallinity [10]. In this context, surfactants are interesting amphiphilic substances in which the balance between the hydrophilic and hydrophobic fractions determines their applications. Polyoxyethylene sorbitan monooleate (Tween 80) has a high hydrophilic/lipophilic balance (HLB) value ( $>10$ ) and is used for oil-in-water-type applications [11]. A reduction in the water absorption capacity of methylcellulose films has been observed with increasing HLB of the mixture of surfactants. Surfactants with higher HLB allow a greater association of their hydrophilic fraction with the hydrophilic film matrix which, in turn, may reduce the amount of water binding sites while the hydrophobic fraction may act as a water vapour permeability (WVP) barrier.

In this work, the preparation of solution-cast blends of PLA and CAB using Tween 80 as a plasticizer has been investigated and their properties as potential packaging materials examined. The structures of the PLA, CAB and Tween 80 are shown in Figure 1.

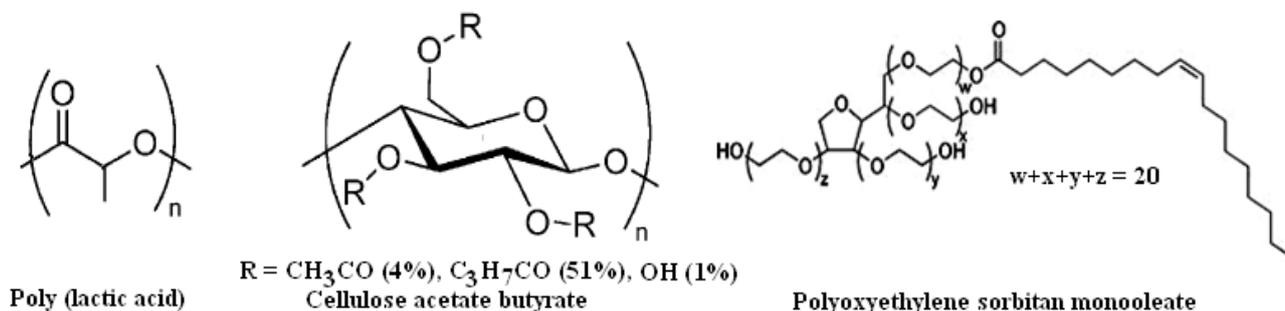


Fig. 1: Molecular structures of PLA, CAB and polyoxyethylene sorbitan monooleate (Tween 80)

## 2. Materials and Methods

### 2.1. Materials

PLA was obtained from NatureWorks (Purac, Netherlands) and had a viscosity-average molecular weight,  $\overline{M}_v$ , of 61,000 as determined by dilute-solution viscosity measurements in chloroform at 25°C. The PLA pellets were translucent and semi-crystalline with a  $T_g$  (mid-point) of 59°C and a  $T_m$  (peak) of 148°C. Cellulose acetate butyrate (CAB) type 500-5 of number-average molecular weight,  $\overline{M}_n$ , 57,000 was obtained from Eastman Chemical Company (Kingsport, Tennessee, USA). The butyryl, acetyl and hydroxyl contents were 51%, 4%, and 1% respectively. Polyoxyethylene sorbitan monooleate (Tween 80) (Sigma-Aldrich, Saint Louis, USA) was used as received.

### 2.2. Preparation of Blends

Specified amounts of PLA, CAB and Tween 80 were placed in a beaker to a total amount of 0.5 g and 10 ml of chloroform were added. After being stirred vigorously for about 5 h, the solution became clear and was then poured into a glass Petri dish. After the chloroform had evaporated at room temperature, homogeneous films of approximately 0.05 mm in thickness were obtained. The dried samples were peeled off from the glass and further dried in a vacuum desiccator for several days to completely remove any

residual solvent. The same procedure was used for blends containing 5, 10, 15 and 20% by weight of plasticizer (Tween 80). The blend films containing a given amount of CAB are subsequently referred to in this paper as  $\Phi_{\text{CAB}} = X$ ; where  $X$  represents the weight fraction of CAB in the blends.

### 2.3. Characterization of Blends

Thermal properties of the blends were measured using a Perkin-Elmer Differential Scanning Calorimeter (DSC7) at a heating rate of 10 °C/min and the glass transition temperature,  $T_g$ , melting temperature,  $T_m$ , and heat of melting,  $\Delta H_m$ , determined. The surface topography of the blends was studied using a Jeol 5910 LV Scanning Electron Microscope at an acceleration voltage of 15 kV. Samples were mounted onto SEM stubs using carbon tabs and the stub surface then coated with gold using a sputter-coater. Tensile testing of the blend films was performed at room temperature using a Lloyds LRX+ Universal Testing Machine at a cross head speed of 10 mm/min and initial gauge length of 50 mm.

## 3. Results and Discussion

### 3.1. Thermal Properties

Figure 2 shows the DSC curves of the (a) PLA ( $\Phi_{\text{CAB}} = 0$ ), (b) CAB ( $\Phi_{\text{CAB}} = 1$ ) and (c) a PLA/CAB 50:50 blend ( $\Phi_{\text{CAB}} = 0.5$ ) using different amounts of Tween 80. For PLA, two endothermic melting peaks could be seen at approximately 148°C in the 5, 10, 15 and 20% Tween 80 samples; this temperature corresponds to the melting point of PLA. Moreover, an endothermic melting peak was also observed at the same temperature when using 20% Tween 80 in  $\Phi_{\text{CAB}} = 0.5$  indicating that this highest Tween 80 content could induce partial crystallization in the PLA microdomains. However, this peak could not be seen when using 0% Tween 80 in pure PLA and the PLA/CAB blend.

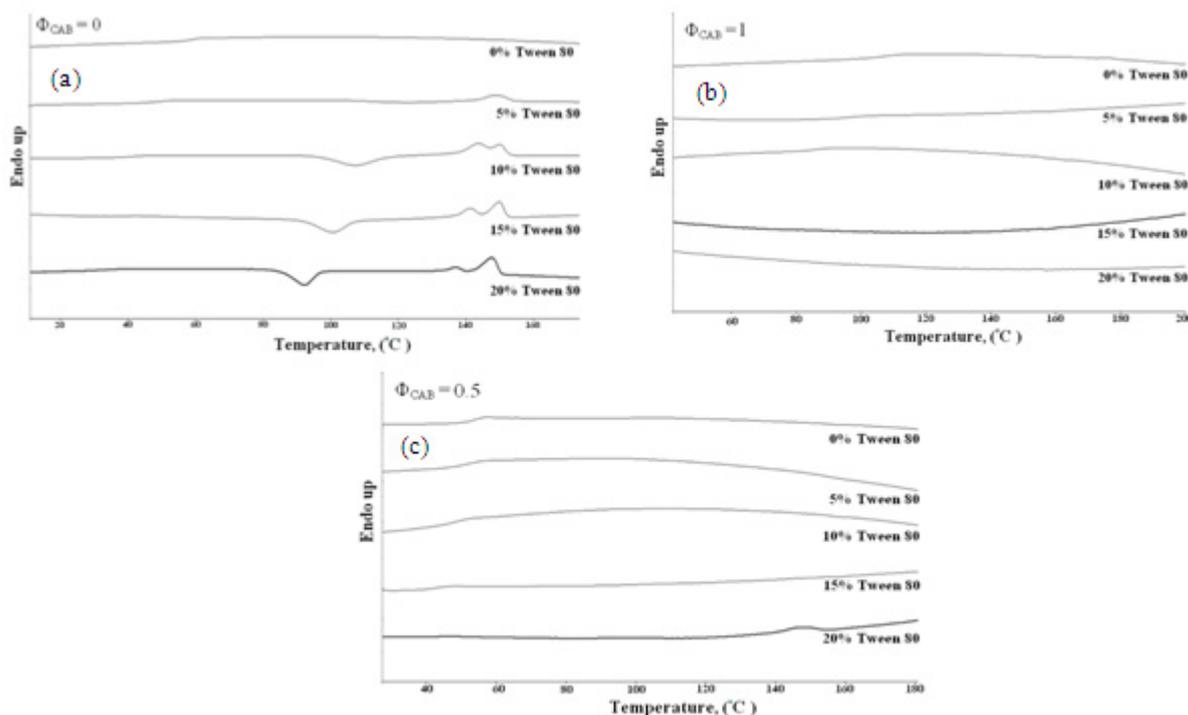


Fig. 2: DSC thermograms (2<sup>nd</sup> run) of (a)  $\Phi_{\text{CAB}} = 0$  (b)  $\Phi_{\text{CAB}} = 1$  and (c)  $\Phi_{\text{CAB}} = 0.5$  with different amounts of Tween 80 as plasticizer

To discuss the effect of the Tween 80 content on the melting behavior, the values of  $T_g$ ,  $T_m$  and  $\Delta H_m$  were evaluated for each of the as-cast samples and the results are shown in Table 1. It can be seen that  $T_m$  increases with increasing Tween 80 content implying that larger PLA crystallites are formed. It can also be seen that the  $T_g$  values decrease with increasing Tween 80. A single  $T_g$  is observed for all blend compositions which indicates that the PLA/CAB blends are compatible in the amorphous phase. It should also be noted that physical ageing was not observed in the second DSC scans as all the samples were

quenched and re-run immediately. An approximate value of the  $T_g$  of binary compatible blends can be calculated from the Fox Equation [12].

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where  $W_1$  and  $W_2$  are the weight fractions of the two components ( $W_1+W_2=1$ ) and  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures in degrees Kelvin of the respective homopolymers.

At 10% Tween 80, the  $\Phi_{CAB} = 0$  blend had a maximum  $\Delta H_m$  value which decreased with further added Tween 80. Notably, the appearance of a  $T_m$  and  $\Delta H_m$  when using 20% Tween 80 in the  $\Phi_{CAB} = 0.5$  blend confirmed that the introduction of the Tween 80 induced crystallization of the PLA.

Table 1: Glass transition and melting temperatures ( $^{\circ}\text{C}$ ) and heats of melting (J/g) of pure PLA ( $\Phi_{CAB} = 0$ ), pure CAB ( $\Phi_{CAB} = 1$ ) and PLA/CAB blends ( $\Phi_{CAB} = 0.5$ ) with and without plasticizer (Tween 80).

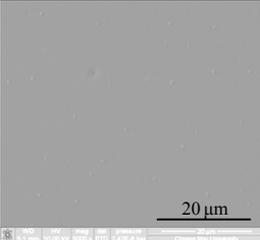
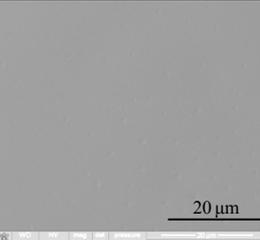
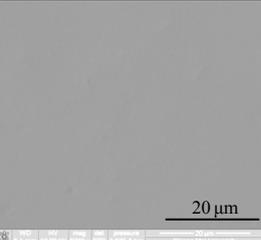
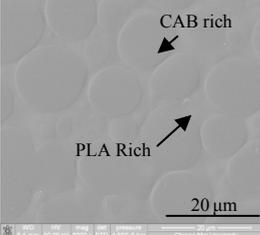
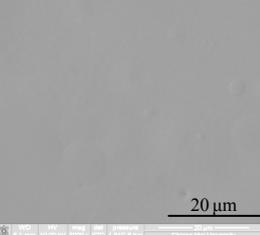
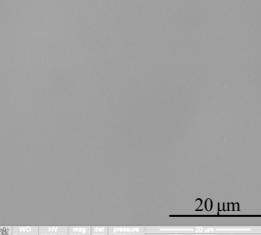
Tween 80 % wt.	$\Phi_{CAB} = 0$			$\Phi_{CAB} = 0.5$			$\Phi_{CAB} = 1$		
	$T_g$	$T_m$	$\Delta H_m$	$T_g$	$T_m$	$\Delta H_m$	$T_g$	$T_m$	$\Delta H_m$
0	58.5	n/d	n/d	52.1, 106.2	n/d	n/d	108.6	n/d	n/d
5	47.7	148.8	9.3	52.5	n/d	n/d	96.2	n/d	n/d
10	41.3	147.8	29.8	48.6	n/d	n/d	86.5	n/d	n/d
15	50.5	148.2	25.4	45.1	n/d	n/d	53.9	n/d	n/d
20	32.0	148.3	3.0	42.3	148.3	2.3	40.5	n/d	n/d

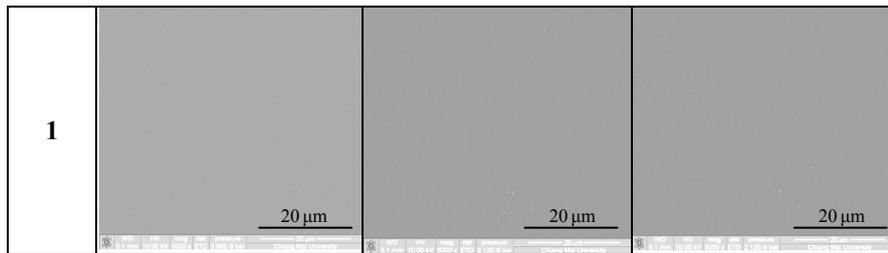
n/d = not detected

### 3.2. Scanning Electron Microscopy

Table 2 shows the SEM images of the film surfaces. Films without Tween 80 ( $\Phi_{CAB} = 0$  and 1) exhibited a continuous phase but the PLA/CAB blend film ( $\Phi_{CAB} = 0.5$ ) showed phase separation between the PLA and the CAB due to their partial incompatibility at the molecular level. However, the addition of Tween 80 appeared to decrease this phase separation due to its plasticizing effect.

Table 2: SEM micrographs (magnification x5000) of pure PLA ( $\Phi_{CAB} = 0$ ), pure CAB ( $\Phi_{CAB} = 1$ ) and the PLA/CAB blends ( $\Phi_{CAB} = 0.5$ ) with and without plasticizer (Tween 80).

$\Phi_{CAB}$	Amount of Tween 80 (%wt.)		
	0	10	20
0			
0.50			



### 3.3. Mechanical Properties

The tensile mechanical properties of the films are summarized in Figure 3. In general, the Tween 80 plasticizer enhances the ductile character of the PLA/CAB blends as expected. The tensile strength is a maximum at 10% Tween 80 in all film samples, while the PLA/CAB blends showed a slight increase in % elongation at break with increasing Tween 80. These findings support the view of the partial compatibility of PLA and CAB. The addition of Tween 80 significantly reduced the Young's modulus of the blend films.

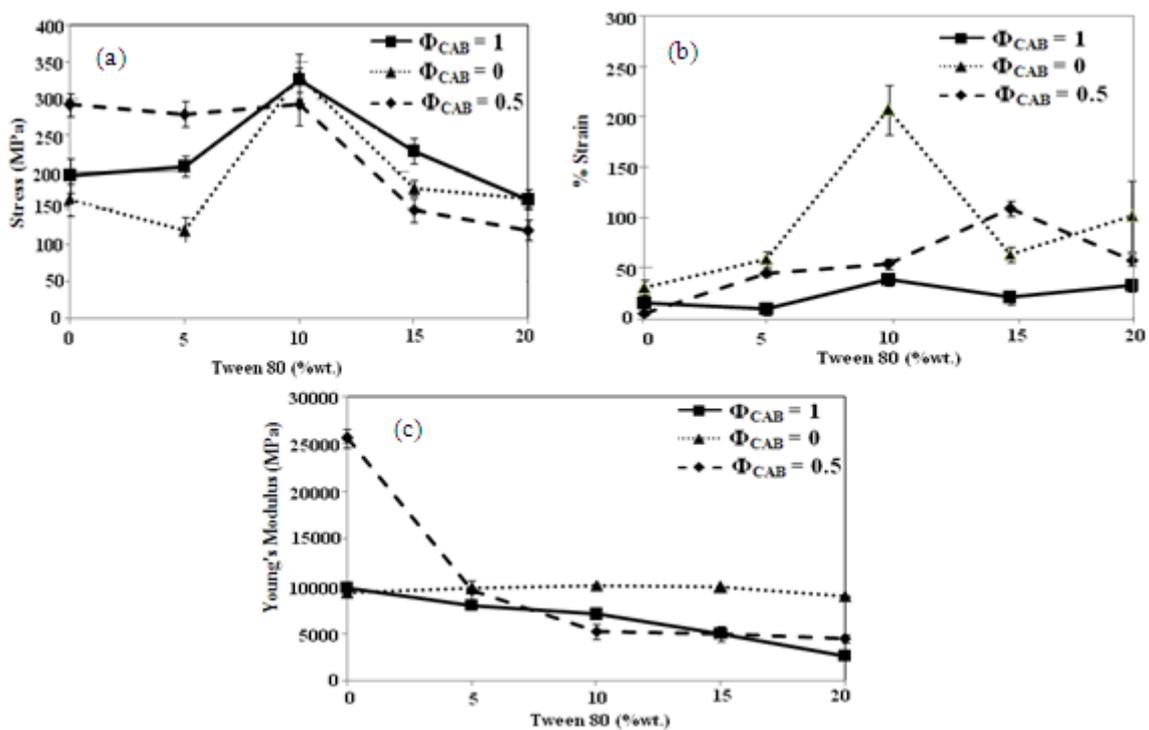


Fig. 3: Mechanical properties of the films ( $\Phi_{CAB} = 0$ ,  $\Phi_{CAB} = 1$  and  $\Phi_{CAB} = 0.5$  with different amounts of Tween 80)

(a) stress at break (b) % elongation and (c) Young's modulus

## 4. Conclusions

PLA is a promising biodegradable polymer which can be blended with CAB and Tween 80 to modify its properties and lower its cost. The properties and compatibility of these biodegradable polymer blends were determined through thermal and mechanical testing and scanning electron microscopy. The changes in the tensile properties and the DSC results suggest that blends of PLA and CAB are partial compatible in the amorphous phase. The addition of Tween 80 to PLA/CAB blends reduced the  $T_g$  and increased the heat of melting of the PLA. From the SEM images, all films were homogeneous when Tween 80 was added. The incorporation of Tween 80 reduced the Young's modulus of the blends, increased the strain at break and increased film flexibility.

## 5. Acknowledgements

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## 6. References

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