

Analysis of the Mechanical Properties of Solvent Cast Blends of PLA/PCL

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**Abstract.** Polylactic acid (PLA) is the most promising material in the biodegradable category. However, brittleness and poor thermal stability restrict its application. To overcome this limitation, PLA may be blended with other biodegradable materials to tailor its properties while maintain biodegradability. In this study a series of blends of PLA and poly ( $\epsilon$ -caprolactone) (PCL) with various mass fractions were prepared by solution method and solvent casting. Films of each blend were formed when the solvent evaporated. Subsequently, tensile test samples were punched out of the film for testing and tensile testing, Fourier transform infrared spectrometry (FTIR), Differential scanning Calorimetry (DSC) and contact angle measurements were carried out. Since PCL is a ductile material, the two materials were blended together in an effort to improve the mechanical properties. However, on thermal analysis of the blends, two individual melting peaks were observed in the DSC thermograms. Furthermore, no significant shift in peaks was observed on the FTIR spectra, and clear droplets and boundaries between two components of the blend can be observed in morphology study, all indicated the immiscibility of PLA and PCL. Tensile test showed poor mechanical properties due to the poor adhesion of the two immiscible components of the blend, and the addition of PCL did not influence the wettability of the surface of the blends as there were no significant differences in contact angle measurements.

## 1. INTRODUCTION

Polylactic acid (PLA) is aliphatic polyester, which is derived from renewable and degradable resources such as corn and rice. Due to its natural origin PLA and similar polymers can help alleviate the energy crisis as well as reduce the dependence on fossil fuels of our society [1]. It is proven to be one of the most promising materials in biodegradable category and has gained increasing attention in the last decade in terms of applications in the medical field due to degradation products which are water and carbon dioxide, neither of which are toxic nor carcinogenic to the human body.

However, the brittleness and poor thermal stability limit the application of PLA [2]. Blending of PLA with other polymers is a useful way to impart flexibility and toughness to the PLA matrix and broaden applications.

Several studies have reported blending of PLA with biodegradable components such as poly(ethylene glycol) (PEG), poly( $\beta$ -hydroxybutyrate) (PHB), poly( $\epsilon$ -caprolactone) (PCL), poly(butylene adipate-co-terephthalate) (PBAT), chitosan, and starch tailors the properties of the composite while maintaining biodegradability [3]. In one such study Al-Itry et.al reported that hot melt extruded blends of PLA with PBAT and branching agent Glycidyl methacrylate (GMA) exhibited an improvement in mechanical properties and thermal stability of the composite [4]. In another study Gan, et.al reported that by melt-mixing PLA with bacterial cellulose (BC) the stiffness of PLA can be improved [5]. Whereas, Prabaharan et al. reported that forming PLA-Chitosan hybrid scaffolds can control the drug release rate [6].

PCL is a hydrophobic, semi-crystalline polymer. It has a low melting point, exceptional blend-compatibility, biocompatibility, superior rheological and viscoelastic properties make it very attractive for use in the biomedical field [7]. PCL is a ductile polymer and don't have the mechanical properties to be applied in high load bearing applications, however, dispersion PCL spherulites in PLA tends to enhance ductile deformation of PLA fibrils [8].

PLA and PCL have similar solubility parameters, 10.1 and 9.2  $\text{cal}^{0.5}/\text{cm}^{1.5}$  respectively [9]. They should be miscible in theory. However, both miscible and immiscible blending of PLA and PCL have been reported. Auras et al. reported that miscible PLA/PCL blends were obtained with blends of low molecular weight PCL (2 and 3 kDa) and low molecular weight PLLA (1.75kDa) or low and high molecular weight PDLLA (2 and 44 kDa, respectively) [2]. Broz et al. reported that above the melting temperature of PCL, 65°C, and below the lower critical solution temperature, 86°C, PLA/PAL blends are miscible. However annealing induces phase separation [10]. Todo et al. found that phase separation originated by immiscibility of PLA and PCL tends to degrade the mechanical properties of PLA/PCL blends [11]. Shin et al. claimed that the PLA/PCL blends were thermodynamically immiscible, which results in poor dispersion and interfacial adhesion [12]. Patricio et al. also reported that PLA/PCL blending produced by physical blending process was immiscible [13]. Yeh et al. found PLA and PCL are partially miscible in their study of PLA/PCL blend [14].

Due to the lack of clarity in the literature, the current study was designed to assess the miscibility of a series of blends of PLA and PCL with various mass fractions prepared using solvent casting methods. Resultant samples were characterised using by DSC, FTIR and visual inspection.

## **2. EXPERIMENTAL**

### **2.1 Materials**

PLA was obtained from NatureWorks LLC, Ingeo biopolymer 7032D. PCL was obtained from Perstrop UK Limited, Capa 6250 with molecular weight of 25,000. Solvent casting was used to produce PLA/PCL blends with 1, 4-Dioxan (Labscan Ltd) utilised as the diluent. Both polymers and the solvent were used as received.

### **2.2 Sample Preparation**

The PLA/PCL blends with mass fractions of 100/0, 90/10, 80/20, 70/30, 60/40 wt% were prepared by dissolving a hand mixed blend of both polymers in 1, 4-Dioxan at 30 °C under constant stirring at 300rpm for 12 hours. When the polymers were completely dissolved the solution was poured in the Petri dishes and left in vacuum dryer overnight which led to the production of thin films when the

solvent evaporated. Finally, the film was removed from the petri dishes and tensile test samples were punched out of the resultant film.

### 2.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was carried out on the PLA/PCL blending samples, using PerkinElmer spectrum one, with 8 scan per sample cycle.

### 2.4 Tensile Tests

The mechanical properties of the PLA/PCL blends were characterised by tensile testing each different blend. Tensile testing was carried out on a Lloyd Lr10k tensometer using a 2.5kN load cell on ASTM standard test specimens at a strain rate of 50mm/min. Data was recorded using Nexygen™ software. The tensile tests were carried out in adherence to ASTM D 882. Prior to testing each sample, the thickness of each sample was measured. The maximum load, percentage of strain at the maximum load and stress at the maximum load of each sample were analysed.

### 2.5 Differential Scanning Calorimetry

Differential scanning Calorimetry (DSC) was carried out using a DSC 2920 Modulated DSC (TA Instruments). Calibration of the instrument was performed using indium as standard. All the samples were dried at 60°C for 8 hours prior to testing. Test specimens weighed between 8 and 12 mg were measured on a Sartorius scales, capable of been read for five decimal places. Samples were crimped in non-perforated aluminium pans, with an empty crimped aluminium pan being used as the reference. The thermal history was removed by heating samples from 20°C to 220°C at the rate of 30°C/min, and then held isothermally at 220°C for 10 min. The samples were then cooled down from 220°C to 20°C at 30°C/min. Finally, the thermal properties of the samples were recorded by heating the samples from 20°C to 220°C at the rate of 10°C/min. Crystallinity and melting temperatures of each batch were analysed.

The percentage crystallinity of PLA in the blends can be calculated by Eq. 1:

$$X_C = \frac{\Delta H_f}{\Delta H_f^\circ \times W} \times 100\% \quad (1)$$

Where,  $\Delta H_f$  is the apparent melt enthalpy of PLA/PCL blend,  $\Delta H_f^\circ$  is the melt enthalpy of completely crystalline PLA, which is 93.6 J/g [2], W is the weight fraction of PLA in the blend.

### 2.6 Morphology

The surface of PLA and PLA/PCL blends were studied by using a Wild M3Z microscope, images were taken at magnification of 400.

### 2.7 Contact angle analysis

The contact angle distilled water made with each sample was recorded using a Firsttenangstroms, FTA32 goniometer. For each individual sample three individual drops were recorded in different locations on each sample giving a total of 33 images for each PLA/PCL blended film.

### 2.8 Statistical Analysis:

Statistical analysis of the tensile data ( $n = 8$ ), contact angle ( $n = 33$ ) between batches, and differences between PCL fractions in the compound ( $n = 5$ ) were performed using one way ANOVA. Differences were considered significant when  $p \leq 0.05$ . The software used to perform statistical analysis was Minitab for windows.

### 3. RESULTS AND DISCUSSION

#### 3.1 Fourier Transform Infrared Spectroscopy

The molecular formula of PLA is  $(C_3H_4O_2)_n$ , while PCL is  $(C_6H_{10}O_2)_n$ . There are CH bonds and CO double bonds, which attribute to the characteristic peaks of PLA and PCL. In figure 1, the peaks located at  $2995\text{cm}^{-1}$  for PLA and  $2945.1\text{cm}^{-1}$  for PCL are responsive for the stretching of CH bonds respectively, while the peaks of  $1759.9\text{cm}^{-1}$  for PLA and  $1723\text{cm}^{-1}$  for PCL are responsible for the vibration of CO double bond [15]. The blends have the peak between  $2997.76$  and  $2945.11\text{cm}^{-1}$ , there is no significant shift in the peaks for PLA/PCL blends, this might suggest that there is very little interaction occurred between PLA and PCL in the blend.

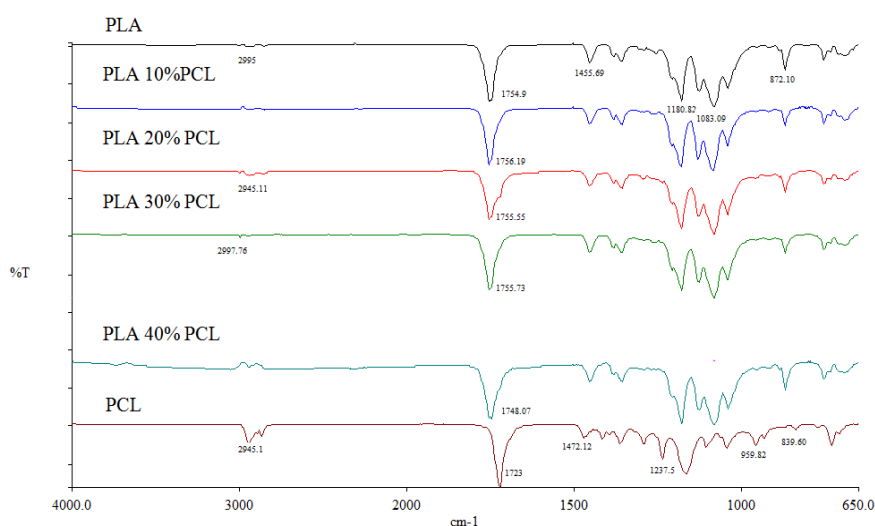


Figure 1: FTIR spectra of PLA, PLA/PCL blends and PCL.

#### 3.2 Differential Scanning Calorimetry

The thermal characteristics of the blends were investigated via DSC. Glass temperature, melting temperature, and heat of fusion of each blend were recorded in table 1 and the thermograms are illustrated in figure 2.

Table 1: Results from DSC for PLA and PLA/PCL blends

	Tm (PCL) °C	Tg (PLA) °C	Tm (PLA) °C	$\Delta H_f$ (PLA) J/g
PLA 0% PCL	N/A	65.44	168.82	107.8

PLA 10% PCL	59.53	N/A	170.17	109.6
PLA 20% PCL	58.8	N/A	171.15	79.46
PLA 30% PCL	59.85	N/A	168.84	64.26
PLA 40% PCL	59.03	N/A	169.44	28.6

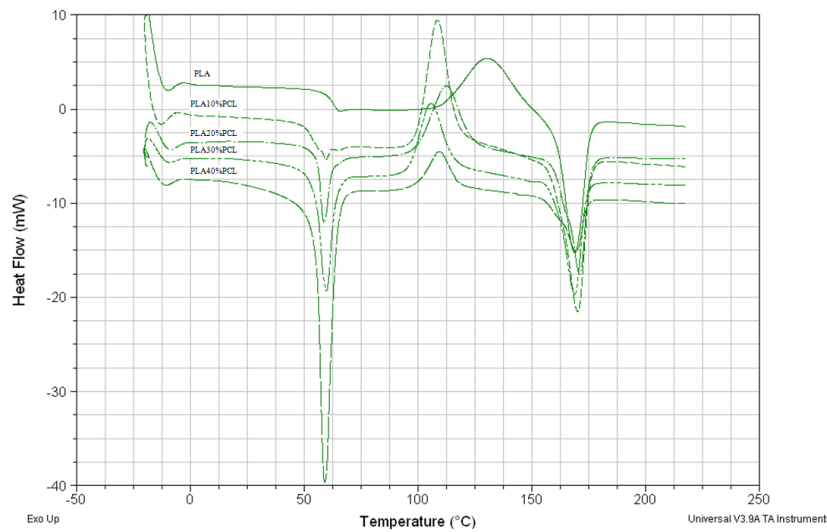


Figure 2: DSC thermograms of PLA and PLA/PCL blends

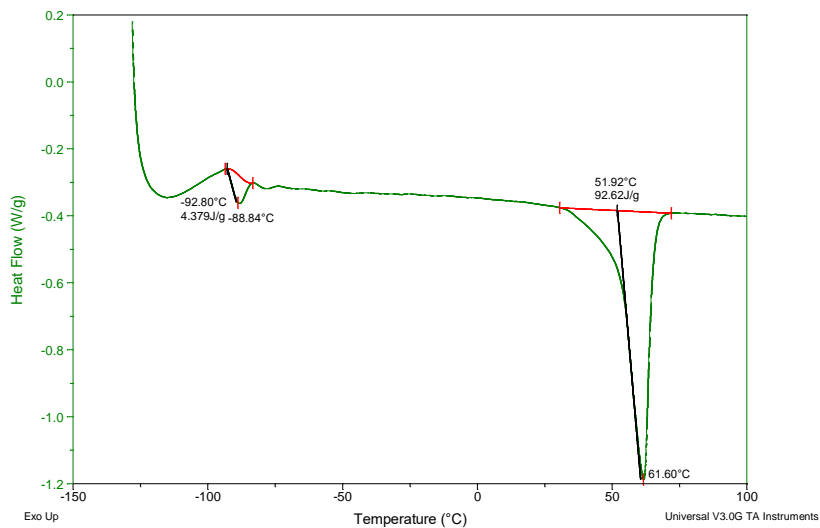


Figure 3: DSC thermograms of virgin PCL

The melting temperature of PCL has been reported as been  $\sim 60^{\circ}\text{C}$  [16] and is measured to be  $61.6^{\circ}\text{C}$  (figure 3). The glass temperature of PLA has also been reported as been  $\sim 60^{\circ}\text{C}$  [2], hence the

overlapping of these transitions can be seen at 60°C, the T<sub>g</sub> peaks of PLA are masked by the melting region of PCL (figure 2) [14, 17].

Two independent melting peaks, one corresponding to PCL ( $59.3 \pm 0.5^\circ\text{C}$ ) and the other one corresponding to PLA ( $169.7 \pm 1.5^\circ\text{C}$ ), suggests that PLA and PCL are not miscible. It has to be noticed that the fusion enthalpy of PLA has reduced dramatically from 107.8J/g for virgin PLA to 28.6J/g for PLA40%PCL, which is indicating a reduction of degree of crystallinity as a consequence of PCL influence on the kinetics of PLA crystallization.

### 3.4 Contact Angle Test

The wettability of the blends was investigated via contact angle when a distilled water interface met PLA/PCL blended films, and the results were recorded in figure 4.

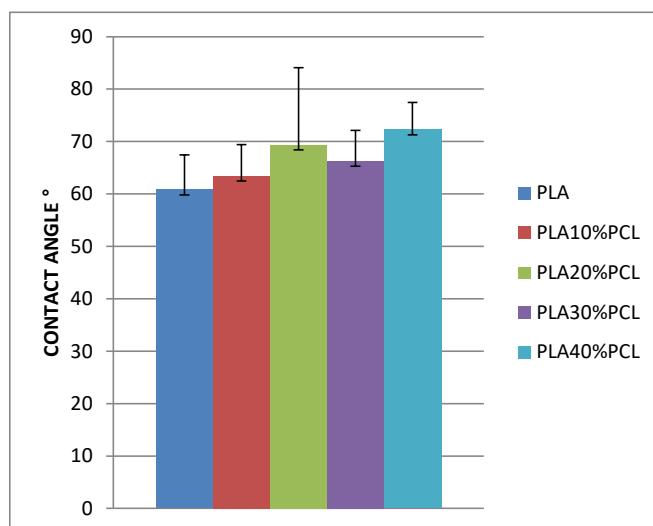


Figure 4: Contact angle for the PLA/PCL film.

From analysis of the results it was found that no significant differences could be detected between groups ( $p = 0.414$ ). These results indicate that the additional of PCL to PLA did not affect the wettability of the surface.

### 3.5 Morphology

Virgin PLA film had a smooth consistent surface. Conversely, the PLA/PCL blends had a roughened surface with clear signs of phase separation between the polymer components (figure 5).

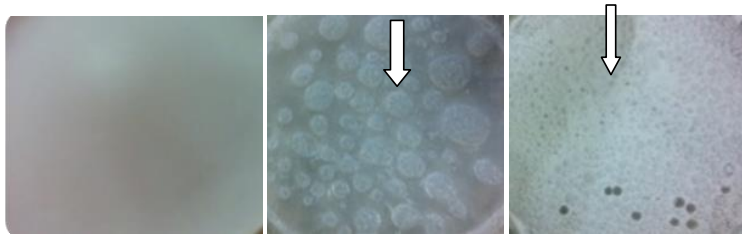


Figure 5: Left, virgin PLA; Middle: PLA/30%PCL; Right, 40%PCL/PLA. The arrows indicate the interface between the PLA and PCL segments in the blend. These boundaries are a clear indication of phase separation

Droplets and the boundaries between the two components can be clearly spotted via a naked eye for the fraction of 30% and 40% PCL in the blends (figure 5). Similar immiscible droplet structures were gained by Yeh et.al and Patricio [14, 17]. The droplet structures were observed under the wild M3Z microscope at the magnification of 400 and the pictures were shown in figure 6.

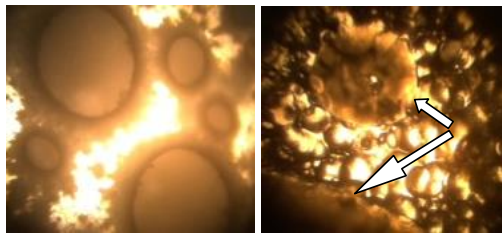


Figure 6: Microscopic images of droplet structures at magnification of 400. Left: PLA30%PCL, Right: PLA40%PCL. The arrows indicate the boundary between the droplet and matrix.

The clear boundaries indicate the poor adhesion and little interaction between the two components. The droplets among the matrix were likely attributed to the PCL component of the blend [14, 17].

### 3.2 Mechanical Properties

PLA is recognized for being a strong biodegradable material with a relatively high tensile strength and Young's modulus. Adding PCL might impair the mechanical strength of PLA but improve toughness.

The results from tensile testing were recorded in table 1. Due to the obvious immiscibility of PLA30%PCL and PLA40%PCL blends which resulted in the breaking point occurring at the boundaries between PCL disperse and PLA matrix, the results were invalid and not included in the table 1.

Table 1: Tensile properties of PLA/PCL blends

	Stress at Maximum Load (MPa)	Percentage Strain at Maximum Load	Young's Modulus (MPa)
PLA0%PCL	12.38024	162.265	430.408
PLA10%PCL	9.906	160.808	367.8722
PLA20%PCL	6.759	175.353	98.428

By adding PCL the tensile strength of PLA reduced from 12 MPa for virgin PLA to 10 MPa for PLA10%wt PCL and further down to 6.7 MPa for PLA and 20%wt PLC blend ( $p = 0.012$  for all comparisons, there are difference among the means that the 0.05 level of significance); while Young's modulus dropped significantly from 430MPa for virgin PLA to 368MPa for PLA10%wt PCL and further down to 98MPa for PLA and 20%wt PLC blend ( $p < 0.05$  for all comparisons, there are significant difference).

PLA is a brittle material with relative low elongation at the maximum load, while PCL is a ductile material with a high elongation at the maximum load, by blending PCL with PLA the elongation of PLA can be improved, which was agreed by the test results that the percentage strain at the maximum load for virgin PLA was 162.265 and increased to 175.353 for PLA and 20%wt PLC blend ( $p = 0.228$ , for all comparisons).

#### 4. CONCLUSION

Various weight fraction of PCL were blended with PLA by solution method and solvent casting in this study. The resultant blends of PLA and PCL indicated that the polymer were immiscible using this preparation method. This finding was supported by two separated melting temperatures from two polymers in DSC test and also the little interaction shown in FTIR result. The droplets which were likely attributed to the PCL component of the blend and the boundaries between these two components were clearly seen through microscope, indicating that a heterogeneous blend was formed. The mechanical properties were impaired due to the poor adhesion between the two polymers. This poor interaction tween the two polymers, may be the reason that PCL did not influence the surface characteristics of the blends, which resulted in no significant differences between detected in contact angle measurements.

#### ACKNOWLEDGMENTS

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