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# CO<sub>2</sub> Assisted blending of poly(lactic acid) and poly(ε-caprolactone)

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## Abstract

Poly(lactic acid) (PLA) is gaining increasing interest from the packaging industry as a biodegradable alternative to oil based polymers such as polypropylene (PP) and polyethylene terephthalate (PET). However, its' inherent brittle nature prevents widescale commercial use. Blending in order to improve the Young's modulus, yield stress and elongation to break, provides a possible alternative although many polymers have been found to be immiscible with PLA. In this study, high pressure carbon dioxide (CO<sub>2</sub>) was utilised during blending to encourage miscibility between two normally immiscible polymers: poly(ε-caprolactone) (PCL) and poly(lactic acid) (PLA). Blends were prepared by melt blending in the presence of carbon dioxide (CO<sub>2</sub>) and compared to solvent casting and melt blending with a single-screw extruder. CO<sub>2</sub> assisted blends demonstrated a significant reduction in the size and number of PCL domains in a PLA matrix, and consequently improved the adhesion between phases at the microscale. The optimum melt blend composition for Young's modulus, yield stress and elongation to break was found to be 75% PLA and 25% PCL. Mechanical properties of PLA 2002D blends were further improved when prepared by CO<sub>2</sub> assisted melt blending.

**Keywords:** Poly(lactic acid), Poly(ε-caprolactone), blends, carbon dioxide, extrusion.

## 1. Introduction

The use of biodegradable polymers is becoming increasingly widespread as their applications broaden into both the biomedical [1] and food packaging industries [2]. Persistent rapid

growth in the consumption of biodegradable plastics is forecast for the foreseeable future [3]. Among biopolymers, poly(lactic acid) (PLA) is the most prevalent in the market place, due to availability and relatively low cost of production compared to other biopolymers [4]. It is extensively used in various medical applications, such as drug delivery [5] and scaffolds in tissue engineering [6]. Additionally, there is a growing interest in the use of PLA as food packaging because PLA can be derived from natural sustainable resources and can biodegrade if correctly composted. PLA is produced from lactic acid which can be obtained from renewable (sustainable) resources such as corn and sugarcane [7, 8]. It has therefore attracted attention as an alternative to synthetic non-biodegradable polymers. However, it has been reported that PLA is relatively brittle [9] and this has limited its range of applications. Blending with other biodegradable polymers offers a possible solution to this problem. If two polymers are miscible, their mechanical, thermal and physical properties combine to generate intermediate properties, relative to their composition. Therefore, by selecting a miscible biopolymer with greater ductility, the brittle characteristics of PLA can be improved. There have been a number of attempts to improve the mechanical properties of PLA in this way by inclusion of a soft elastomeric heteropolymer into PLA. This has been identified as a method to improve the Young's modulus of the polymer blend [10, 11].

Poly( $\epsilon$ -caprolactone) (PCL) is a partially crystalline, biodegradable, aliphatic polyester with a low glass transition temperature in the region of  $-60$  °C. PCL has a relatively low tensile Young's modulus and yield stress and is ductile at room temperature. PCL can exhibit elongation-to-break values in the region of 800%. Despite immiscibility being previously reported for PLA and PCL, the ductility of PCL makes it a desirable blend component for PLA [12].

PLA/PCL blends, produced through solvent casting from chloroform [10, 13] and methylene chloride [14], were found to be immiscible using DSC, DMA and SEM. Choi *et al.* [13] studied the effect of compatibilisers; P(LLA-*co*- $\epsilon$ CL) and P(LLA-*b*- $\epsilon$ CL), on the morphology of PLA/PCL blends. Miscibility was not obtained, however there was a reduction in size of the dispersed PCL domains.

Broz *et al.* [14] found poor adhesion at the phase boundary interface and confirmed immiscibility and phase separation through NMR. It was hypothesised that to improve the mechanical properties of the blend, the samples should be annealed in the single-phase region of the LCST phase-diagram to enhance interfacial adhesion. It was concluded that interfacial adhesion may occur when the majority phase is PCL [10].

PLLA/PCL blends have also been produced through a conventional melt-mixer followed by reprocessing into plaques [9, 15]. Improvements were seen in the mechanical properties and the fracture toughness of PLA with the addition of just 5% PCL. The improvement is a result of multiple craze formation, nucleated by debonding of spherulite interfaces. SEM and DSC confirmed phase separation using this production method, although some adhesion was seen between phases.

In other polymer blend systems, high pressure and supercritical carbon dioxide (CO<sub>2</sub>) assisted blending has been exploited in the production of PCL/PHB [16], PE/PS [17, 18] and PLA/PEG blends [19]. However, it has yet to be explored in the blending of PCL and PLA. The introduction of CO<sub>2</sub> into the melt has been seen to promote miscibility in polymer systems [16-18]. CO<sub>2</sub> is able to diffuse into the free volume of the system allowing Lewis acid-base reactions to occur, reducing the chain entanglements by inhibiting the secondary interactions between the chains [20]. This expands the chain separations and facilitates chain motions. Blends of PE/PS prepared in the presence of CO<sub>2</sub> demonstrated a reduction in the size of the dispersed phase from a few microns to submicrons [17].

It can be seen from previous research that the blending of PCL and PLA has been found to be immiscible when prepared through solution and melt blending. Blending PLA and PCL in the presence of CO<sub>2</sub> has not been reported. Therefore, the aim of this work is to compare the domain size and mechanical and thermal properties of PLA/PCL blends formed by solution, melt and CO<sub>2</sub> assisted blending. More specifically, to determine whether CO<sub>2</sub> can induce miscibility in polymer blend systems that has been shown otherwise to be immiscible.

## 2. Materials and Methods

### 2.1 Materials

Poly-DL-(lactic acid) (PLA) grades; semi-crystalline 2002D and amorphous 4060D in the form of pellets were supplied by NatureWorks LLC (Nebraska, USA). Poly( $\epsilon$ -caprolactone) (PCL) grade CAPA 6800 ( $M_w$  212,000 g mol<sup>-1</sup>) was supplied as pellets by Perstorp UK Ltd (Warrington, UK). The properties of all three polymers can be found in Table 1. CO<sub>2</sub> (purity 99.9 %v/v) was obtained from BOC (Birmingham, UK) and used as received.

Table 1: Properties of the polymers used within this paper (\*[21] \*\*[22])

Polymer	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	D-lactide Content (%)	M <sub>w</sub> (g mol <sup>-1</sup> )
PLA 2002D	55	154	4*	194,000
PLA 4060D	52	-----	11-13**	181,000
PCL CAPA 6800	-60	60	-----	212,000

### 2.2 Blend Preparation

Blends were prepared by solution casting, melt extrusion and CO<sub>2</sub> assisted melt extrusion. The following PLA/PCL compositions were produced for each preparation method; 0/100, 25/75, 50/50, 75/25 and 100/0 by weight.

#### 2.2.1 Solution Blending

Dichloromethane was chosen as a common solvent to dissolve both PLA and PCL. The required masses of each polymer (totalling 4 g) were dissolved in dichloromethane (40 ml) to give a 10% w/v solution. The solutions were then covered and stirred for 2 hours to ensure complete dissolution of both polymers. Films were cast into petri dishes, 9 cm in diameter, covered with glass lids and left to slowly evaporate for 2-3 days. Slow evaporation prevented the development of voids in the blend samples.

#### 2.2.2 Production of Melt Blends by Extrusion

Prior to extrusion, the PLA grades were dried to remove any residual moisture. Drying

temperatures and times were selected in accordance with the processing data sheets provided by Natureworks. Consequently, PLA 4060D was subjected to 4 hours at 45 °C and 2002D for 2 hours at 90 °C. The dried polymer was subsequently stored in desiccators with silica gel (previously dried).

The melt blends were produced using a Rondol (Staffordshire, UK) bench top linear 25 mm rotating single-screw extruder with a L/D (length/diameter) ratio of 25:1. The screw possesses a general purpose profile of 3:1 compression ratio. It was made of high strength carbon steel, heat-treated, polished and removable to enable cleaning. The screw speed was infinitely variable between 0 and 120 rpm. The barrel was also composed of heat-treated high strength carbon steel, fitted with a pressure relief valve for over pressure protection. The temperature was controlled through a series of heaters, one in each of the three zones. The barrel and die temperatures were controlled between 0-300 °C and cooled using a tangential water cooling system. A stainless steel two roll take-off unit (with cooling / polishing rolls) placed after the die, cooled the extrudate before passing onto a conveyor belt.

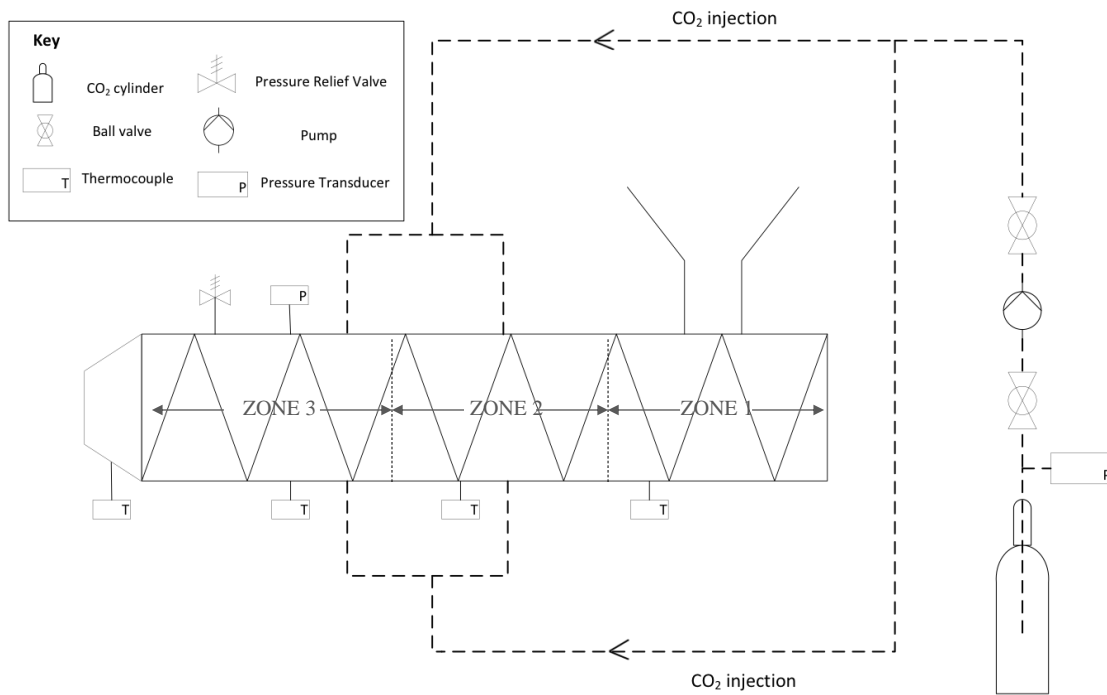
Blends of pellets, pre-mixed by mass, were added to the hopper of the extruder in 200 g batches. Barrel and die temperatures were set to 160 °C and 170 °C, respectively. The pressure in the screw was monitored using an external pressure transducer. Samples were extruded through a 1 mm slit die and passed through the cooled rollers onto a conveyor belt. Screw speeds of 20 and 30 rpm were selected.

### *2.2.3 Production of Carbon Dioxide Assisted Blends*

Blends were also produced in the presence of CO<sub>2</sub> using the same extruder as discussed above, however the extruder was modified to allow the injection of CO<sub>2</sub> into the polymer melt.

CO<sub>2</sub> was injected via a custom made design of 4 injection ports, 2 on either side of the barrel, into zones 2 and 3 (see figure 1 for extruder set-up). A Jasco pump (Model PU-2086 Plus)

fitted with a chiller head enabled CO<sub>2</sub> to be pumped in liquid form. A pressure relief valve was installed to prevent over pressurisation in the extruder. The pressure in the extruder was monitored using a pressure transducer to within 0.1 bar using a Druck PTX (Leicester, UK) transducer.



**Figure 1.** Schematic of the extruder set-up illustrating the injection of CO<sub>2</sub>.

CO<sub>2</sub> was added at a specific concentration in relation to the polymer flow rather than at a set pressure to maintain consistency throughout the polymer. This resulted in an average combined CO<sub>2</sub>/polymer pressure of 67 bar in the extruder. In order to calculate the CO<sub>2</sub> concentration for addition into the extruder, each polymer was extruded at both 20 and 30 rpm and the average of three extruded masses per minute was calculated for each screw speed. The CO<sub>2</sub> flow rate (g/min) was then calculated as a wt% of the measured polymer mass extruded per minute using equation 1. This enabled the input of a given concentration of CO<sub>2</sub>, in relation to the polymer, into the extruder. This calculated value was converted into ml/min as CO<sub>2</sub> was injected as liquid. Equation 2 shows this conversion. The density of CO<sub>2</sub> was calculated by NIST web-book [23] as 0.91898 g/ml based on the CO<sub>2</sub> pressure (4.8 MPa) and temperature (4 °C) in the pump.

$$\mathit{Flow\ rate}_{CO_2} \text{ (g/min)} = \frac{\mathit{CO}_2 \text{ Concentration (wt\%)}}{100} \times \mathit{Flow\ rate}_{\text{polymer}} \text{ (g/min)} \quad [\text{Eq. 1}]$$

$$\mathit{Flow\ rate}_{CO_2} \text{ (ml/min)} = \frac{\mathit{Flow\ rate}_{CO_2} \text{ (g/min)}}{\mathit{Density}_{CO_2} \text{ (g/ml)}} \quad [\text{Eq. 2}]$$

CO<sub>2</sub> is known to depress the melting point of semi-crystalline polymers, it was found that blends of PLA and PCL could be readily extruded at reduced barrel and die temperatures of 150 °C and 160 °C, respectively. As the Gibbs free energy equation states that blending is proportional to temperature, the reduced processing conditions will not enhance miscibility and therefore any effects observed will be due to the presence of CO<sub>2</sub> alone.

### 2.3 Microstructural, Mechanical and Thermal Analysis

Fracture surfaces were produced by a flexural loading of the blend samples following immersion in liquid nitrogen. The fracture surfaces were mounted on an aluminium stub using conductive carbon adhesive discs and coated in gold using a Polaron SC7640 sputter coater. Coating the samples for 3 minutes deposited approximately 10 to 12 nm of gold, which provided sufficient conductivity to minimize charging of the sample surface. Samples were imaged using a Phillips (XL30 ESEM) scanning electron microscope. An accelerating voltage of 10 kV was selected.

Tensile tests were carried out using a mechanical test instrument (Instron 5566) interfaced to a PC. The instrument was controlled using proprietary Instron Merlin software. Samples were cut into a standard 25 mm (L<sub>0</sub>) 'dog-bone' shape. The width of the narrow central section was 4 mm and the thickness was recorded from a three-point average. Stress-strain curves were recorded at 25 °C and at a strain rate of 10 mm/min. Young's modulus, elongation to break and yield stress were determined from the resulting stress-strain curves. A minimum of 5 repeats were performed for each blend system.

Thermal analysis of the blends was performed using a Mettler Toledo DSC1 (Greifensee, Switzerland) purged with nitrogen at a gas flow rate of 100 cm<sup>3</sup>/min. The instrument was

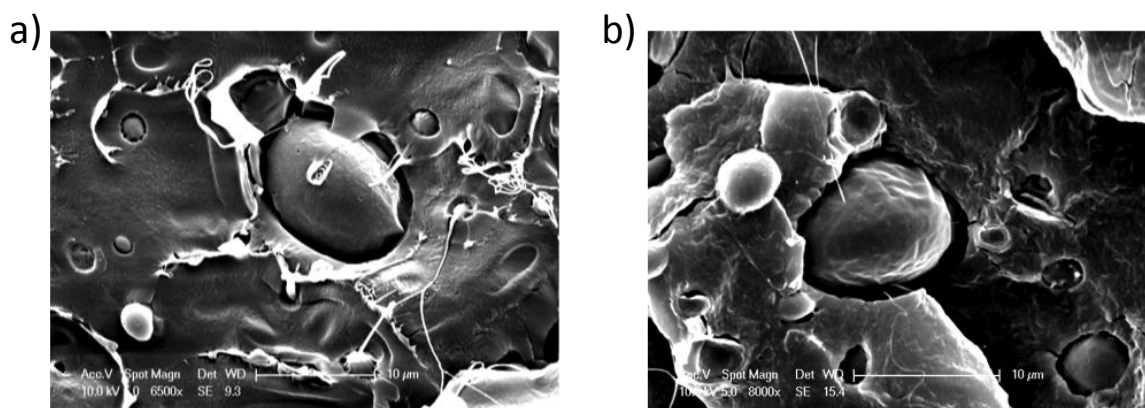


interfaced to a personal computer and controlled using proprietary STARE software (version 11). The thermal response of the instrument was calibrated from the enthalpy of fusion of a known mass of indium (99.999% pure). The temperature of the calorimeter was calibrated using the melting point of tin. Samples of around 5-7 mg were contained in aluminium pans with an empty pan used as a reference. The glass transition temperature ( $T_g$ ), melting point ( $T_m$ ) and enthalpy of fusion ( $\Delta H_f$ ) of the blends were measured from the initial heating run at 10 °C/min.

### 3. Results and Discussion

#### 3.1 Microstructural Characterisation

The blends created by solvent casting from dichloromethane showed clear evidence of gross phase separation for each of the blend systems. Relatively large domains (up to 10  $\mu\text{m}$ ) were observed by SEM (Figure 2a, 2b and supplementary information). This observation is in accordance with other studies in which clear phase separation is reported, although it should be noted that these observations were made in blends produced from different grades of PLA and PCL [24]. No difference was observed between the two grades of PLA.



**Figure 2a and b.** SEM images of solvent cast **(2a)**: 75/25 PLA 4060D/PCL and **(2b)**: 75/25 PLA 2002D/PCL.

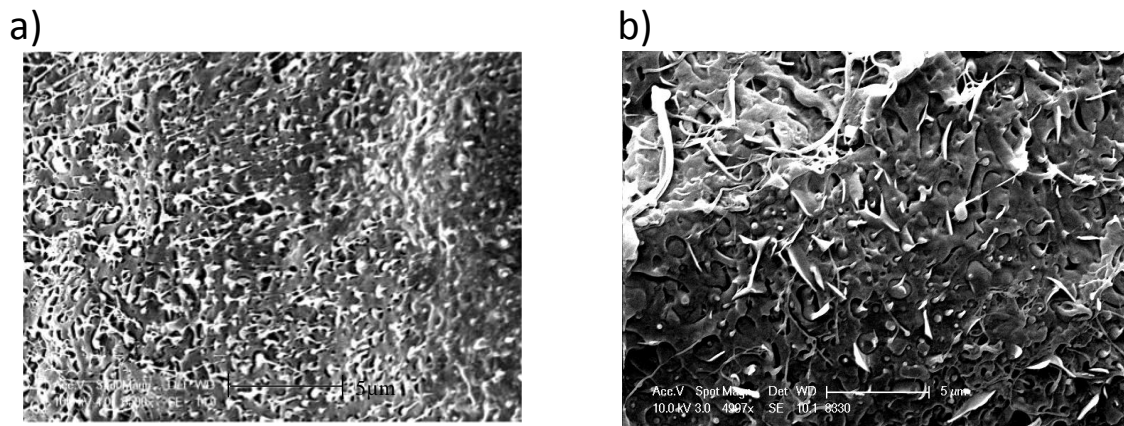
Solution casting from dichloromethane dissolves both polymers allowing constituent polar groups to interact. However, slow evaporation of the solvent (which was required in order to reduce the formation of voids) provides time for the polymers to phase separate and encourages crystallinity to develop causing further phase separation. The observation of

phase separation in previous PLA/PCL solvent-cast blends was attributed to crystallisation of PCL and expulsion of PLA in these crystalline regions through spherulitic growth [25]. It was noted that phase separation may also be induced by the presence of a third component, the solvent. Solvent-casting these blends promotes phase separation and may not reflect the true morphology of the two component systems.

The polymer blend solution was initially transparent and no interfacial boundary layers were observed as a result of any solution density differences. Therefore, molecular level mixing was assumed to have taken place. Subsequently, no boundary layers were observed to develop on evaporation of the solvent, yet the final blend was grossly phase separated. Clearly, the phase separation observed in this preparation method was induced by crystallisation of the homopolymers from solution.

As seen above for solvent cast blends, at a composition of 75/25 PLA/PCL, the immiscibility results in the formation of PCL spheres within the PLA 4060D and 2002D matrices. On fracturing the material prior to SEM analysis, PCL spheres can drop out of the fracture surface resulting in the formation of concave holes. The number and dispersion of these concave holes and PCL spheres can be used to assess the miscibility.

Melt blending with a single screw extruder was also found to yield a phase separated system at all compositions, screw speeds and PLA grades investigated. However, a clear improvement in dispersion and domain size (reduced from 10  $\mu\text{m}$  by solvent casting to around 1  $\mu\text{m}$  by melt blending) was observed in the 75/25 PLA/PCL composition (Figures 3a, 3b and supplementary information).



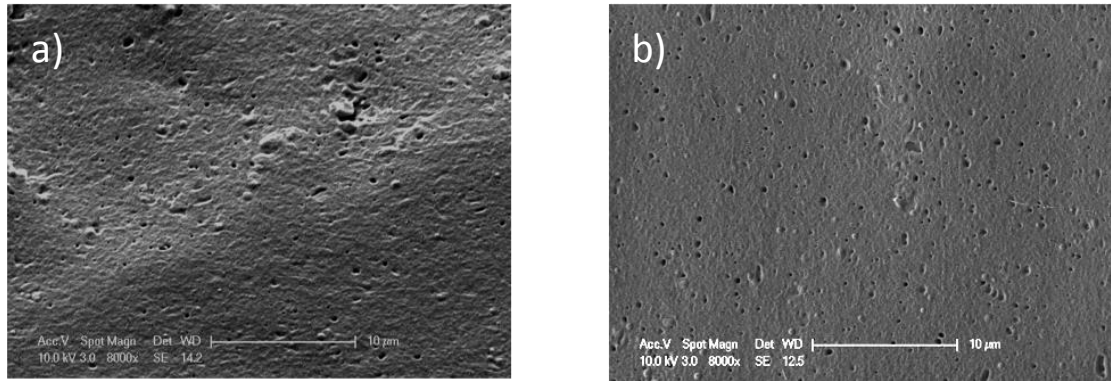
**Figure 3a and b.** SEM images of melt blends produced with a single screw extruder at 160 °C. **(3a):** 75/25 PLA 4060D/PCL at 20 rpm. **(3b):** 75/25 PLA 2002D/PCL at 30 rpm.

The application of heat (160 °C which is above the melting points of both polymers) combined with the shear forces of mechanical mixing during melt blending, initially creates a higher level of dispersion allowing the blends to transform from the two phase into the one phase region of the LCST curve [12]. Previous work has also shown that the low interfacial tension and similar viscosities of the two polymers contribute to both size and homogeneity of the dispersed phase and final sample morphology [26].

The morphology of the blend system is stabilised on cooling after exiting from the die at the end of the barrel. If there is vitrification of the PLA component prior to the crystallisation-induced phase separation of PCL from the blend, a miscible system will be retained. However, in this case, the cooling rate was insufficient to limit the phase separation of PCL, although an enhanced dispersion was still evident.

A further improvement in the dispersion, as indicated by a reduction in the size and quantity of the PCL domains, was observed when the blends were prepared in the presence of CO<sub>2</sub> (Figures 4a, 4b and supplementary information). Similar to the melt blends, the blend composition that showed the greatest reduction in size and dispersion of domains was 75/25 PLA/PCL for both PLA grades. Domain sizes in these blends were around 0.2 μm in diameter. However, all blends produced in the presence of CO<sub>2</sub> showed a high degree of porosity (around 100 nm in diameter) due to the effect of depressurisation of the blend system on

exit from the extruder. These are easily distinguishable from the concave holes formed by loss of PCL domains as small cylindrical voids. Similar images were obtained for PLA 4060D and PLA 2002D.



**Figure 4a and b.** SEM images of blends produced in the presence of 10% carbon dioxide at 150 °C. **(4a):** 75/25 PLA 4060D/PCL at 20 rpm. **(4b):** 75/25 PLA 2002D/PCL at 30 rpm.

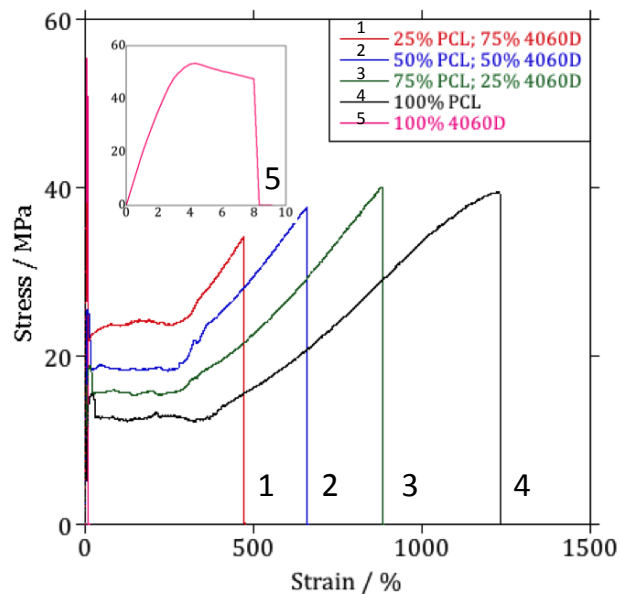
Similar enhanced miscibility in the presence of CO<sub>2</sub> has been previously reported [16-19]. The gaseous properties of CO<sub>2</sub> enables its diffusion into the free volume of polymers, between the individual chains. Once inside, CO<sub>2</sub> forms Lewis acid-base interactions with the carbonyl groups (present in both PLA and PCL). This disrupts the inter/intra molecular interactions, decreasing the number of chain entanglements within the polymers and consequently reduces their melting point and viscosity [20]. The creation of additional free volume and increased chain mobility enables better interaction and mixing between the two polymers, enhancing the potential for miscibility in this system. Blend morphology has been investigated in other polymer systems: PE/PS blends and PS/PMMA using carbon dioxide [17, 18, 27]. These blends showed a significant decrease in the size of the dispersed phase from a few microns to submicron by injecting CO<sub>2</sub>. This enhanced miscibility means more intimate mixing of PLA and PCL resulting in consistency throughout the material.

A completely miscible blend system will display only one phase in an SEM image. Large spherical domains of the minor phase dispersed within the major phase were found by SEM following solvent blending, indicating poor miscibility. Melt extrusion was found to reduce

the size of these domains and CO<sub>2</sub> assisted melt extrusion reducing them further, indicating the highest miscibility of the two polymers.

### 3.2 Mechanical characterisation

Figure 5 shows a representative example of the engineering stress-strain curves for all PLA 4060D/PCL blends produced by melt blending. The curve for 100% PLA is shown as an inset due to the dramatic change in elongation-to-break. It is clear that with increasing PCL content in the blend, the tensile behaviour of the blend system changed dramatically: the reduction in yield stress was compensated by a significant increase in elongation at break. The same trend was also apparent in the PLA 2002D/PCL system.

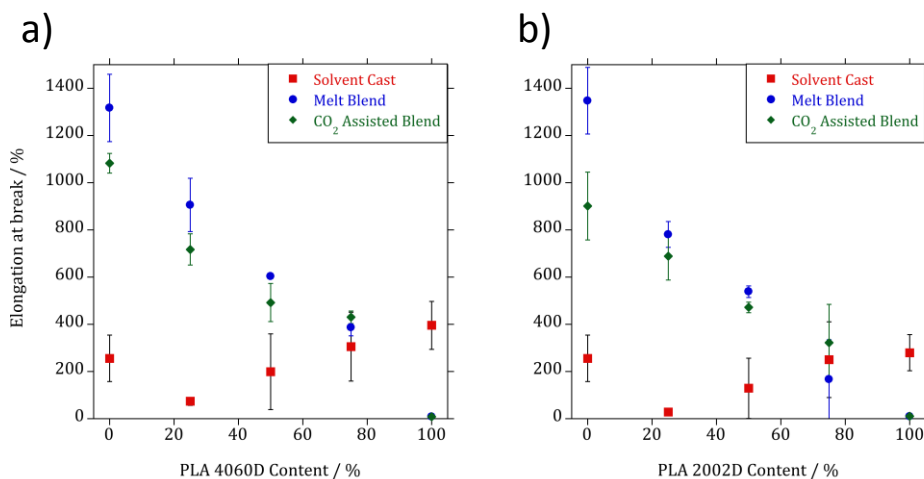


**Figure 5.** An example of the engineering stress-strain curves for the mechanically blended PLA 4060D/PCL blend system. Inset top left is the result for 100% PLA.

Figures 6, 7 and 8 illustrate the variation of mechanical properties with composition for both blend systems and all three preparation methods. The mechanical properties of the blends

produced by melt and CO<sub>2</sub> assisted extrusion generally change linearly with composition, suggesting that they are obeying the rule of mixtures.

Pure PCL has a much higher elongation to break than both PLA 4060D and 2002D. The results (Figure 6) show a reduction in the elongation to break as the content of both grades of PLA is increased, indicative of blending. This coincides with the SEM for both melt and CO<sub>2</sub> assisted blending. No significant difference was observed between the two methods. The porosity generated on venting the CO<sub>2</sub> from the polymer following extrusion introduces stress concentration sites into the structure, resulting in premature breakage. Further evidence is the reduction in elongation to break values for pure PCL produced in the presence of CO<sub>2</sub> compared to melt blending.



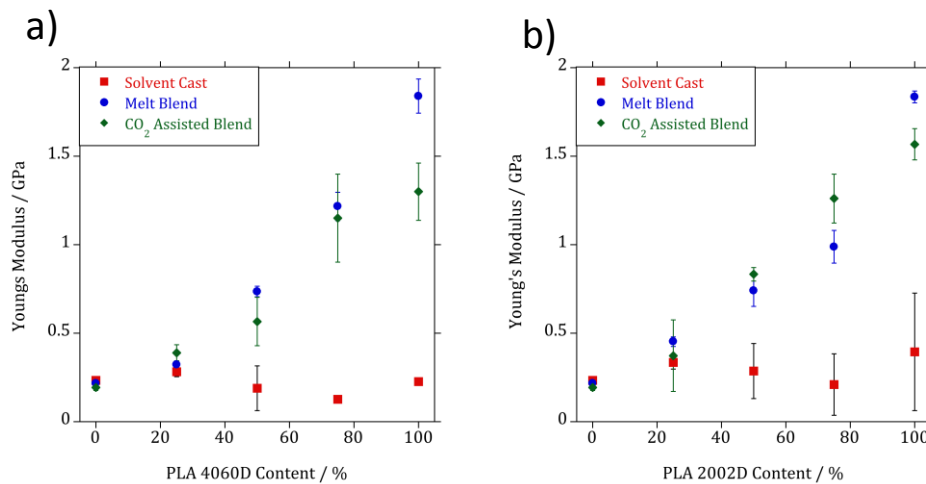
**Figure 6a and 6b.** A comparison of elongation at break for solvent cast, melt and CO<sub>2</sub> assisted blends of **(6a)**: PLA 4060D and **(6b)**: PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

In contrast to these results, the blends formed through solvent casting are markedly different. An initial reduction in the elongation is observed on the addition of both PLA 4060D and 2002D, which increases again as the proportion of PLA rises. The much lower values obtained compared to the other processing techniques are attributed to gross phase separation of the two components. Residual solvent is also known to act as a plasticiser in

solvent cast polymers and blends which accounts for the increase in elongation to break for pure PLA 4060D and 2002D compared to the other blending methods. In contrast, the elongation to break of PCL is reduced to below the value of PLA following solvent casting. This leads to an increase in elongation to break as the PLA content is increased within the blend.

Figure 7 shows an increase in Young's modulus as PLA 4060D and 2002D content increases for melt blending with and without the presence of CO<sub>2</sub>. There are little differences in the values between the two blending methods, with exception of 75% PLA 2002D, where there is a marked increase in the Young's modulus when blended in the presence of CO<sub>2</sub>, suggesting enhanced miscibility for this blend.

The solvent blending produced samples with a much lower modulus as a result of phase separation between the individual components.

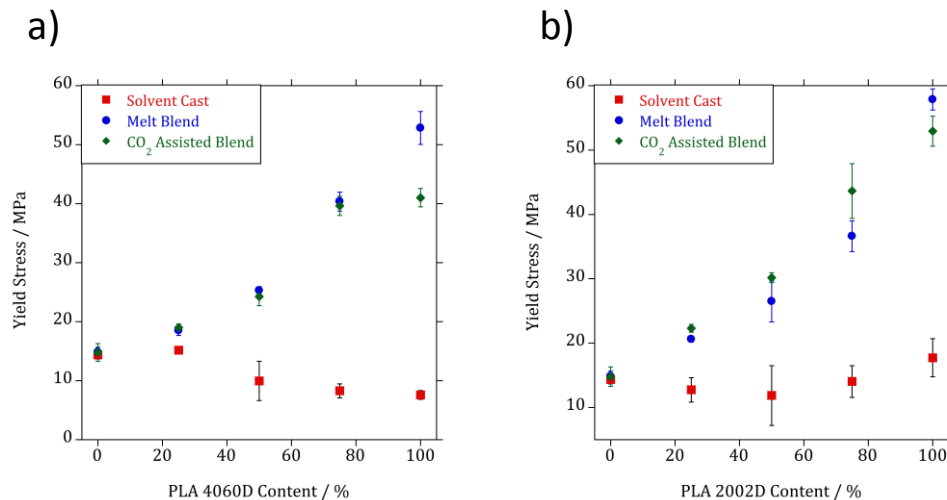


**Figure 7a and 7b.** A comparison of Young's Modulus for solvent cast, melt and CO<sub>2</sub> assisted blends of **(7a):** PLA 4060D and **(7b):** PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

There is little difference in the yield stress between the two melt blending techniques for PLA 4060D and PCL blends (Figure 8a and b). Interestingly, an improvement in the yield

stress was observed in the PLA 2002D/PCL blends when blended in the presence of CO<sub>2</sub>, becoming more significant as the PLA content increased. This is likely to be a result of enhanced mixing when processed with CO<sub>2</sub>, creating smaller PCL domains in the material and therefore smaller inclusions that cause the material to fracture. Solvent blended samples displayed a significantly lower yield stress compared to melt blended methods. Solvent casting was found to have no effect on yield stress of pure PCL, however, the strength of pure PLA was significantly reduced due to plasticisation by solvent residue. This coupled with poor miscibility resulted in the low yield stress values obtained.

The melt blend results differ from those published previously where complete phase separation resulted in a negative deviation from linearity in all mechanical properties [10]. A likely explanation is that the method mentioned in the paper included an additional thermal processing step using a hot-press, to produce suitable samples for mechanical testing. As this involves heating in a static environment it will promote phase separation.



**Figure 8a and 8b.** A comparison of yield stress for solvent cast, melt and CO<sub>2</sub> assisted blends of **(8a)**: PLA 4060D and **(8b)**: PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

A suitable packaging material must have a sufficiently high Young's modulus and yield stress to prevent weakening under load in addition to a high elongation to break, preventing brittle fractures of the product. In light of this, the most suitable melt blend was found to be 75%



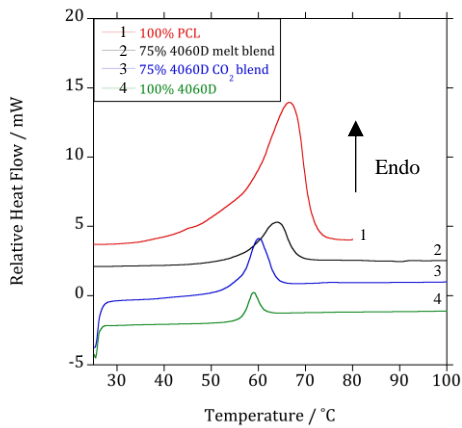
PLA (both 4060D and 2002D) with 25% PCL. However, the properties of the 2002D blend were enhanced further through melt blending in the presence of CO<sub>2</sub>, denoted by a higher Young's modulus and yield stress with no change in elongation to break. This concurs with the above SEM results, which show a smaller PCL domain size and quantity when processed in the presence of CO<sub>2</sub>, indicating increased miscibility.

Although not fully evident from mechanical testing analysis, due to porosity created during CO<sub>2</sub> venting, a clear improvement in the miscibility of PLA and PCL when melt blended in the presence of CO<sub>2</sub> is observed by SEM. This indicates that CO<sub>2</sub> has influenced the interfacial tension between both polymers enabling better mixing and dispersion of phases. The finer dispersion of PCL domains results in lower number of stress concentration points throughout the sample. This result is consistent with Todo *et al.* [9] who found that larger PCL domains within PCL/PLA blends hasten the initiation of fracture by inducing more severe stress concentrations than smaller phases within the blends.

### 3.3 Thermal Analysis

DSC was used to explore changes to the thermal transition temperatures in 75/25 PLA/PCL blends, where the best mechanical properties and smallest domain sizes were observed. Figures 9a and 9b show the DSC traces of 75/25 PLA/PCL and respective homopolymers for the PLA 4060D/PCL and PLA 2002D/PCL blends produced with and without the presence of CO<sub>2</sub>. As a result of the completely amorphous nature of PLA 4060D, only one melting endotherm corresponding to PCL was observed by DSC in the subsequent blends (Figure 9a). The temperature of this transition was found to decrease following blending, indicative of miscibility, by the larger reduction of the CO<sub>2</sub> assisted blend's melting point. The observation of two melting peaks in figure 9b confirms that phase separation has taken place in blends made by both techniques, and that any interactions in the melt were not significant enough to develop / retain complete miscibility on cooling. However, the melting point of PCL was again found to decrease following melt and CO<sub>2</sub> assisted blending, illustrating partial miscibility.

a)



b)

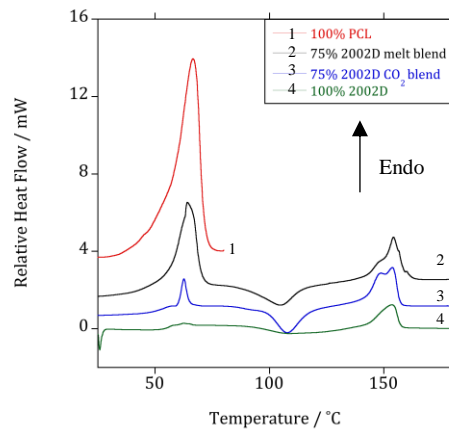


Figure 9a and 9b. A comparison of DSC traces of **(9a)**: 75/25 PLA 4060D/PCL and **(9b)**: 75/25 PLA 2002D/PCL produced by melt and CO<sub>2</sub> assisted blending with their homopolymers.

The pure PCL samples exhibit much larger melting endotherms for the PCL component (figure 9a and 9b) than those observed for the blended systems. In the PLA 2002D blend, this peak is further reduced when blended in the presence of CO<sub>2</sub>, exhibiting corresponding  $\Delta H_f$  PCL values of 62.66 J/g for 100% PCL, 46.6 J/g for the melt blend and 17.14 J/g for the blend produced in the presence of carbon dioxide. Division of these enthalpies of fusion by the value for 100 % crystalline PCL, 139 J/g [28], gives the crystallinity of the PCL component within the blend. From this it can be seen that there is a surprisingly low degree of crystallinity in the CO<sub>2</sub> assisted blend with PLA 2002D (12.3% compared with 33.5 % for melt blended). The reduction in crystallinity may be associated with fractionated crystallisation of the PCL component, influenced by a decreased number of nuclei per domain as the size decreases [29]. Similar results have been observed in PCL/PHB blends, where fractionated crystallisation also occurs in the PCL component [30]. This result was attributed to the dispersion of PCL into isolated domains, greater in number than the available active heterogeneities usually present in the bulk homopolymer [30]. A reduction in PCL crystallinity corresponding with decreased domain size has also been reported in PLLA/PCL blends [13].

The glass transition of PLA 4060D in each of the blends (Figure 9a) and PLA 2002D in the melt blend (Figure 9b) cannot be determined as a result of the overlapping transition with the melting endotherm of PCL. However, the glass transition of PLA 2002D (Figure 9b) can be partially seen immediately prior to the PCL melting endotherm in the PLA 2002D blend produced in the presence of carbon dioxide. The midpoint of this transition was found to be 52 °C compared to 56 °C exhibited by the homopolymer. This slight reduction in the  $T_g$  of PLA 2002D suggests the development of partial miscibility.

Cold crystallisation is observed between the melting peak of PCL and PLA 2002D (figure 9b) suggesting that PCL may be acting as a nucleating agent for PLA. The finer distribution of PCL domains (acting as more nucleating points) within the CO<sub>2</sub> assisted blend may allow additional crystallisation to occur upon heating. It has been commonly reported [31, 32] that PLA exhibits relatively slow crystallisation kinetics and it has been found that within the time-scales of a conventional DSC experiment run at 10 °C/min, PLA will not undergo crystallisation (on cooling) from the melt. Therefore, it is unusual to observe a melting endotherm post processing. The double melting peak on the PLA component for the CO<sub>2</sub> assisted blend indicates the formation of different lamellae sizes, often explained by the melt-recrystallisation model [8, 9]. The appearance of multiple melting peaks is reported in numerous partially crystalline polymers [33] such as poly(ether-ether-ketone) (PEEK) [34, 35], poly(ethylene terephthalate) (PET) [36], poly(butylene naphthalate) (PBN) [37], nylon-6 [38] and biodegradable polymers such as poly(L-lactide-co-glycolide) (PLGA) [39], and poly(lactic acid) (PLA) [40]. Many explain the double melting behaviour using the melt-recrystallisation model [41]. According to this model, the low temperature and high temperature endothermic peaks in the DSC melting trace are attributed to melting of original crystals (formed upon previous cooling) and to the melting of crystals formed within the heating scan of the experiment.

The reduced size of the PCL melting endotherm in the CO<sub>2</sub> assisted 75/25 PLA 2002D/PCL blend is an indication of increased miscibility over the PLA 4060D polymer and may explain the enhanced Young's modulus and yield stress results observed previously. The smaller

endotherm is indicative of lower crystallinity, arising due to a greater dispersion of PCL within the PLA 2002D domain. This greater dispersion will also result in fewer weak points within the structure and a strength comparative to PLA 2002D as observed in the mechanical testing results.

#### **4. Conclusions**

Blends produced by solvent casting display immiscibility across all compositions. A significant improvement in mechanical properties and polymer domain size was observed through melt blending using a single screw extruder. The 75/25 PLA (4060D and 2002D)/PCL blend was identified as having the optimum mechanical properties with the highest Young's modulus and yield stress with a high elongation to break. Although the mechanical properties of the CO<sub>2</sub> assisted blends showed little improvement on samples made by melt blending, the SEM images clearly indicate an improvement at the microscale with smaller and fewer PCL domains observed. However, porous structures have been observed which may explain the lack of a significant improvement in mechanical properties. Regardless of the porosity, an improvement in mechanical properties was found for the 75/25 PLA 2002D/ PCL blend following CO<sub>2</sub> assisted extrusion, corresponding to an increase in both the Young's modulus and yield stress compared to the other blending techniques.

Data sets from the above work may be requested from the authors by email (M.J.Jenkins@bham.ac.uk).

#### **5. References**

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### List of Captions

Figure 1. Schematic of the extruder set-up illustrating the injection of CO<sub>2</sub>.

Figure 2a and b. SEM images of solution cast (2a): 75/25 PLA4060D/PCL and (2b): 75/25 PLA2002D/PCL.

Figure 3a and b. SEM images of melt blends produced with a single screw extruder at 160 °C. (3a): 75/25 PLA4060D/PCL at 20 rpm. (3b): 75/25 PLA2002D/PCL at 30 rpm.

Figure 4a and b. SEM images of blends produced in the presence of 10% carbon dioxide at 150 °C. (4a): 75/25 PLA4060D/PCL at 20 rpm. (4b): 75/25 PLA2002D/PCL at 30 rpm.

Figure 5. An example of the engineering stress-strain curves for the mechanically blended PLA4060D/PCL blend system. Inset top left is the result for 100% PLA.

Figure 6a and 6b. A comparison of elongation at break for solution cast, melt and CO<sub>2</sub> assisted blends of (6a): PLA 4060D and (6b): PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

Figure 7a and 7b. A comparison of Young's Modulus for solution cast, melt and CO<sub>2</sub> assisted blends of (7a): PLA 4060D and (7b): PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

Figure 8a and 8b. A comparison of yield stress for solution cast, melt and CO<sub>2</sub> assisted blends of (8a): PLA 4060D and (8b): PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

Figure 9a and 9b. A comparison of DSC traces of (9a): 75/25 PLA4060D/PCL and (9b): 75/25 PLA2002D/PCL produced by melt and CO<sub>2</sub> assisted blending with their homopolymers.