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Co_2 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_2) 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_2) and compared to solvent casting and melt blending with a single-screw extruder. CO_2 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_2 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

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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(ε-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 compatibilsers; P(LLA-*co*-εCL) and P(LLA-*b*-εCL), 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_2) 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_2 into the melt has been seen to promote miscibility in polymer systems [16-18]. CO_2 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_2 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_2 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_2 assisted blending. More specifically, to determine whether CO_2 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(ε-caprolactone) (PCL) grade CAPA 6800 (M_w 212,000 g mol^{-1}) was supplied as pellets by Perstorp UK Ltd (Warrington, UK). The properties of all three polymers can be found in Table 1. CO_2 (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_g (˚C)	T_m (˚C)	D-lactide Content (%)	M_w (g mol^{-1})
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_2 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_2 using the same extruder as discussed above, however the extruder was modified to allow the injection of CO_2 into the polymer melt.

CO_2 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_2 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.

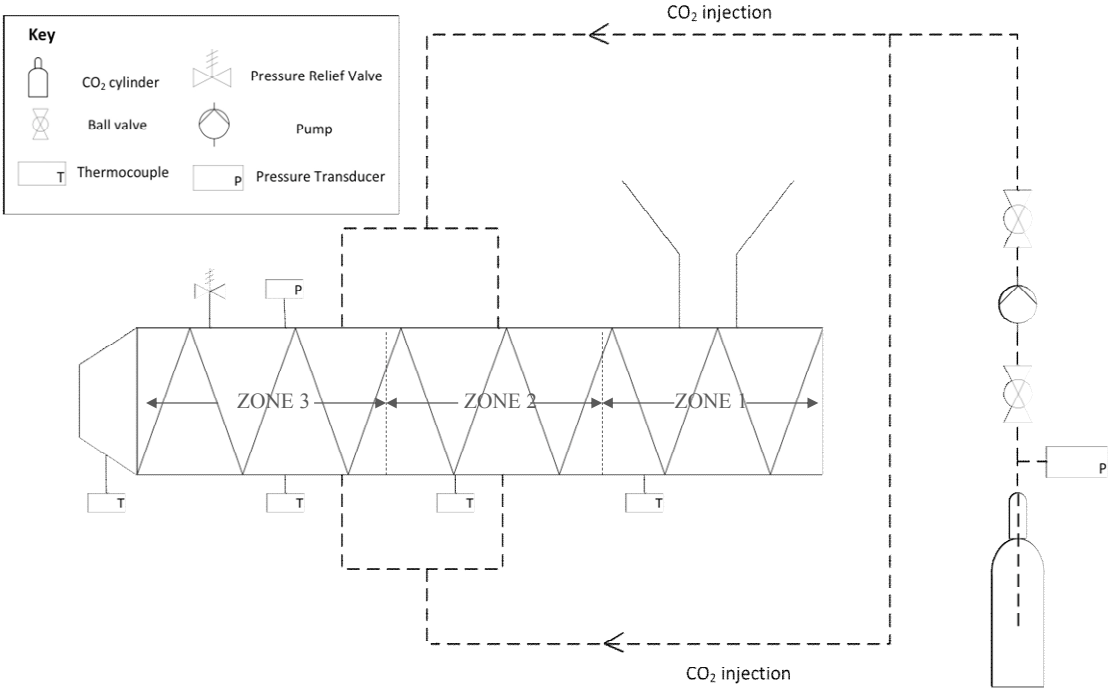

Figure 1. Schematic of the extruder set-up illustrating the injection of CO_2.

CO_2 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_2/polymer pressure of 67 bar in the extruder. In order to calculate the CO_2 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_2 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_2, in relation to the polymer, into the extruder. This calculated value was converted into ml/min as CO_2 was injected as liquid. Equation 2 shows this conversion. The density of CO_2 was calculated by NIST web-book [23] as 0.91898 g/ml based on the CO_2 pressure (4.8 MPa) and temperature (4 ˚C) in the pump.

$$Flow\ rate_{CO2}\ (g/min) = \frac{CO_2\ Concentration\ (wt\%)}{100} \times Flow\ rate_{polymer}\ (g/min\ ) \quad \textbf{[Eq. 1]}$$

$$Flow\ rate_{CO2}\ (ml/min) = \frac{Flow\ rate_{CO2}\ (g/min)}{Density_{CO2}\ (g/ml)} \quad \textbf{[Eq. 2]}$$

CO_2 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_2 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_o) '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^3/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 (ΔH_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 μm) 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.

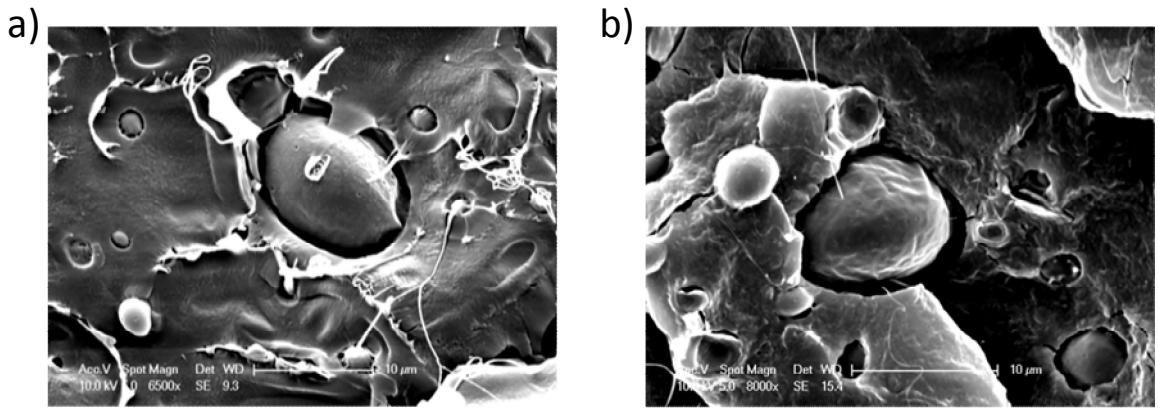

Figure 2a and b. SEM images of solvent cast **(2a):** 75/25 PLA 4060D/PCL and **(2b):** 75/25 PLA 2002D/PCL.

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 μm by solvent casting to around 1 μm by melt blending) was observed in the 75/25 PLA/PCL composition (Figures 3a, 3b and supplementary information).

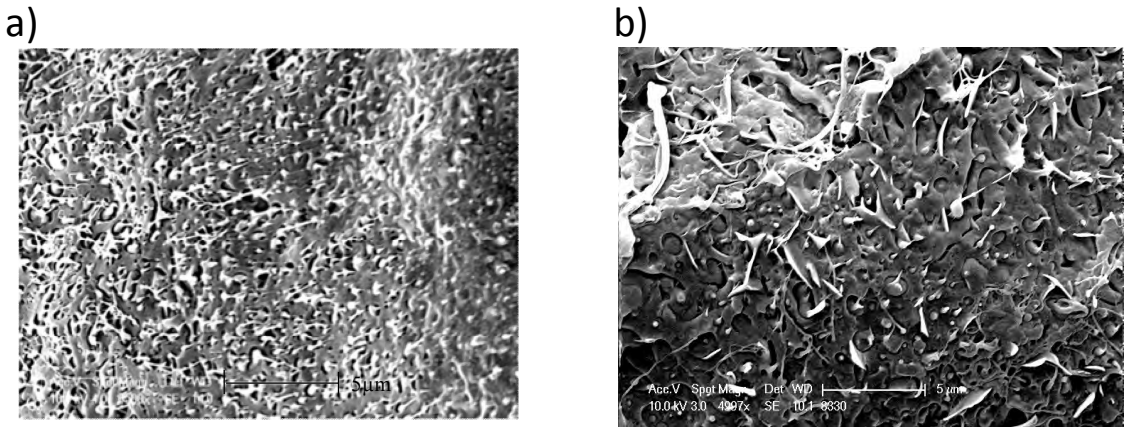

Figure 3a and b. SEM images of melt blends produced with a single screw extruder at 160 ˚C. **(3a):** 75/25 PLA 4060D/PCL at 20 rpm. **(3b):** 75/25 PLA 2002D/PCL at 30 rpm.

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_2 (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_2 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.

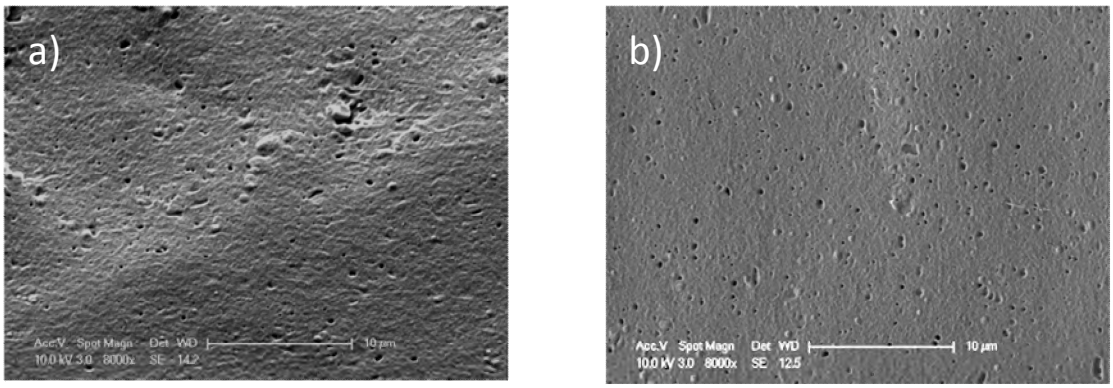

Figure 4a and b. SEM images of blends produced in the presence of 10% carbon dioxide at 150 ˚C. **(4a):** 75/25 PLA 4060D/PCL at 20 rpm. **(4b):** 75/25 PLA 2002D/PCL at 30 rpm.

Similar enhanced miscibility in the presence of CO_2 has been previously reported [16-19]. The gaseous properties of CO_2 enables its diffusion into the free volume of polymers, between the individual chains. Once inside, CO_2 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_2. 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_2 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.

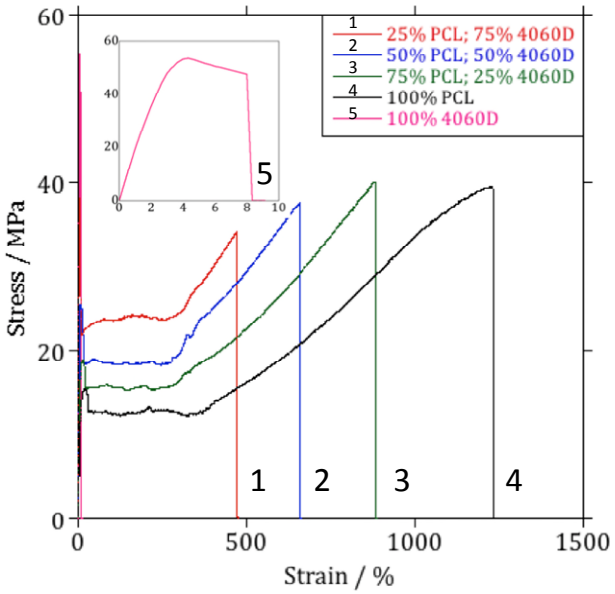

Figure 5. An example of the engineering stress-strain curves for the mechanically blended PLA 4060D/PCL blend system. Inset top left is the result for 100% PLA.

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_2 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_2 assisted blending. No significant difference was observed between the two methods. The porosity generated on venting the CO_2 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_2 compared to melt blending.

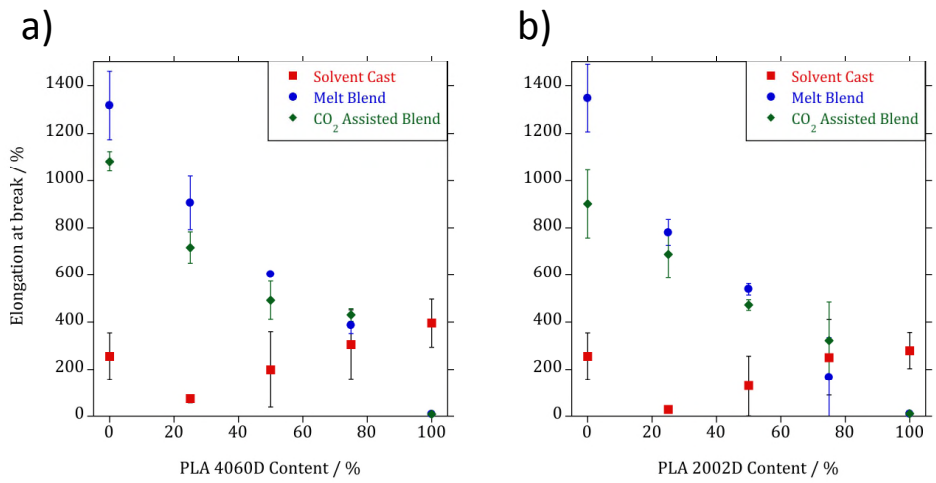

Figure 6a and 6b. A comparison of elongation at break for solvent cast, melt and CO_2 assisted blends of **(6a):** PLA 4060D and **(6b):** PLA 2002D/PCL at various compositions. The standard uncertainty is denoted by error bars, which represents the standard deviation averaged over multiple experiments.

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

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CO2 assisted blending of poly(lactic acid) and poly(-caprolactone)

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