Acceleration of crystallisation rate in injection moulded PLLA by stereocomplex formation

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Abstract
An experimental study has been performed to examine the crystallisation rate of poly(L)-lactic acid (PLLA) blended with poly(D)-lactic acid (PDLA) in order to reduce injection moulding cycle time. Optically pure PLLA was melt blended with up to 15wt% of its enantiomer PDLA in a twin screw extruder. Flow properties, melt strength and thermal properties of the blends were assessed. PLLA/PDLA blends were then injection moulded and allowed to crystallise using two different methods, either non-isothermally in a high temperature injection mould tool or isothermally by annealing moulded samples in a hot oven after conventional injection moulding. Mechanical and thermo-mechanical properties of the moulded samples were investigated and optical measurement of crystal formation using polarised light microscopy was performed at conditions representative of both crystallisation methods. Addition of PDLA was found to accelerate crystallisation rate by up to 80% and the resulting morphology demonstrated increased heat resistance, melt strength and stiffness, with a corresponding reduction in strain at break.

1. Introduction

Polylactic acid (PLA) is an aliphatic polyester derived from natural sources which is biodegradable and can be industrially composted [1]. PLA was first synthesised in 1932 by Carothers and then patented by DuPont in 1954 [2] and has recently been attracting growing interest due to its sustainable nature and good mechanical properties. PLA typically has a tensile strength of 44–70 MPa, high stiffness with elastic modulus of 2–3 GPa [3] and is brittle below its glass transition temperature of 50 °C–60 °C, above which it softens. This limits its uses in many applications to those requiring relatively low temperatures, for example cold food packaging. In addition, PLA has low melt strength which can restrict its usage in melt processing techniques which involve a stretching deformation. Currently PLA is used primarily in disposable packaging and textile applications where the glass-transition temperature of the material is not restrictive. Numerous attempts have been made to modify the properties of PLA, either by blending it with other organic materials (such as polymers, nucleating agents and solvents), inorganic materials (such as chalk, talc and graphene) or by changing the properties during or after processing (orientation, annealing and control of processing conditions) [4]. PLA is produced from the chiral monomer lactic acid. Lactic acid (2-hydroxy propionic acid), has an asymmetric carbon atom and can exist in two optically active configurations (enantiomers), the L (levo-lactic acid) and D (dextro-lactic acid) forms respectively. The concentration of L and D isomers can affect the morphology and properties of the material, with high optical purity homo-polymers (PLLA and PDLA) exhibiting a higher glass transition temperature and eventual crystallinity than the more typically amorphous co-polymer PDLLA, [5]. Commercially, the most widely used form of polylactic acid is PLLA containing a small percentage of D lactide.

The crystal formation and behaviour of PLA is controlled by polymerisation kinetics but as previously mentioned can be manipulated by addition of nucleating agents and other polymers, or by inducing orientation within the polymeric chains. However, the chirality of PLA provides another method of modification of
crystallinity through control of its stereochemistry. PLA has a slow crystal formation rate, which means that achieving high crystallinity in a process with a short timescale such as injection moulding is challenging [6]. However, increasing crystallinity is desirable as it improves mechanical and thermal properties. There are two potential methods to increase the crystallinity of PLA during manufacturing; isothermal and non-isothermal crystallisation [7]. Isothermal annealing of PLA depends on temperature, time and molecular weight of the material. Crystal formation and spherulite growth has been shown to depend on molecular weight (Mw), where PLLA with lower molecular weight showed higher crystallinity than the higher Mw PLA under the same conditions [8]. As PLA is sensitive to thermal processing, this finding suggests also that thermal history may influence Mw and therefore crystal formation. Annealed PLA can exhibit up to 70% crystallinity, resulting in a corresponding increase in melting temperature and \( T_m \) [4].

The crystallisation temperature of PLLA at molten state is around 100 °C and it has been shown from polarised microscopy that spherulite number and size are affected by annealing time and temperature [4, 9]. In general, increasing the crystallinity of PLA provides an increase in strength (impact, tensile, flexural) and stiffness even at temperatures higher than \( T_m \). However the material exhibits low values of elongation at break [10–12]. Non-isothermal crystallisation occurs when the material is cooled at a specified rate. The cooling rate has an inversely linear relationship with crystallisation enthalpy and crystal formation, where lower cooling rates achieve higher levels of crystal formation. When the cooling rate of PLLA is higher than 10 °C min \(-1\), low amounts of crystal formation is achieved, whilst cooling rates higher than 20 °C min \(-1\) lead to amorphous PLLA [13].

Various materials have been used as nucleating agents for PLA, mostly with particle sizes below 100 μm. Table 1 in the supporting information shows a list of PLA studies with nucleating agents and a summary of the property modifications achieved. Commonly used nucleating agents include talc and starch, which provided a significant range of properties, dependent on the material type, particle size and molecular weight of PLA.

Table 1. Injection moulding conditions of PLLA/PDLA blends (2 cavity tensile bar mould).

| Injection settings | Extrusion settings | Temperature settings |
|--------------------|--------------------|---------------------|
| Injection speed    | 100 (mm s\(^{-1}\)) | Back pressure        |
| Position transfer  | 10 (mm)            | Speed               |
| Pack pressure      | 500 (bar)          | DCMP distance       |
| Packing time       | 30 (sec)           | DCMP velocity       |
| Shot size          | 48 (mm)            | Cool time           |
|                    |                    | Feed zone           |
|                    |                    | Zone 1              |
|                    |                    | Zone 2              |
|                    |                    | Zone 3              |
|                    |                    | Zone 4              |
|                    |                    | nozzle              |

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Blending both enantiomers of polyactic acid together changes PLA properties because, due to their chirality, when crystallised the enantiomeric polymeric chains can be oriented more rapidly, resulting in acceleration of crystallisation. Therefore, PDLA can act as an effective nucleating agent for PLAG[20]. Tsuji et al [6] investigated PLA stereocomplex formation in detail, describing stereocomplexation as the stereo-selective association which takes place between the interaction of polymers having different tacticities or configurations. In PLA, when both enantiomeric chains are blended, various types of crystals can be formed. Crystals between chains of the same isomers are referred as homo-crystals (hc) and crystals formed by chains of different enantiomers represent stereocomplex (sc) crystal formation. By presenting a simple matrix model, Tsuji et al [6] explained that creating a fully sc formation does not happen automatically by blending the two materials; the crystallinity of PLA blends that have both enantiomers is higher and in most cases formation of both sc and hc occurs. Blending PLAG and PDLA creates microcrystals which do not occur for optically pure PLLA in which the crystalline area consists of conventional spherulites. For this reason scPLA exhibits higher mechanical and thermomechanical properties than pure PLLA [21]. Both optically pure enantiomers of PLA have the same thermal properties, but when blended together, the new crystalline structure leads to a sc melting temperature of around 230 °C.

Saeidlo et al [22] added small amounts of PDLA to PLLA (1, 3 and 5 w/w % and melt blended them using a twin screw extruder. Stereocomplex spherulitic structures were found to act as particulates inside the PLLA matrix. This resulted in increasing viscosity and a modification in morphology and melt enthalpy. The stereocomplex spherulites (\( T_m = 218 \) °C) exhibited a radiated structure while the crystalline network (\( T_m = 180 \) °C) formed a less organised worm-like structure. XRD and optical microscopy analysis showed a trans-crystalline layer of homocrystals on the surface of the stereocomplex spherulites, explaining the nucleating effect of PDLA. Tsuji et al [23] investigated the nucleating effect on homocrystal growth of PLLA with the addition of small amounts of PDLA (0.1%, 0.3%, 1%, 3% and 10% w/w %). The materials were blended via solution casting where the films had been quenched at 0 °C. During isothermal crystallisation from the melt, results showed that the growth mechanism of the homocrystals was not affected by the presence of...
stereocomplex formation. However, the sc crystallites resulted in an increasing number of spherulites per unit volume, showing that during isothermal crystallisation PDLA decreased crystallisation time and spherulite size. During non-isothermal crystallisation, a nucleating effect was detected from the addition of 1% w/w PDLA and above.

Attempts have also been made to form stereocomplex PLA using polymerisation and solution blending. Shao et al.[24] synthesised low molecular weight PLA enantiomers together using ring-opening polymerisation. Then, using solution casting, various PLLA-PDLA blends were mixed to investigate the morphology and growth of PLA stereocomplex formation. Increased PDLA content was found to favour stereocomplex formation. Annealing at temperatures between 130 and 190 °C was shown to result in formation of many nucleation points with smaller spherulites whereas the opposite effect occurred when the blends were annealed at higher temperatures, with fewer nucleation points and larger spherulites. It was also observed that blends with higher than 10% PDLA produced a different spherulitic morphology, where on the surface of the spherulites spiked edges could be seen.

Whilst a significant amount of research has been performed into the science of stereocomplex formation, relatively few studies have attempted to investigate how low levels of stereocomplex PLA can be used to influence thermomechanical properties and crystallisation rate of PLLA in industrially relevant processes such as injection moulding. This aim of this research was to study the effect of melt blending small amounts of PDLA with optically pure PLLA on its rheological, mechanical and thermomechanical properties and to quantify the impact on rate of crystallisation. Increased crystallisation rate and heat deflection temperature would offer significant benefits in the application of injection moulded PLA products.

2. Methods

2.1. Materials and sample preparation

Optically pure PLLA grade Ingeo 3260HP (NatureWorks™), with a melt flow rate (MFR) of 65 g/10 min (210 °C 2.16 kg ASTM D1239) and D-lactide content <0.5% was blended with optically pure PDLA Sulzer polylactide D100M (L-isomer <0.3%) having MFR of 14–15 g/10 min (2.16Jg, 190 °C ISO 1133–1). The materials were dried under vacuum for 24 h at 60 °C and then compounded in an APV 19mm twin screw extruder with L:D ratio of 25:1 at a rate of 1.44 kg/hr. Five compounds were extruded: pure PLLA and blends containing 1,5,10 and 15% weight by weight of PDLA. The blends are hereafter referred to by their PDLA content, as D0 (0 wt% of PDLA), D1 (1 wt% PDLA) up to D15 (15 wt% PDLA). The extrusion temperature settings, from feed zone to die, were 160 °C → 170 °C → 180 °C → 190 °C → 200 °C at a screw speed of 60rpm. Extruded strand was cooled and cut into pellets of approximately 3mm diameter for further processing.

A Fanuc s-200i 100A injection moulding machine was used with to mould rectangular tensile bars with dimensions of (length/depth/width) 80 × 4 × 10 mm (ISO 527). Compounded PLLA/PDLA blends were dried in a vacuum oven for 24 h at 90 °C prior to moulding. Details of the injection moulding conditions are shown in table 1.

The crystallisation study was performed using two crystal formation methods; by injection moulding samples into a cold mould (30 °C) followed by annealing of the moulded samples in an oven at 95 °C for up to 20 min, and by injection moulding into a hot mould tool at 95 °C and held for times ranging from 1 to 5 min. Hot stage polarised microscopy was also performed on a thin film of each blend formed using a Specac manually operated hydraulic press (15-ton capacity); heated to 220 °C and pressed using a 100μm thick ring spacer, prior to cooling.

2.2. Characterisation techniques

Shear viscosity of the PLLA/PDLA blends was measured using a Rosand RH10 twin bore capillary rheometer at 200 °C with 1.0 mm diameter dies with 16.0 mm and <0.2mm lengths. Three repeats of each test were made for every blend which were dried prior to testing. Materials were examined over a shear rate range from 30 s⁻¹ to 5,000 s⁻¹. To investigate melt strength of the materials, a haul off test was performed on all blends at a set temperature of 200 °C. During this test, extruded filament exiting a 2.0 mm diameter capillary die was threaded around a low friction pulley wheel positioned on a high precision balance, and then fed to a motorised winding assembly. Melt tension was measured by the precision balance was recorded by the rheometer control software as the motor speed (haul off rate) was increased, allowing force to be measured as a function of speed.

Mechanical properties of injection moulded samples were measured using a Messphysik BETA 20–10/8 × 15 tensometer with maximum load capacity of 20 kN and a Pixelink Monochrome camera (3.1 megapixels and 95 fps) for the video extensometer data. A 1% strain rate was used for all samples and a test speed of 50 mm min⁻¹ on the tensile test equipment was set. An Instron Dynatup POE 2000 pendulum impact test machine was used to measure IZOD impact strength of injection moulded samples which had been notched in
the middle of the gauge section. All mechanical characterisation techniques were repeated for 5 specimens from each blend.

DSC analysis was performed using a TA Instruments Discovery DSC under a nitrogen purge. Heat−cool−heat tests were carried out on extruded pellets and moulded bars using 10 °C min−1 heating and cooling rates between 30 °C and 240 °C. Extruded pellets were also tested using a customised test procedure, first heated to 240 °C at 10 °C min−1, then held for 3 min to delete the thermal history of the material and cooled at 10 °C min−1 to the crystallisation starting point (determined from heat−cool−heat tests) and held at this temperature for 15 min. The material was then cooled to 10 °C and re-heated to 240 °C.

Deflection temperature under load (DTUL) of moulded specimens was measured using a TA instruments DMA800. The instrument was run in controlled force mode using a 3-point bending clamp at a constant force of 1.21 N and a temperature ramp of 2 °C min−1 from 40 °C to 120 °C. From the resulting temperature−deflection graph, the HDT value was taken as the temperature in which the magnitude of deflection reached 80.7 μm. This method was adapted from ASTM D648 but using a smaller sample geometry, as described in [25] and used by [26].

Hot stage polarised optical microscopy was performed using an Olympus BH−2 microscope, with a SPlan 10PL lens. Images were captured using a Canon EOS550D digital camera mounted onto the microscope. Temperature was controlled using a Linkam LTS420 stage with Linksys software. Film samples were placed on a glass microscope slide. To investigate the annealing route, samples were heated at a rate of 40 °C min−1 and held at 95 °C for 10 min, with images taken every 5 s. To investigate crystallisation during cooling from the melt, samples were heated to 240 °C, held for 3 min then cooled at 40 °C min−1 to the crystallisation starting point (based on DSC results). The samples were then held at that temperature for 10 min, with the camera recording images every 5 s. Images were then analysed in Adobe Photoshop, allowing luminosity values to be calculated. The rate of luminosity increase provided an indication of crystallisation rate, supporting the results obtained from moulded samples.

3. Results & discussion

3.1. Rheology

Figure 1(a) shows that, of the two virgin enantiomers, PDLA exhibited higher viscosity than PLLA at 200 °C. Addition of PDLA caused a significant change in flow behavior even at low addition levels. At 5% w/w addition of PDLA the viscosity of the blend reached that of pure PDLA. At higher PDLA loadings shear viscosity was increased by a factor of five and eight for 10 and 15 wt% PDLA respectively. In figure 1(a) the shear viscosity of each PLLA/PDLA blend is displayed at a constant shear rate of 360 s−1. The viscosity increase can be explained by the existence of the stereocomplex crystals formed during blending. As these crystals melt at higher temperatures (210 °C−230°C) than the homocrystals of PLLA and PDLA (150 °C−170°C) they act as particulate fillers, resulting in an increase in shear viscosity of the blends [27]. This was also visible during testing and during twin screw extrusion as the amount of PDLA increased the transparency of the blend was observed to decrease. At the highest amounts of PDLA (10% and 15 wt%) the molten materials exhibited a paste-like appearance.

As shown in figure 1(b) the addition of PDLA also increased melt strength. This indicates formation of either a solidified core of sc crystals surrounded by molten PLLA or by a network [22, 28, 29] of sc crystals within PLLA causing it to exhibit higher viscosity, producing a higher tensile stress during melt drawing. The melt strength test could not be performed on the blend containing 15 wt% of PDLA because it was too brittle to be melt drawn, solidifying almost immediately on exiting the capillary die.

Figure 1. (a) Capillary rheometry results of PLLA/PDLA blends at 200 °C with a 1mm diameter die. Shear viscosity Versus D% content at 360/s shear rate; (b) Average haul off force Versus speed results of PLLA/PDLA blends.
3.2. Thermal analysis

DSC results for the virgin materials measured individually are shown in the supporting information. Both PLA enantiomers exhibited a similar thermal behavior with glass transition and melting observed at 60 °C and 175 °C respectively. The only difference in thermal behavior was that PDLA had a narrower cold crystallization peak between 90 °C and 110 °C and PLLA a wider one between 100 °C and 120 °C. Blending with PDLA resulted in a significant change in all thermal transformations with the exception of glass transition. Cold crystallisation results are shown in figure 2(a); the addition of PDLA shifted the crystal formation peak of the homocrystals to lower temperatures. Adding 1wt% of PDLA did not have a significant effect on crystal formation during heating, but additions of 5, 10 and 15wt% decreased the cold crystallisation peak by up to 10 °C. During cooling (figure 2(b)), addition of PDLA caused a significant increase in crystal formation of the PLA homocrystals. With 0 wt% PDLA the crystal formation peak was barely visible, whilst addition of just 1wt% of PDLA caused a notable change. As the amount of PDLA increased, the start of the crystal formation peak shifted to higher temperatures by 10 °C–20 °C. This shows that adding PDLA allowed the material to reach the point of crystal formation earlier during the cooling cycle.

The result also shows that PDLA resulted in narrower crystal formation peaks with higher peak values, indicating that the temperature formation window was smaller for blends containing higher amounts of PDLA. During cooling of PLLA/PDLA blends, formation of stereocomplex crystals has been shown to reduce the energy of neighbouring molecules allowing molecular packing to be more readily initiated [22] and [23].

In figure 3 a comparison of the time required to form PLLA homocrystals at isothermal conditions is presented. Pure PLLA showed a significantly slower crystal formation requiring 10 min. Addition of PDLA was found to accelerate crystallisation, with 1% loading reducing the crystallisation time to 5 min. Increased PDLA loading further reduced crystallisation time, to D10 and D15 both requiring 2 min. This indicates that stereocomplex formation also had a nucleating effect on hc formation, up to 10wt% of PLDA, with 15wt% having negligible further effect.

In figure 4 (a) & (c), homocrystal melting enthalpy for the different blends is presented and compared to the enthalpy of stereocomplex crystal formation (b & d) for both crystallisation methods of the injection moulded samples. Neat PLA exhibited a maximum of 55% of homocrystals (51 J g⁻¹ enthalpy) when annealed for 6 min at 95 °C (figure 4(a)). The addition of 1% PDLA resulted in a similar homocrystal enthalpy but required 4 min to reach a fully crystallised formation. Increasing PDLA content also resulted in a reduced melting enthalpy, indicating a lower level of homocrystal formation. Similar results were observed from injection moulded bars produced in the hot mould (figure 4(c)), where increased PDLA content resulted in a lower level of homocrystal formation but achieved in a shorter time.

The results from the stereocomplex formation enthalpy from both annealed (figure 4(b)) and hot moulded (figure 4(d)) samples showed that the amount of the stereocomplex crystals formed was independent of the crystal formation technique. In both cases the value of stereocomplex formation enthalpy was close to twice the w/w % of optically pure PDLA loading, indicating that a majority of 1:1 PLLA-PDLA stereocomplex formation had been achieved. Annealing and moulding time had a negligible effect on the levels of stereocomplex crystals formed.
3.3. Mechanical properties

Tensile properties were found to depend on the time in which each blend was crystallised and the PDLA loading, as shown in figure 5. Increase in annealing time resulted in an increase in elastic modulus, up to a time of around 10 min, above which modulus remained unchanged (figure 5(a)). Interestingly, the highest modulus was recorded at a PDLA loading of 5wt%, with further addition causing a decrease. Modulus also increased with time during injection into a hot mould (figure 5(b)) with 5wt% PDLA also exhibiting highest modulus.

In contrast, tensile strength (figure 5(b) and (d)) decreased with increase in annealing and moulding time (figure 5(b)). Results showed that when samples reached full crystallisation after approximately 6 min, tensile strength dropped, most significantly for the 1% PDLA loading blend. Tensile strength increased as the amount of PDLA was increased. During annealing there was a notable warpage effect on the samples, especially as the sample was held for longer times in the oven. As the amount of PDLA increased though, warpage was less...
significant. To minimise warpage, a cooled metallic load was placed on top of the samples when they were removed from the oven, to maintain the shape, although the shoulders of the samples were exposed which may have resulted in premature failure during the tensile tests in some cases. A similar effect was observed for non-isothermally crystallised tensile bars (hot mould). Increasing the amount of PDLA resulted in increased tensile strength, as shown in figure 5.

Increase in crystallinity also resulted in a decrease in toughness, as indicated by the strain at break results shown in figure 6. Fully annealed samples exhibited strain at break values of between 1.8 and 3% which was significantly lower than that of un-annealed neat PLA (7.5% strain at break). Blends which had been injection moulded exhibited lower strain at break results between 0.6 and 1.8%. Increasing PDLA content resulted in increased strain at break, in general.

Impact strength results from the crystallised PLLA/PDLA blends showed a difference between the two crystallization techniques. Annealed PLLA/PDLA blends exhibited impact strength values roughly proportional to the level of homocrystal enthalpy measured in DSC tests (figure 4(a)). Neat PLLA when fully crystallised produced highest impact strength, above 6 KJ m\(^{-2}\) compared to 1.5 KJ m\(^{-2}\) for un-annealed samples. Increasing loadings of PDLA had a less significant effect on impact strength after annealing, with blends containing 10 and 15 wt% demonstrating negligible improvement over un-annealed samples. These results suggested that crystallised neat PLLA had a more uniform structure, with crack growth during impact being decelerated, by smaller, uniform crystals. The addition of PDLA and subsequent formation of stereocomplex crystals in the PLLA matrix may have created areas between lower strength interactions in the regions between homocrystals and stereocomplex crystals [24]. Corresponding impact strength data from non-isothermally crystallised (hot moulded) PLLA/PDLA blends showed similar results, but at a lower intensity and with higher variation (figure 7(b)).

3.4. Thermomechanical properties

HDT results are shown for all blends and both crystallization techniques in figure 8. Non-crystallised samples exhibited HDT values between 60 °C–65 °C, only marginally higher that of neat PLLA. However, HDT increased significantly, up to above 95 °C with addition of PDLA using both crystallization techniques. This result indicates that the higher melting temperature of stereocomplex crystals had a pronounced effect on deformation temperature of the blends in addition to reducing crystallization time.
3.5. Polarised optical microscopy (POM)

Figure 9 shows images taken during crystallisation of PLLA/PDLA blends from the start of crystallization (a) to 350 s (h) at 50 s intervals. Blends were cooled from their melt to crystallization start temperature (determined from DSC) and held at temperature whilst images were taken every 50 s. Temperatures used for D0, D1, D5, D10

Figure 6. Strain at break results of PLLA/PDLA blends during tensile testing of annealed samples (a) and hot moulded samples (b) with 1% strain rate during testing (50 mm min⁻¹).

Figure 7. IZOD impact testing results of PLLA/PDLA blends, crystallised isothermally at 95 °C (annealed) and injection moulded in a heated mould (95 °C) at different holding times.

Figure 8. DMA results (Controlled force, temp ramp) of Strain at maximum deflection of PLLA/PDLA blends in non-crystallised (30 s holding time at 30 °C mould temperature), annealed (oven set at 95 °C for 20 min holding time), and high temperature injection moulded (mould set at 95 °C held for 5 min) morphologies.
and D15 blends were 125 °C, 130 °C, 135 °C, 140 °C and 145 °C respectively. Increasing levels of PDLA addition was found to result in more nucleation points with corresponding formation of smaller spherulites. This resulted in reaching a fully crystallised morphology more rapidly as the amount of PDLA increased. From visual analysis of the images, neat PLLA appeared to be fully crystallised only after 350 s, compared to D1 at 250 s, D5 at 200 s, D10 at 150 s and D15 after 100 s. In figure 1 of the supporting information the POM images of the blends when crystallised during annealing (at solid state) are shown.

In figure 10(a), the luminosity of raw images taken every 5 s is shown from the moment the materials reached the crystallisation start point (cooled down from melt). Crystallising the PLLA/PDLA blends by heating and annealing at 95 °C did not yield as useful visual results. The materials reached a fully crystallised state more rapidly as shown in figure 10(b) but with lower luminosity value (supporting data figure 2 available online at stacks.iop.org/MRX/7/105308/mmedia). This can be explained by the solidified condition of the samples during crystallisation. The movement of the molecules in solid state is limited resulting in creation of small spherulites that do not have room to grow, compared to crystal formation from melt state. In supporting data table 2, the change in transparency Versus time for the annealed tensile bars of each blend is shown with their corresponding DSC results. These show that the samples transitioned from an amorphous to a crystallised within a relatively brief period of one minute, but only after the material had to be maintained at temperature for a prolonged period (e.g. 5 min for pure PLLA).

The rate of increase in luminosity was calculated by measuring the gradient of a linear fit (as shown in figure 10(c) for neat PLLA and 15% PDLA). These rates were then compared for all blends for both crystallisation methods, in figure 10(d). Crystallisation rate can be inferred from these calculated rates of luminosity increase. For both crystallisation methods the gradient of normalised luminosity increase was around 6.5, which supports the previous observations that addition of PDLA accelerated crystallisation, as previously shown in the DSC results displayed in figure 2. This result provides a more detailed understanding of the acceleration effect in crystallinity by the addition of PDLA to PLLA.

![Figure 9. Hot stage polarised microscopy images showing homocrystal formation in PLLA/PDLA blends. Images recorded after crystallisation start temperature was reached, following cooling from the melt. Image (a) represents time = 0, each subsequent image represents an increase of 50 s.](image-url)
4. Conclusions

Low molecular weight PLLA was melt blended with its enantiomer PDLA in loadings up to 15% w/w and the effects on morphology and properties were investigated by two crystallisation methods: injection moulding following by annealing and by injection into a heated mould. Neat PLLA was found to exhibit a slow crystal formation, with properties heavily dependent upon degree of crystallinity. Stereocomplex crystal formation was shown to occur in all blends, leading to an increase in viscosity and melt strength. PDLA was found accelerate homocrystal formation in PLLA by up to approximately 80% during both crystallisation routes. Crystallised PLLA/PDLA blends had higher stiffness but a corresponding decrease in strain at break and impact strength, which suggests that the addition of PDLA affects the distribution of the crystals as indicated by impact strength. The addition of PDLA resulted in an increase in heat deflection temperature to above 95 °C due to the higher melting temperature of the stereocomplex crystals. These results show that addition of relatively low fractions of PDLA can lead to significant reduction in cycle time and improvement in heat deflection temperature of PLLA through stereocomplex formation and its influence on crystallisation. Crystallisation in a heated mould is more applicable to industrial manufacturing compared to oven annealing, which required longer holding times and led to sample warpage. Further strategies are being investigated to improve the toughness of these blends, such as incorporation of materials which have a plasticising effect [30, 31].

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