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Effects of Liquid CO_2 Exposure on Semi-Crystalline Polylactic Acid

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Summary: In this work, the effect of low temperature (approximately −50°C to −20°C) liquid CO_2 treatment on the morphology of semi-crystalline polylactic acid (PLA) was studied. This investigation was carried out by means of differential scanning calorimetry (DSC) and Synchrotron wide-angle X-ray scattering (WAXS). Under the experimental conditions used, DSC and WAXS revealed the existence of two main crystalline structures, namely the α" crystal structure and a mesomorphic structure. The α" crystals were found to be preferentially formed at higher temperature, whereas only the mesomorphic structure was detected at lower temperature. The transition between these two morphologies was observed at around −35°C.

Keywords: carbon dioxide; crystallinity; plasticisation; polylactic acid

Introduction

Polylactic acid (PLA) is renewable and compostable polyester that is increasingly used in packaging and textile applications[1,2]. PLA has a glass transition temperature (T_g) of 55 to 60°C, and a melting temperature (T_m) typically between 120 and 180°C, which strongly depends on its composition in D- and L-lactic acid enantiomers.[3] The D and L composition of PLA also influences its crystallisation behaviour,[3] but generally PLA is considered as a slowly crystallising polymer which is a major drawback for the manufacturing of durable goods or applications involving temperatures above T_g. Several crystalline forms are described in the literature. The commonly observed α form is produced by various ways including crystallisation from the melt[4,5] or strain-induced crystallisation.[6,7] This crystalline form is characterised by a pseudo-orthorhombic unit cell. A disordered version, the α' form, has also been observed and characterised.[8,9] The less-common β form is produced in fibres produced with high draw ratios.[10,11] More recently, several authors observed a distinct crystalline structure in PLA following exposure to carbon dioxide (CO_2) under certain conditions.[12–14] Marubayashi *et al.* named this form α" and suggested that it was produced by the inclusion of CO_2 molecules within the crystalline unit-cell, thus widening the distance between the PLA chains and leaving cavities after removal of the guest molecules.[12,15,16] A similar phenomenon has been reported with syndiotactic polystyrene crystallised in various solvents.[17]

Much research work is currently being devoted to carbon dioxide as a processing medium for polymers, some of which is already in use in the industry.[18] The "green" solvent can be utilised to lower the viscosity of polymeric materials to aid processing, to improve crystallisation, to produce a cellular structure, or to clean or even to impregnate polymers with additives. This interest has been motivated by the low price, the non-toxicity and the lower environmental impact of CO_2 in comparison with traditional solvents.

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Some of this work on CO_2 involves PLA, for example for the manufacturing of biomedical implants[19] or for extrusion foaming.[20,21] A noticeable sign of interaction between PLA and CO_2 is the accelerated crystallisation of the polymer. CO_2 is a well known plasticiser for PLA, as for other thermoplastic polymers.[22] This plasticisation is characterised by a decrease of the polymer's T_g, allowing crystallisation at much lower temperatures than typically required.[23] This phenomenon has been described by many authors, generally using supercritical CO_2 or CO_2 in its gaseous phase. Marubayashi *et al.* exposed PLA to CO_2 at temperatures between 0 and 70°C and pressures up to 15 MPa, therefore covering the gas, liquid and supercritical states.[12] They showed that these CO_2 treatment parameters affected the morphology of the crystallised PLA, in terms of crystalline form (α or α") and crystalline superstructure (spherulites or nanorods).

In this paper, we studied the crystalline morphology of PLA treated with liquid CO_2, and in particular the effect of the treatment temperature in the -50 to –20°C range. To our knowledge, this temperature range is an unexplored area in the literature. Differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) were employed to characterise the crystalline structures obtained through the CO_2 treatment.

Materials and Methods

A commercial PLA, NatureWorks LLC PLA grade Ingeo 3001D, was used in this study. This grade is mainly composed of L-lactic acid monomer units, with 1.4% D-lactic acid.[24] Its weight-averaged molecular weight is approximately 100 kDa as measured by size exclusion chromatography in chloroform at 30°C (results relative to a polystyrene standard). The dried material was extruded on a 20 mm single-screw extruder, and quickly cooled from the melt in a water bath ensuring that the material was frozen into an amorphous state. The 2 mm diameter strands were then cut into 15 mm long rods and conditioned for at least 48 hours at 23°C and 50% relative humidity before use.

Table 1.
Liquid CO_2 treatment parameters.

	Pressure (bar)	Time (minutes)
−50	27	200
−40	30	167
−35	32	154
−30	34	142
−20	40	122

The liquid CO_2 treatment of the samples was performed in a 10 mL pressure vessel at temperatures from −50 to −20°C. For each tested temperature, the pressure was set 20 bar above the vapour saturation pressure, and the treatment time was chosen so that the samples were saturated with CO_2. The treatment times were based on previous absorption experiments not described here. The treatment parameters are summarised in Table 1. After a fast depressurisation (less than 1 minute), the samples were stored in a freezer at −18°C for 3 weeks, then under vacuum at room temperature for 1 week. This procedure allowed a complete removal of the CO_2 from the samples.

Differential scanning calorimetry (DSC) was performed on samples sliced from the rods (treated and non-treated) using approximately 5 mg of material heated from 20 to 200°C at 5°C per minute. A TA Instruments Q1000 apparatus was used.

The wide-angle X-ray scattering (WAXS) experiments were carried out on the WAXS/SAXS beamline at the Australian Synchrotron in Melbourne. The X-ray samples were sliced (approximately 0.5 mm thick) from the rods and encapsulated into Kapton tape. The wavelength used was 0.8266 (15 keV) and the camera length was approximately 120 mm, calibrated with silver behenate. The diffracted X-rays were collected on a Mar165 CCD detector. From the resulting X-ray spectra, the Kapton and air background was first removed. Then, the contribution of the amorphous fraction of the samples was subtracted by modelling the amorphous halo with Gaussian functions as performed by Mano.[25] For this purpose, a non-treated extruded sample was used as reference. The crystallinity of the samples was then assessed using the ratio between the areas under the crystalline-only spectrum and the total spectrum.

Results

The DSC traces of a non-treated sample and samples treated at various temperatures are displayed in Figure 1. The main features of the trace obtained on the non-treated sample are the glass transition (onset at 57°C), cold-crystallisation at around 100°C, pre-melting crystallisation likely associated with a perfection of the crystals, and finally melting (peak at 170°C). A small endotherm can also be observed at the glass transition. This feature is attributed to a physical ageing of PLA occurring during conditioning.[26] The DSC traces of the samples treated with liquid CO_2 are substantially different and, among them, two distinct behaviours are observed. The traces of the samples treated at −30 and −20°C exhibit a rather small cold-crystallisation exotherm with its peak at approximately 75°C, i.e. soon after the glass transition. This obviously suggests that these samples significantly crystallised during the liquid CO_2 treatment. On the contrary, the traces of the samples treated at −50 and −40°C exhibit a deep endotherm at the glass transition, immediately followed by a sharp exotherm at around 75 – 80°C. A significant pre-melting exotherm is also observed. These DSC traces are similar to what observed on heating of stretched PLA film or fibre samples. Some authors working predominantly on fibres found that the endotherm at the glass transition was likely to be due to the relaxation of the stretched amorphous polymer chains re-heated above T_g,[27,28] while the subsequent exotherm was attributed to a "strain-induced nucleation enhanced crystallisation".[29] However, more recently, other authors including Stoclet *et al.*, claimed these features to be caused by the formation of a "mesophase" in PLA drawn at temperatures slightly above T_g, which melted when re-heated above T_g, thus producing the observed endotherm.[30,31]

On these DSC traces, the post-T_g endotherm was integrated. The crystallinity, X_c (J/g), was also calculated as $X_c = \Delta H_m - \Delta H_{cc}$,

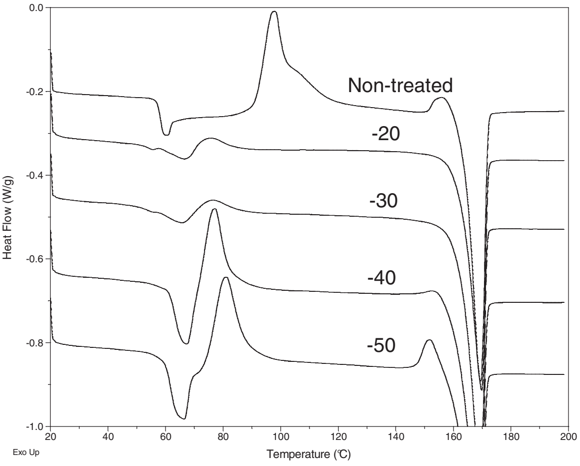

Figure 1.
DSC traces of the samples (non-treated and treated from −50 to −20°C).

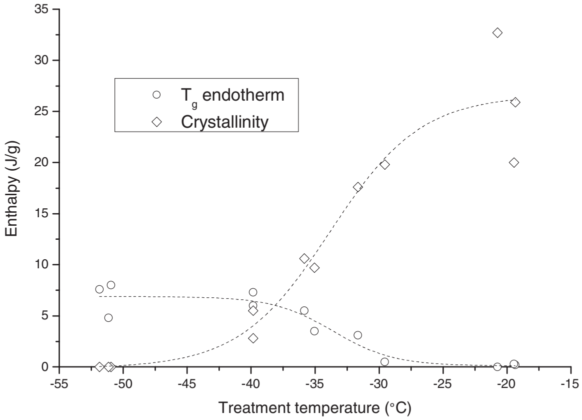

Figure 2.
Post-T_g endotherm and crystallinity (in J/g) calculated from the DSC traces, and plotted as a function of the treatment temperature.

where ΔH_m and ΔH_{cc} are the enthalpy of melting and cold-crystallisation respectively. These results are displayed in Figure 2, plotted against the treatment temperature. One can see a clear change of morphology at around −35°C. The enthalpy associated with the post-T_g endotherm increased with decreasing treatment temperature, reaching about 8 J/g at −50°C. On the contrary, the crystallinity decreased with decreasing treatment temperature. Samples treated at −50°C are virtually amorphous according to these calculations.

The wide-angle X-ray experiments provided additional information on the morphology of these samples. Firstly, these experiments confirmed that, prior to CO_2 exposure, the samples were completely amorphous. The processed spectra, with the background and amorphous contributions removed, of the treated samples are displayed in Figure 3. One can observe a gradual transformation of the spectra with decreasing treatment temperature, with a widening of the main crystalline peak and disappearance of some weaker peaks, for example at $2\theta \approx 12°$ and $2\theta \approx 13°$.

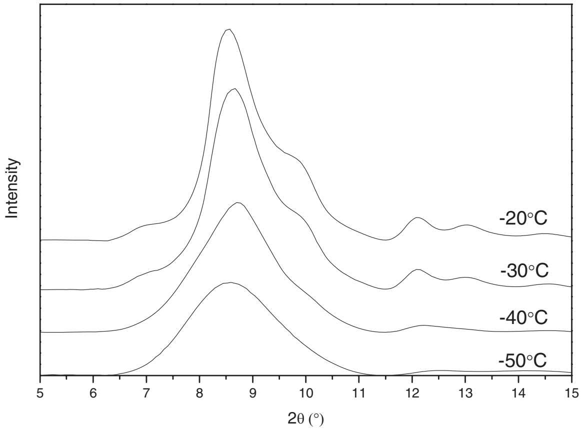

Figure 3.
Crystalline-only WAXS spectra obtained on the samples treated at -50, -40, -30 and −20°C ($\lambda = 0.8266$ Å).

The crystalline spectra obtained at −30 and −20°C correspond well with those published by several authors, including Marubayashi *et al.*,[12] which indicates that the α" crystalline structure was formed under CO_2 exposure at these temperatures. The spectra of the samples treated at the lower temperatures are similar to what was observed by Stoclet *et al.* on PLA samples stretched at temperatures slightly above T_g.[30] These authors stated that this type of spectrum was associated to a distinct mesomorphic structure, and not small or defective crystals of the more usual α or α' form. This is well supported by the crystallinity calculations based on our DSC experiments indicating that the samples treated at −50°C were free of crystallinity. Stoclet *et al.* also stated that this mesophase melted when heating the samples through the glass transition.

In order to clarify whether the mesophase formed under CO_2 exposure at low temperature melted above T_g as suggested by Stoclet *et al.*, WAXS and DSC were used in parallel on a sample treated at −50°C. Slices taken from a treated sample were reheated in the DSC apparatus up to various temperatures, quickly cooled down, and then subjected to WAXS. The results are illustrated by Figure 4 where the evolution of the WAXS spectrum through re-heating is shown. The initial peak associated with the mesophase disappeared when going through the post-T_g endotherm, confirming that this DSC feature was produced by the melting of the mesophase. With further heating, the sample re-crystallised, first into the α' form which was then converted into the more stable α form. This conversion from one to the other can be identified with the appearance of weaker peaks as well as a slight shift of the main peaks towards larger angles.

With this confirmation of the melting of the mesophase, and the correct assignment

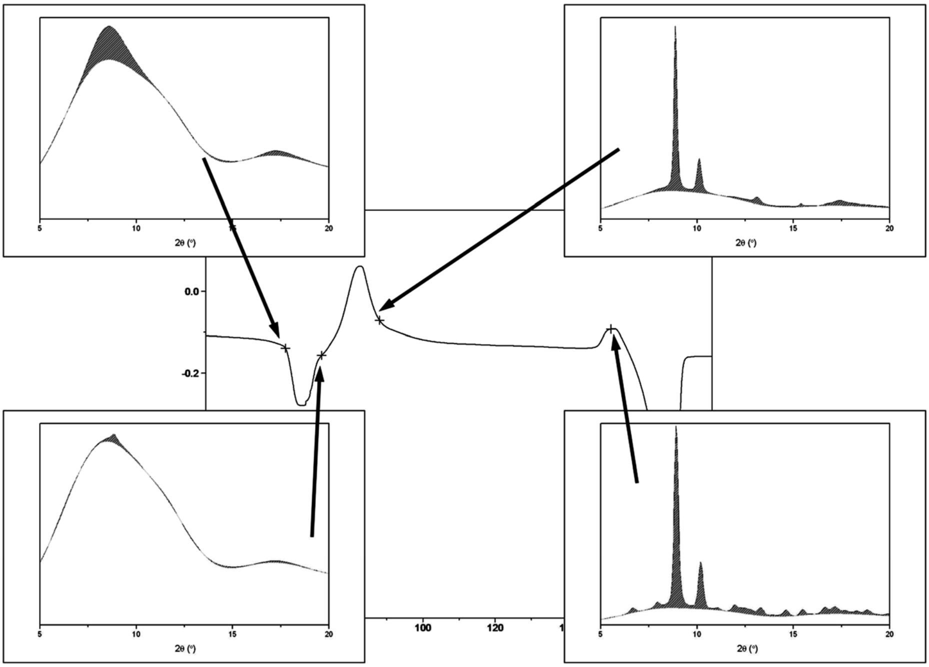

Figure 4.
Evolution of the WAXS spectrum of a sample treated at −50°C when re-heated in the DSC apparatus. Spectra acquired after re-heating up to 62, 72, 88 and 152°C are shown. On these spectra, only the background, and not the amorphous contribution, was subtracted.

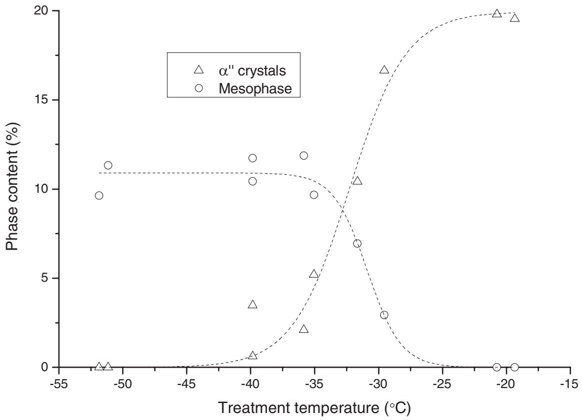

Figure 5.
Mesophase and α” content calculated from the WAXS spectra, and plotted as a function of treatment temperature.

of the features of the DSC traces, the melting enthalpy of the mesophase was calculated (using 93 J/g as the melting enthalpy of the α form[32]). The value of 73 J/g was found. This value is close to what published by Stoclet *et al.* (70 J/g[30]). From the WAXS spectra of the samples treated at different temperatures, the α” crystal and mesophase content were then assessed. The corresponding results, shown in Figure 5, are qualitatively similar to what was determined by DSC (Figure 2).

Discussion

From the WAXS and DSC results presented here, it is clear that the ordered structure observed in the samples exposed to liquid CO_2 below −35°C is the mesophase described by previous authors. This mesophase has already been observed in stretched PLA but, to our knowledge, its creation through CO_2 exposure has not been reported in the literature. In the case of strain-induced crystallisation, the ratio between mesophase and α crystals is governed by stretching temperature and strain rate. If the stretching temperature is sufficiently high (e.g. $T_g + 20°C$), PLA will form α crystals. If the stretching temperature is close to the glass transition temperature (e.g. $T_g + 5°C$), the thermal activation is not sufficient to allow crystallisation into the α form. However, the mesophase will emerge through alignment of the polymer chains. It is therefore suggested that the transition between mesophase and α” form in the CO_2 treated samples originated from a similar mechanism. This is a rather complex process as the CO_2 absorbed decreased the glass transition temperature of the samples being treated. This decrease of the T_g was reversed by the CO_2 removal as proved by the DSC traces in Figure 1. Describing accurately the mechanisms responsible for the transitions between the two morphologies would require further study but it is likely that similar mechanisms as for the case of stretching were involved. At the higher end of the treatment temperature range tested, thermal activation was sufficient to allow molecular motion and ordering of the PLA chains into crystals. The α crystals observed when stretching PLA were replaced by the α” due to the likely inclusion of CO_2 molecules in the unit-cell. At the lower end of the treatment temperature range, thermal activation was probably not sufficient to allow this crystallisation despite the induced plasticisation. However, the CO_2-induced swelling of the polymer generated enough chain alignment to create an ordering of the PLA chains and thus the development of a mesomorphic structure.

Conclusion

In this paper, the effect of liquid CO_2 treatment on polylactic acid was studied in the -50 to −20°C temperature range. As previously reported, CO_2 exposure induced the crystallisation of PLA. However, in the present work, we showed the existence of two distinct polymer morphologies, respectively produced through treatment below and above −35°C. When treated above −35°C, PLA predominantly crystallised into the α" form. This crystalline form has been previously suggested to be due to CO_2-PLA co-crystallisation. When treated below −35°C, this crystalline form was replaced by a mesomorphic structure. This mesophase was found to be identical to the the mesophase observed when stretching PLA at temperature just above its glass transition. Additionally, this mesophase was shown to melt when reheated above T_g. Its melting enthalpy was calculated at approximately 73 J/g. Mechanisms similar to the ones responsible for the strain-induced mesophase formation were suggested for the development of a mesophase under low temperature liquid CO_2 exposure, namely alignment of the PLA chains without sufficient thermal activation and molecular relaxation for PLA to crystallise effectively.

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