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Miscibility in blends of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(ε-caprolactone) induced by melt blending in the presence of supercritical CO_2

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Abstract

Blends of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(ε-caprolactone) (PCL) have been produced by melt blending in the presence of supercritical CO_2. Infrared spectroscopy has shown that supercritical CO_2 can induce melting in PHBV at temperatures below the melting point. The miscibility of the PCL–PHBV blend system produced by both mechanical and supercritical means has been characterised by a combination of differential scanning calorimetry and dynamic mechanical thermal analysis. It has been shown that PHBV–PCL blends produced using mechanical means were immiscible, whereas the same blends produced using supercritical methods were found to be miscible as evidenced by a decrease in the glass transition temperature of the PHBV component. The development of miscibility is discussed in terms of enhanced interdiffusion resulting from the action of supercritical CO_2. In addition, the infrared spectrum of the blends produced using supercritical CO_2 showed negligible levels of the degradation product crotonic acid. Whereas in the samples produced using mechanical blending without supercritical CO_2, there was a significant increase in the level of crotonic acid, which was interpreted as evidence of degradation.

Keywords: PHBV; Blends; Miscibility

1. Introduction

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) is a semi-crystalline thermoplastic copolymer that can be produced by bacterial fermentation [1]. The repeat unit of PHBV is shown in Fig. 1. PHBV is also biodegradable and has been used in a variety of applications including plastic containers, films and bottles [2]. The biodegradability of the polymer may offer the possibility of biomedical applications, including the controlled release of therapeutic agents in drug delivery [3,4].

Although PHBV exhibits increased flexibility and reduced brittleness in comparison to the related material, polyhyroxybutyrate, attempts have been made to further improve the physical properties of PHBV by blending with other polymers [5].

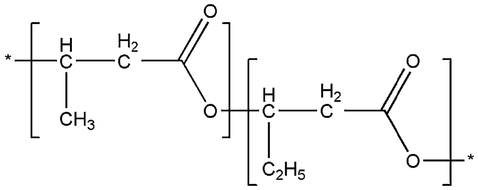

Fig. 1. The repeat unit of PHBV.

Polycaprolactone (PCL) is an aliphatic polyester produced using a ring-opening polymerisation of ε-caprolactone. The repeat unit of PCL is shown in Fig. 2. PCL is also biodegradable and as a result has recently been the subject of a number

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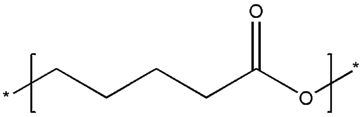

Fig. 2. The repeat unit of PCL.

of studies that have aimed to investigate applications of PCL in the area of controlled release [6].

A number of previous studies have investigated the creation of blends of PHBV and PCL, but the preparation methods that were adopted utilised a solution blend methodology [7,8]. In these studies the blends were found to be immiscible. Although solution blending prevents thermal degradation of the PHBV during processing, the method is likely to limit biomedical applications of the blend due to the problems associated with the presence of residual solvent. Conversely, melt blending by mechanical means avoids contamination of the material by solvent residues, but the process can lead to the thermal degradation of the PHBV component, which may preclude the use of the blend in a biomedical application.

The use of supercritical carbon dioxide as a solvent in conjunction with mechanical melt blending offers a processing route that does not result in solvent residues and minimises the possibility of thermal degradation. The method is currently of significant interest in a range of applications including recycling, the preparation of tissue scaffolds and polymeric drug delivery systems. Melting point depression by supercritical CO_2 has been observed in a number of semi-crystalline polymers [9,10]. Moreover, our laboratory has previously studied the solubility of carbon dioxide in PCL [11]. Supercritical CO_2 can also facilitate the formation of blends by acting as a solvent, reducing the intermolecular interactions and increasing the chain separation, in effect acting as a molecular lubricant [12].

The purpose of this paper is to extend current work on the PHBV−PCL blend system by fabricating blends in the melt by mechanical means both with and without the presence of supercritical CO_2. The miscibility of melt-blended PHBV and PCL will be investigated using a combination of differential scanning calorimetry and dynamic mechanical thermal analysis. This will be accomplished through the analysis of the variation of the peak temperature of the α relaxation and the variation of the glass transition temperature in PHBV with blend composition. The interaction of carbon dioxide with the PHBV component will be investigated using infrared spectroscopy. Futhermore, infrared spectroscopy will be used to characterise the level of degradation in the samples following processing.

2. Materials, apparatus and experimental procedure

2.1. Materials

Polycaprolactone (CAPA 6500) was supplied in pellet form from Solvay Interox Ltd (UK). The number and weight average molecular weights of the CAPA 6500 were 47500 and 84500, respectively (manufacturers data). Poly(hydroxybutyrate-*co*-8%hydroxyvalerate) (PHBV D400G) was supplied in pellet form from Zeneca Bioproducts (UK). The number and weight average molecular weights for PHBV were 131,000 and 539,000, respectively.

2.1.1. Preparation of blends using a two-roll mill (mechanical blends)

Polymer blends of PCL and PHBV in the composition range 25/75 (PCL/PHBV)−75/25 (PCL/PHBV) (by weight) were produced using a two-roll mill (Swabenthan, Germany). The rollers were pre-heated to 175 °C to limit thermal degradation of the PHBV polymer. Pellets of PCL were then introduced into the rollers, followed by PHBV. This allowed initial melting of the PCL and limited the amount of heating, hence thermal degradation of the PHBV. The polymers were then mixed thoroughly for 4 min to ensure maximum dispersion of the polymers. Samples were stored for one month prior to testing to enable any secondary crystallisation to develop fully.

2.1.2. Preparation of blends with supercritical CO_2 (supercritical blends)

Polymer blends of PCL and PHBV in the composition range 25/75−75/25 (by weight) were also produced using a supercritical carbon dioxide rig manufactured by Thar Ltd, illustrated in Fig. 3. Pellets of the polymers were introduced to a sealed vessel (100 ml) equipped with a mechanical stirrer. The vessel was initially heated to 125 °C at which point PCL was in the melt and PHBV remained a semi-crystalline solid. The vessel was then pressurised to 320 bar with CO_2. Under these conditions, both PCL and PHBV were in the melt. The pressure was maintained through the pump system and the temperature was controlled by a computer programme which monitored the thermocouples inside the vessel and on the heating element surrounding the vessel.

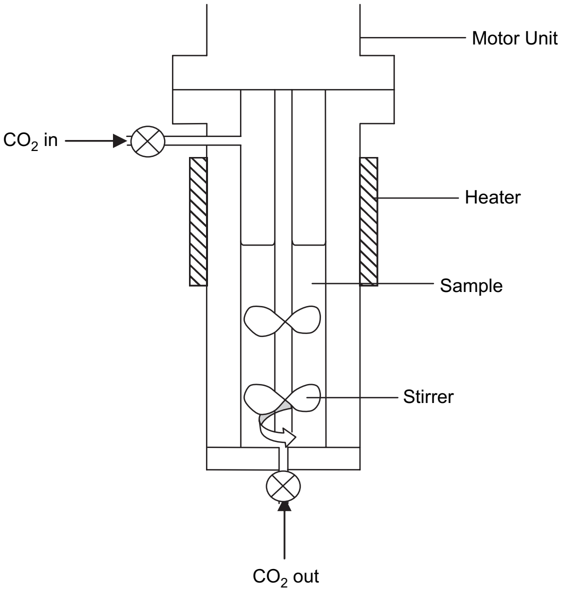

Fig. 3. A schematic diagram illustrating the apparatus used to produce a blend of PCL and PHBV in the presence of supercritical carbon dioxide.

Blends were stirred at 1000 rpm for 2 h to ensure thorough mixing and complete melting by dissolution of CO_2 in the polymer. After this period the pressure was released and the vessel cooled to allow extraction of the polymer blend.

2.1.3. Differential scanning calorimetry (DSC)

The glass transition behaviour of PHBV was measured using a Perkin Elmer differential scanning calorimeter (DSC 7) interfaced to a personal computer. 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 points of benzoic acid, stearic acid and octadecane. Corrections were made for thermal lag by extrapolation to zero heating rate. Plots of actual vs. experimental melting points were linear and were used to calibrate the calorimeter temperature.

Samples in the form of discs (1-mm thick and 3-mm diameter) were contained in aluminium pans, and an empty pan was used as a reference. Sample masses were typically 15 mg except in the case of the 75/25 (PCL/PHBV) blend. In this instance, the sample mass was deliberately increased to 30 mg to increase the deflection of the heat flow trace at the glass transition temperature of PHBV, thereby providing an increase in sensitivity. The glass transition temperature of the PHBV component was measured according to the following procedure. Samples were melted and stored at a temperature of 210 °C for 3 min to ensure thorough melting of the sample. The samples were quenched in liquid nitrogen by manual extraction from the DSC cell. The samples were then reheated at 10 °C/min from −35 °C through the glass transition temperature of the PHBV component and the temperature of the process was measured according to the procedure described by Richardson [13]. The melting behaviour of PHBV was also characterised using DSC. At a heating rate of 10 °C/min, the melting point of PHBV was found to be 163.5 °C (as shown in Fig. 9).

2.1.4. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical measurements were performed on the mechanical blends using a Polymer Laboratories DMTA MKII. Samples in the form of rectangular beams (50 × 10 × 2 mm) were mounted in dual cantilever geometry and the loss and storage moduli were recorded over a range of frequencies from 0.1 to 10 Hz. The temperature scan range was from −120 to 40 °C at 1 $°C\ min^{-1}$. The loss tangent was calculated from the ratio of loss and storage moduli. DMTA on the blends produced with supercritical carbon dioxide was not performed as these measurements would have required further re-processing to create suitable plaques. Further re-processing was likely to introduce the possibility of degradation and was therefore not attempted.

2.1.5. Infrared spectroscopy

Changes to the infrared spectrum of PHBV during either heating (at ambient conditions) or pressurisation with CO_2 (at 130 °C) were monitored using a Nicolet 860 FT-IR. Measurements were made using a Golden Gate ATR supercritical fluids analyser supplied by Specac (p/n 10585). The ATR unit also facilitated measurement of the infrared spectra at pressures up to 300 bar. A schematic diagram of the ATR unit with supercritical top-plate is shown in Fig. 4. The supercritical CO_2 was delivered to the high pressure cell by the use of a hand operated high pressure generator (HiP 62-6-10). The pressure in the cell was measured by a pre-calibrated transducer (Druck, UK) which had an uncertainty of 0.014%. The temperature was controlled and monitored by a dedicated heater unit, which had an uncertainty of ±0.1 °C.

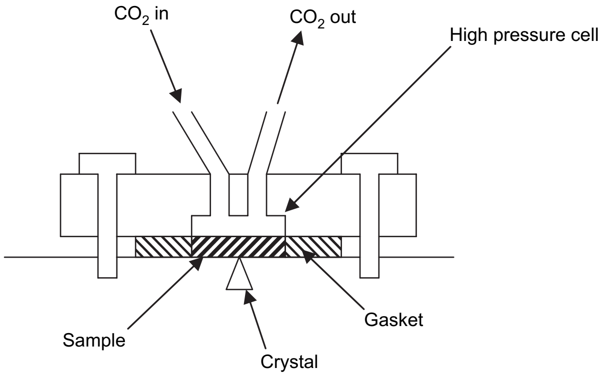

Fig. 4. A schematic diagram illustrating the apparatus used to measure the infrared spectrum of PHBV under isothermal and isobaric conditions.

3. Results and discussion

3.1. Blend miscibility in mechanical blends of PCL and PHBV

The behaviour of the glass transition temperature (T_g) with blend composition is generally taken as a measure of the miscibility of a polymer blend system, with a single, composition dependent transition being synonymous with miscibility and the associated molecular level mixing of the component polymers. The variation of the relative heat flow with temperature for the PCL–PHBV mechanical blends shown in Fig. 5

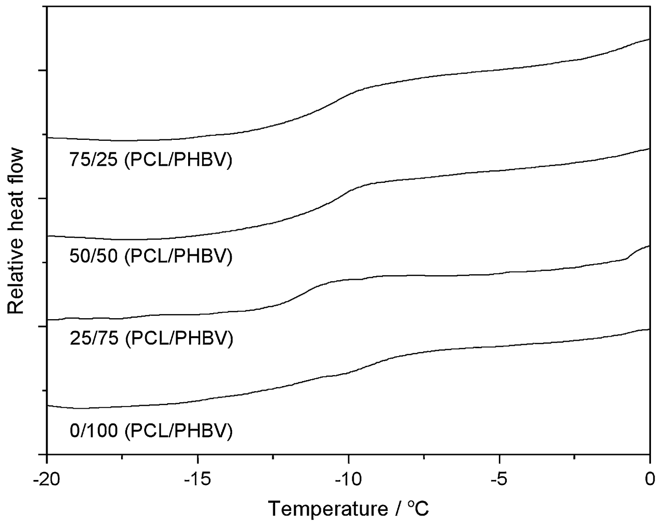

Fig. 5. The glass transition region of the PHBV blend component (mechanical blend) as measured by DSC. No compositional dependence was apparent.

Table 1
The glass transition temperatures of the PHBV blend component for the mechanical and supercritical CO_2 blend preparation methods

Blend composition/wt% PHBV	Glass transition temperature/°C ± 1	
	Mechanical blend	Supercritical blend
100	−11.73	−11.63
75	−11.52	−13.40
50	−11.19	−16.05
25	−11.19	−16.32

illustrates that the glass transition region does not shift with composition. From the above definition of miscibility, it is clear from the associated T_g data presented in Table 1 that the blends of PCL and PHBV produced using mechanical means (described in Section 2.1.1) were immiscible. Any miscibility that may have developed during the mixing process was lost on cooling to room temperature. The mechanism that leads to immiscibility in the PCL–PHBV system is likely to involve a phase separation process that is driven by initial crystallisation of the PHBV component followed by the crystallisation of the PCL phase. The results presented in Table 1 and Fig. 5 are in accordance with previous research that found the PCL–PHBV blend system produced using a solution blend method to be immiscible [8].

The glass transition temperature of the PCL component was not accessible by DSC due to a limitation in the degree to which the block temperature could be cooled. Therefore, to facilitate the measurement of the glass transition process of the PCL component in the mechanical blends of PCL and PHBV, dynamic mechanical thermal analysis was attempted. The variation of the loss tangent with temperature for the mechanical blends of PCL and PHBV in the composition range 0/100 (PCL/PHBV)–50/50 (PCL/PHBV) is shown in Fig. 6. In the selected temperature range, a prominent α relaxation process was apparent, the relaxation was centred at a temperature of −40 °C. The α process in PCL originates from the segmental motions that occur following the glass to liquid transition process [14]. In addition to the α process, at −100 °C, a low intensity β relaxation originating from PCL can also be observed. The origin of the β process is often attributed to rotations of the constituents of the main-chain and is believed to originate in the amorphous phase of the polymer.

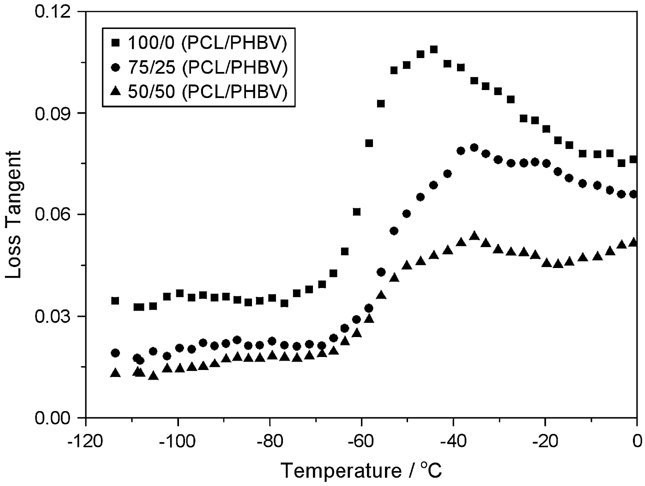

Fig. 6. The variation of the loss tangent with temperature for the mechanical blends of PHBV and PCL in the composition range 100/0–50/50.

The variation in intensity of the α relaxation process can be easily explained in terms of the variation of blend composition, but the most significant observation is the fact that the peak temperature of the PCL α relaxation process does not shift significantly with increasing PHBV content. This is another indication that the blend system produced using mechanical means is immiscible. This finding is in accordance with the results obtained from DSC. Consideration of the results presented above in relation to those described in the literature for blends produced from solution leads to the conclusion that the additional mechanical work introduced using the two-roll mill mechanical blending process does not increase the level of miscibility and therefore, under these conditions, the blend can be described as immiscible.

3.2. Production and miscibility of PCL–PHBV blends produced using supercritical CO_2

The infrared spectrum of a polymer can often contain information that relates to the morphology of the sample under investigation. Vibrational bands can have components in the amorphous regions of the sample and in the crystalline lamellae. In the case of PHBV, the crystalline component of the carbonyl band appears at 1720 cm^{-1} in the infrared spectrum [15–17]. Therefore, the intensity of the crystalline carbonyl peak is in effect related to the degree of crystallinity of the material and can be used to not only monitor the morphology but also the melting of the crystallites in the sample. The morphological sensitivity of the carbonyl peak in PHBV is illustrated in Fig. 7. It is clear that on heating from a temperature of 145 °C (at which point PHBV is a semi-crystalline solid)

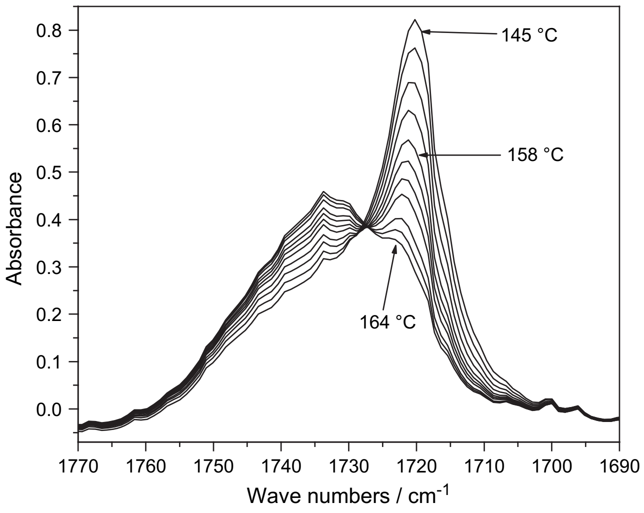

Fig. 7. The infrared spectrum of PHBV illustrating the variation of crystalline phase carbonyl peak intensity with increasing temperature (at atmospheric pressure).

through to a temperature of 164 °C (at which point PHBV is a liquid), there was a marked decrease in the intensity of the crystalline carbonyl peak at 1720 cm^{-1}. There was also a concomitant increase in the amorphous component of the carbonyl band at 1735 cm^{-1}. Therefore, it can be concluded that on heating, the decrease in intensity of the peak at 1720 cm^{-1} is directly related to the melting process in PHBV and can indeed be used to monitor the morphology of the sample.

The interaction of CO_2 with PHBV under pressure can be investigated with an approach similar to that described above. Since the intensity of the carbonyl peak at 1720 cm^{-1} is sensitive to the morphology of the material, any changes to the morphology that are induced by the presence of CO_2 in the material will be apparent in the infrared spectrum. Fig. 8 illustrates the effect of increasing CO_2 pressure on the carbonyl band PHBV at an isothermal temperature of 130 °C. At this temperature, under ambient pressure, PHBV is a semicrystalline solid. It is clear that as the pressure was increased from 100 bar to 300 bar, the intensity of the crystalline component of the carbonyl band decreased, showing a marked similarity to the trend observed in Fig. 7, thereby indicating that melting had been induced by the presence of CO_2. This observation of pressure induced melting is in accordance with Flory–Huggins theory that shows that as the solvent concentration in the polymer increases, there is a corresponding decrease in the melting point [18].

The melting trace of PHBV obtained from DSC under ambient pressure is shown in Fig. 9. The peak melting temperature was 163.5 °C and the last trace of crystallinity was 173.1 °C. The peak melting temperature of PHBV apparent in Fig. 9 can be related to the decrease in crystalline carbonyl peak intensity illustrated in Fig. 7 in that there is good agreement between the temperature of the minimum peak intensity and the peak melting temperature obtained from DSC. From this observation it can be inferred from Fig. 8 that at a temperature of 130 °C and a pressure of 300 bar, PHBV had melted. This corresponds to a melting point depression under these conditions of 33.5 °C. Additional experiments showed that as the isothermal temperature increased, the CO_2 pressure required to melt PHBV decreased: at 140 °C and 150 °C the pressure required to induce melting decreased to 140 bar and 80 bar, respectively.

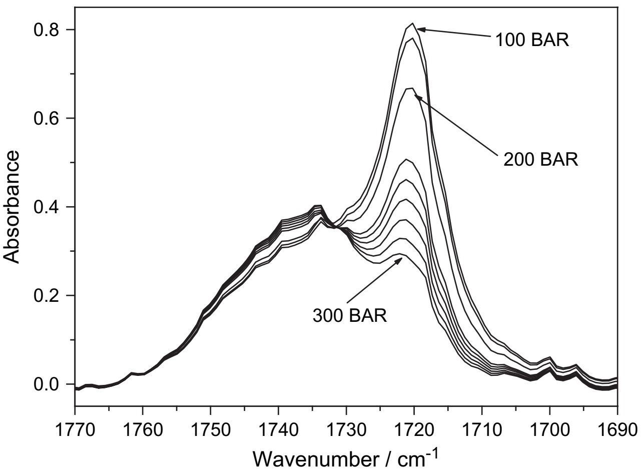

Fig. 8. The infrared spectrum of PHBV illustrating the variation of crystalline phase carbonyl peak intensity with increasing pressure (at a temperature of 130 °C).

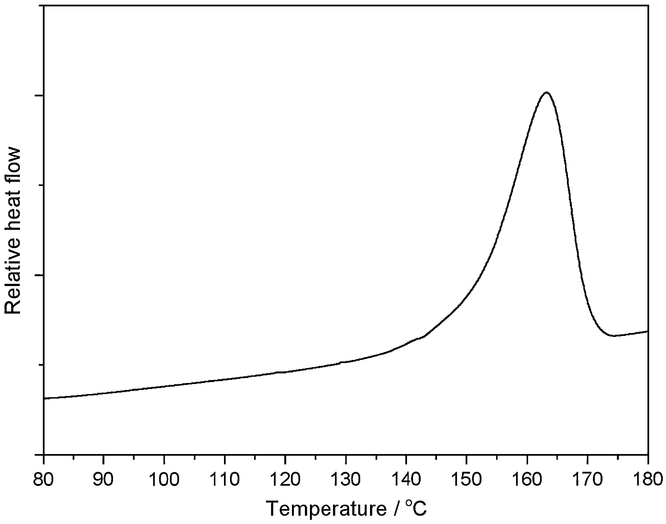

Fig. 9. A typical melting trace of PHBV obtained from DSC. The melting point was found to be 163.5 °C.

The variation of relative heat flow with temperature for the PCL–PHBV blends produced in conjunction with supercritical CO_2 is shown in Fig. 10. In contrast to the glass transition temperatures of the mechanical blends, those of the supercritical blends appear to show evidence of miscibility in the glass transition temperature of the PHBV component whose composition is dependent over the range 25/75 (PCL/PHBV)–50/50 (PCL/PHBV). The measured glass transition temperatures for the supercritical blends are shown in Table 1. Further supporting evidence of the development of miscibility is derived from

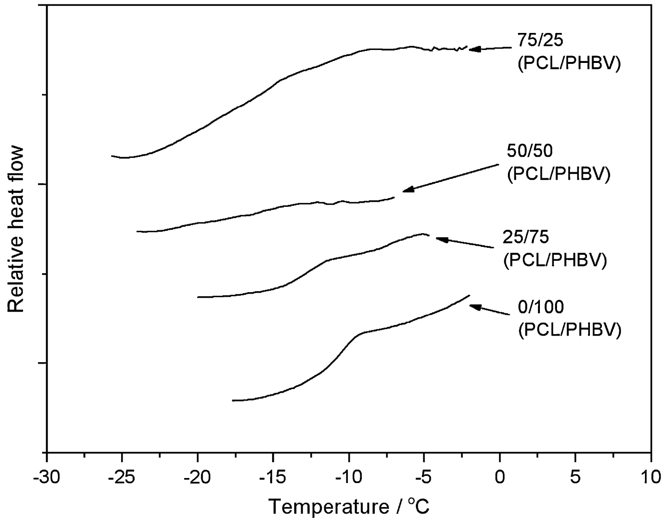

Fig. 10. The glass transition region of the PHBV blend component (supercritical blend) as measured by DSC. Compositional variation and miscibility was apparent.

the comparison of measured T_g values with those predicted by the Fox equation, given below,

$$\frac{1}{T_g} = \frac{w_A}{T_{g_A}} + \frac{w_B}{T_{g_B}} \qquad (1)$$

where T_g, T_{g_A} and T_{g_B} are the glass transition temperatures of the blend, polymer A and polymer B, respectively. The weight fractions of the components are given by w_A and w_B. From Fig. 11, it is apparent that there is a reasonably good agreement with theoretical T_g data over the range 25/75 (PCL/PHBV)–50/50 (PCL/PHBV).

To address the question of why the PCL–PHBV blend can become miscible, the effects of the blend preparation methods must be considered. In the case of the mechanical blend production method, the two-roll mill assists the dispersion of the phases through the introduction of mechanical work by the application of shear forces caused by a difference in the rotation rates of the front and rear rollers. If the level of intermolecular interaction between the homopolymers is insufficient, phase separation will dominate the formation of the microstructure. In the case of the production method that utilises supercritical CO_2, recent work has demonstrated that high pressure CO_2 can enhance the interdiffusion and dissolution of polymers [19]. The action of supercritical CO_2 in the PCL–PHBV blends may be similar and enable the phases of PCL and PHBV to interdiffuse. The resulting miscibility may be retained on cooling due to the effects of intermolecular interactions between the ester groups (present in both polymers) that may be able to operate as a result of CO_2 assisted interdiffusion.

It has been suggested above that the use of supercritical CO_2 may offer a production method that could minimise the occurrence of degradation during processing. Thermal degradation becomes apparent in a variety of ways including a reduction in the glass transition temperature which originates from a decrease in molecular weight. The glass transition temperature data shown in Table 1 suggest that thermal degradation has not occurred in either of the processing methods adopted in this study. However, the sensitivity of infrared spectroscopy provides a deeper insight into the effects of the processing methods described above. The infrared spectrum for a 25/75 (PCL/PHBV) blend in the region 1500–900 cm^{-1} is shown in Fig. 12. It is apparent that a series of additional peaks appear in the spectrum obtained from the blend produced using the mechanical two-roll mill. This is indicative of the formation of C–O moieties. More specifically, a peak becomes apparent in the mechanical blend spectra centred at 978 cm^{-1}, which can be attributed to bending vibrations of the olefinic C–H component of the main degradation by-product, crotonic acid (*trans*-2-butenoic acid) [20]. This observation suggests that the degradation of PHBV has been initiated during melt blending on the two-roll mill, but not during the supercritical CO_2 preparation method.

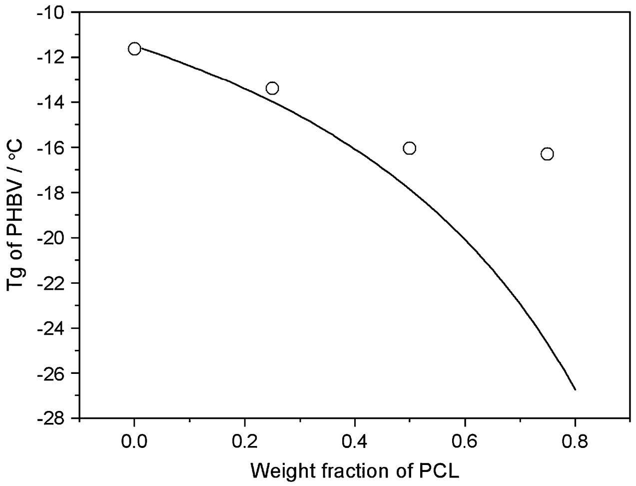

Fig. 11. The variation of PHBV glass transition temperature with blend composition (supercritical blend). Solid line represents the Fox dependence.

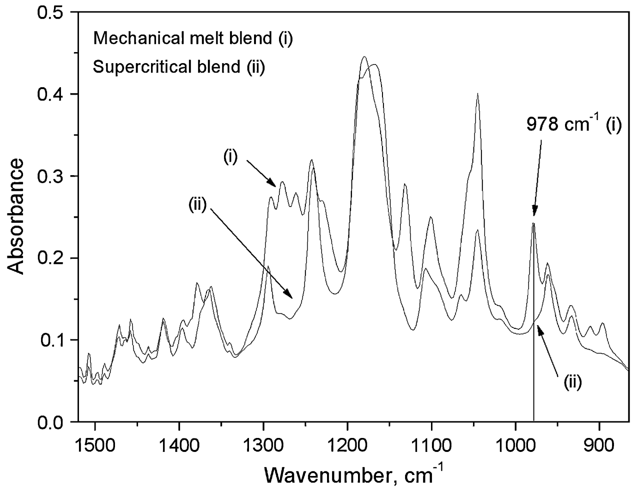

Fig. 12. The finger-print region of the infrared spectrum of a 25/75 (PCL/PHBV) produced using (i) mechanical melt blending (mechanical blend) and (ii) mechanical melt blending in the presence of supercritical CO_2 (supercritical blend). Note the presence of a peak at 978 cm^{-1} in (i) relating to crotonic acid, a degradation product of PHBV.

4. Conclusions

This study has extended existing work on the PHBV–PCL blend system by the use of mechanical blending in the presence of supercritical CO_2. The use of supercritical CO_2 during processing results in a reduction of the melting point of the PHBV component as demonstrated by FT-IR. This enables melt processing to take place at significantly lower temperatures, which is likely to minimise thermal degradation to the PHBV blend component. The presence of crotonic acid is a measure of the degradation of PHBV and it was clear from the finger-print region of the infrared spectrum of the blend produced in conjunction with supercritical CO_2 that the presence of crotonic acid was negligible, whereas in the mechanical blend, the formation of crotonic acid was clearly apparent. Furthermore, preparation of the blends of PCL and PHBV in the presence of supercritical CO_2 resulted in the development of miscibility over the lower wt% PHBV compositions.

Mechanical blending alone did not develop any miscibility. In summary, the use of supercritical CO_2 in the preparation of a blend of PCL and PHBV offers a way of inducing miscibility and at the same time minimising the occurrence of degradation during blend production.

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