

Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol)

Kelly, Catherine; Fitzgerald, Annabel; Jenkins, Michael

DOI:

[10.1016/j.polymdegradstab.2018.01.003](https://doi.org/10.1016/j.polymdegradstab.2018.01.003)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Kelly, C, Fitzgerald, A & Jenkins, M 2018, 'Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol)', *Polymer Degradation and Stability*, vol. 148, pp. 67-74. <https://doi.org/10.1016/j.polymdegradstab.2018.01.003>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked for eligibility: 22/01/2018

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

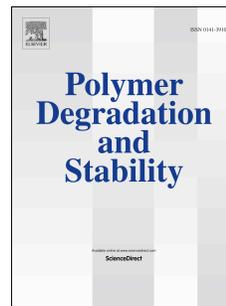
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol)

Catherine A. Kelly, Annabel V.L. Fitzgerald, Mike J. Jenkins



PII: S0141-3910(18)30010-7

DOI: [10.1016/j.polymdegradstab.2018.01.003](https://doi.org/10.1016/j.polymdegradstab.2018.01.003)

Reference: PDST 8428

To appear in: *Polymer Degradation and Stability*

Received Date: 21 September 2017

Revised Date: 21 December 2017

Accepted Date: 4 January 2018

Please cite this article as: Kelly CA, Fitzgerald AVL, Jenkins MJ, Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol), *Polymer Degradation and Stability* (2018), doi: 10.1016/j.polymdegradstab.2018.01.003.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol)

Running head: Reducing the secondary crystallisation of PHB-co-HV with poly(ethylene glycol)

Catherine A. Kelly¹, Annabel V.L. Fitzgerald¹, Mike J. Jenkins^{1*}

¹School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, B15 2TT. UK

*to whom correspondence should be sent: email: m.j.jenkins@bham.ac.uk; tel: +44 (0)121 414 2841; fax - +44 (0)121 414 7468

Abstract

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-co-HV) is a sustainable and biodegradable polymer, but as a potential packaging material, it suffers from a narrow processing window and embrittlement over time due to secondary crystallisation. This study aims to extend previous research by exploring the effect of the addition of poly(ethylene glycol) (PEG), in a range of molecular weights and compositions, on the rate of embrittlement. On blending, it was apparent that there was a reduction in both the melting point (of up to 7 °C) and the melt viscosity. Furthermore, there was a reduction in both the modulus and tensile strength indicating that PEG acts as an effective plasticiser in PHB-co-HV. In terms of the secondary crystallisation process, the addition of PEG could not prevent the process from occurring, only hinder it. PEG 600 in relatively high concentrations was found to be the most effective in this regard with a 53% reduction in the change in Young's modulus compared to pure PHB-co-HV. This observation, together with the melting point reduction which extends the

processing window for PHB-co-HV, makes PEG a worthwhile additive to an otherwise fundamentally brittle polymer.

Keywords: Poly(hydroxybutyrate-co-hydroxyvalerate); poly(ethylene glycol); secondary crystallization; blending; stability

1. Introduction

Poly(hydroxybutyrate) (PHB) and its copolymers are biodegradable polymers formed through bacterial synthesis [1]. Cells generate the polymer as a means of energy storage when they are in the presence of an excess carbon source coupled with depleted levels of nitrogen, oxygen, sulphur or phosphorus [2]. The polymer is formed as discrete granules and can occupy up to 90% of the dry cell mass. This bacterial synthesis results in a sterically pure material and high crystallinities of 50-80% [3, 4]. The biodegradable nature of PHB and its copolymers coupled with barrier properties comparable to polypropylene (PP) and polyethylene terephthalate (PET) [5, 6] has resulted in great interest from the packaging industry.

The mechanical properties of PHB and its copolymers are initially comparable to polymers currently used in packaging applications (for example PP and PET), but these properties deteriorate over time preventing its commercial use. This is because PHB possesses a low glass transition temperature (T_g), of approximately 4 °C [3], causing the polymer chains in the amorphous phase to have a degree of mobility at room temperature. The chains are therefore able to rearrange and undergo secondary crystallisation on storage, thickening the lamellae and/or creating new thinner lamellae. Embrittlement ensues leading to significant

reduction in ductility [7-9]. Another limitation of PHB and its copolymers is their narrow processing window. The high melting point of PHB requires processing temperatures in excess of 180 °C; however above 180 °C bond cleavage can occur, resulting in the production of crotonic acid and degradation of the polymer [10, 11]. Degradation has also been observed to occur at temperatures below the melting point during prolonged exposure [9, 12].

To improve the initial mechanical properties, increase the processing window and hinder secondary crystallisation, two strategies have become apparent; the incorporation of alternative bulkier monomeric units into the polymer chain [1, 13] and blending with other polymers [14] and low molecular weight species [15-18]. The incorporation of additional materials offers a cost-effective route to the improvement of the properties of PHB. The focus of blending additives with PHB and its copolymers has been the formation of intermolecular hydrogen bonds between hydroxyl groups in the additive and the carbonyl groups of PHB. It is believed that this interaction effectively produces cross links between adjacent PHB polymer chains in the amorphous phase. Although these interactions are relatively weak they are still able to alter the properties of the resulting blend. The addition of both Bisphenol A (BPA) and 4,4'-thiodiphenol (TDP) to PHB and its copolymers have been previously investigated [15-18]. Results have demonstrated the formation of hydrogen bonds which in turn increased the glass transition temperature, reduced the melting point and crystallinity and produced a more ductile material. Despite these obvious advantages, BPA is no longer approved for use in food packaging due to its possible estrogenic and endocrine disrupting effects [15]. This work will therefore attempt to replace these additives with a more suitable option.

BPA and TDP consist of two alcohol groups that can hydrogen bond to the carbonyl groups of PHB, thereby hindering mobility in adjacent chains. These alcohol groups are separated by two bulky rings which prevent the polymer chains from approaching each other and therefore primary and secondary crystallisation from the melt is hindered. Given the presence of hydroxyl groups separated by long aliphatic chains biodegradable [19, 20] poly(ethylene glycol) may be a suitable alternative to BPA. Previous work has analysed the blending of PHB-co-HV and PEG over a range of molecular weights and concentrations and the resulting effects on the initial thermal and mechanical properties [21-25]. Miscible blends have been reported with PEG containing a molecular weight of 400 Da, however partial miscibility was found when the molecular weight exceeded 1500 Da [22]. In addition Li *et al.* observed that smaller PEG molecular weights were more favourable during blending with poly(lactic acid) as their smaller size facilitates their insertion into the free volume of the molten state [26]. To date, only Requena *et al.* [21] has reported the effect of PEG on the secondary crystallisation of PHB-co-HV, however, the study only evaluated one concentration and was performed over a relatively short time scale (5 weeks). Therefore, this study aims to extend both the range of PEG molecular weights and concentrations and the length of storage time to assess the long-term effectiveness of the use of PEG as a means to hinder the secondary crystallisation process and resulting embrittlement. If successful, this will prolong the shelf life of PHB products enabling wide scale adoption as a biodegradable packaging material.

In standard polymer blending studies the weight fraction of the materials is generally kept constant as the molecular weight of additive is varied. This results in a greater number of low molecular weight chains compared to longer polymers. As PEG interacts with PHB-co-HV through its terminal hydroxyl groups this would also lead to a variation in the number of chain ends and therefore interactions. This study aims to overcome this issue by keeping the

mole ratio of PEG to PHB-co-HV repeat units constant and therefore the true effect of the size of PEG can be evaluated.

PHB-co-HV : PEG blends are produced using a wide range of molecular weights, within the previously defined miscibility region (<1500 Da)[22], and composition ratios and the thermal and mechanical properties of each are analysed over time to enable any deterioration in their strength, stiffness and elongation to break to be determined. In addition, the viscosity of PHB-co-HV : PEG blends are analysed for the first time.

2. Materials and Methods

2.1. Materials

Poly(hydroxybutyrate-co-hydroxyvalerate) (PHB-co-HV) containing 3% hydroxyvalerate (Tianan ENMAT Y1000P) was obtained from Helian Polymers (Venlo, Netherlands) and dried at 100 °C for 1 hour prior to use. The molecular weight has previously been determined as 215 kDa by gel permeation chromatography in chloroform using polystyrene standards.[9] BioUltra poly(ethylene glycol) (PEG) (M_w 200, 400 and 600 as specified by the manufacturer), was purchased from Sigma Aldrich (Dorset, UK) and used as received. Nitrogen (O_2 free) was purchased from BOC gases (Guildford, UK).

2.2. Methods

2.2.1. Melt blending

A Haake PolyLab QC mechanical mixer (ThermoScientific, Loughborough, UK) was used to blend PHB-co-HV with PEG of various molecular weights. The mixer was preheated to 170 °C. The required mass of PEG was mixed into the PHB-co-HV pellets by hand and this material (50 g) added to the Haake mixer. The system was left for 10 minutes at a screw

speed of 100 rpm to allow the materials to intimately mix before the blend was collected and stored in a freezer (-22 °C) until required in order to limit the potential for phase separation.

2.2.2. Determination of the amount of PEG required

Previous studies on the blending of poly(lactic acid) and PEG have shown a region of high miscibility to occur between PEG concentrations of 8 and 25 wt% [27]. In light of this, compositions of 5, 10 and 15 wt% PEG 400 were used. As the main focus of these studies is to assess the effect of PEG interactions it is important that the ratio of PEG molecules, and therefore the number of end groups able to participate in potential interactions, to repeat units of PHB-co-HV remains consistent throughout. The mass of additive was therefore adjusted accordingly for the various molecular weights (PEG 200, 400 and 600).

Hydroxybutyrate has a mass of 86 and hydroxyvalerate a mass of 100. As ENMAT Y1000P consists of 3 % valerate this gives an average repeat unit mass of 86.42. The PEG molecule : PHB-co-HV repeat unit ratio, can be calculated using the molecular weights of PEG 400 and the repeat unit of PHB-co-HV (Equation 1, Table 1):

$$\text{Moles PEG : PHB-co-HV repeat unit ratio} = \left(\frac{\text{mass}_{\text{PEG400}}}{M_{\text{wPEG400}}} \times \frac{M_{\text{wPHB-co-HV repeat unit}}}{\text{mass}_{\text{PHB-co-HV}}} \right)$$

Equation 1: Calculation of the required moles PEG : PHB-co-HV unit ratio

In order to keep the number of PEG chains, and therefore end groups, to PHB-co-HV repeat units consistent the ratios detailed above are used for each of the PEG molecular weights.

The quantity of each PEG required can therefore be calculated as:

$$\text{PEG}(\% \text{wt}) = \frac{\text{moles}_{\text{PEG}} \times M_{\text{wPEG}}}{(\text{moles}_{\text{PEG}} \times M_{\text{wPEG}}) + (\text{moles}_{\text{PHB-co-HV unit}} \times M_{\text{wPHB-co-HV unit}})} \times 100\%$$

Equation 2: Calculation of the weight percent of PEG required

Due to the difficulties in precisely weighing polymer pellets, flakes and liquids the actual PEG weight percent used and PEG : PHB-co-HV repeat unit mole ratio generated for each sample were calculated (Table 2) and used when comparing the results.

2.2.3. Hot pressing

Plaques (152 x 158 x 0.266 mm) of the PHB-co-HV blends were produced by compression moulding using a Moore E1127 hydraulic hot press (George E. Moore & Sons Ltd, Birmingham, UK) which was preheated to 180 °C. Briefly, the blended polymer samples (9 g) were placed into a mould (152 x 158 x 0.266 mm) which was then inserted into the press. The mould was allowed to warm for 3 minutes before a load of 10 tonnes was applied for a further 5 minutes. The plaques were cooled at a rate of 17 °C min⁻¹ for 20 minutes by passing water through the plates. For the rheology analyses, plaques of 77 x 77 x 1 mm were produced using 8 g of the polymer blend. Following production the plaques were immediately cut into the required shapes and stored at -22 °C to prevent any further crystallisation prior to the start of the stability study.

2.2.4. Stability study

In order to determine the effect of PEG on the rate of secondary crystallisation and embrittlement, time studies were performed. Hot-pressed material was removed from the freezer, left for 10 minutes to equilibrate to room temperature and then immediately analysed. This was taken as time zero. The remaining samples were stored at room temperature and analysed periodically by differential scanning calorimetry (DSC) and mechanical testing at 1, 2, 3, 4, 8 and 12 weeks.

2.2.5. Rheology

The viscosity of the polymer blends was measured using a Rheometric Scientific ARES rheometer (Surrey, UK) with a 25 mm parallel plate geometry. In a typical experiment, discs of 25 mm in diameter were cut from the 1 mm hot pressed plaques and inserted into the rheometer. The rheometer was heated to 180 °C and the sample left for 5 minutes to ensure complete melting. The top plate was lowered until a vertical load was experienced, indicating contact between the plates and sample. Oscillation tests were performed, at a frequency of 10 Hz, in which the shear strain was increased logarithmically from 1 to 350 %. Three samples were analysed for each blend and the averages and standard deviations presented.

2.2.6. Infra-red spectroscopy

A Nicolet 8700 Specac Fourier Transform Infra-red (FTIR) spectrometer, controlled by OMNIC software, (Thermo Scientific, Loughborough, UK) was used to analyse the blending of PHB-co-HV and PEG. Measurements were made on the hot pressed plaques using a Golden Gate ATR supplied by Specac (Thermo Scientific). Infra-red spectra were recorded using 50 scans at a resolution of 4 cm⁻¹ and a background spectra was ran prior to each analysis.

2.2.7. Differential Scanning Calorimetry (DSC)

A Mettler Toledo DSC 1/500 (Mettler Toledo, Leicester, UK), calibrated with indium, tin and zinc standards, was used to determine the melting point and crystallinity of the PHB-co-HV : PEG blends and pure components. The samples (~5 mg) were cut from the hot pressed plaque and weighed into standard 40 µl aluminium DSC pans (Mettler Toledo). This pan was capped with an aluminium DSC lid (Mettler Toledo) and sealed with a press (Mettler Toledo)

before inserting into the DSC at room temperature. The temperature was held at $-40\text{ }^{\circ}\text{C}$ for 5 minutes before raising it to $200\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. The melting point was taken at the peak of the transition. The crystallinity of PHB-co-HV in the blends was determined by raising the temperature to $220\text{ }^{\circ}\text{C}$, at a rate of $50\text{ }^{\circ}\text{C min}^{-1}$ after holding it at $-40\text{ }^{\circ}\text{C}$ for 5 minutes. A linear baseline was drawn from the first onset of melting to the last trace of crystallinity and the enthalpy of fusion was then calculated from the area under the endotherm. The crystallinity of the PHB-co-HV component of the blend (X_c) is defined as:

$$X_c = \frac{\Delta H_f(T_m)}{\Delta H_f^0(T_m^0)} \times \frac{1}{M_{\text{PHB-co-HV}}} 100\%$$

Equation 3: Calculation of the crystallinity of PHB-co-HV in the blend where $\Delta H_f(T_m)$ is the enthalpy of fusion measured at the melting point, $\Delta H_f^0(T_m^0)$ is the enthalpy of fusion of the completely crystalline polymer and $M_{\text{PHB-co-HV}}$ is the mass fraction of PHB-co-HV in the blend.

A literature value of 146 J g^{-1} was used for the $\Delta H_f^0(T_m^0)$ of PHB-co-HV [28]. As heat can alter the miscibility of blends, resulting in further mixing/demixing, the melting points and crystallinity were calculated from the first heating run only.

2.2.8. Mechanical testing

The ultimate tensile strength, elongation to break, and tensile modulus of the blends were determined using an Instron 5566 (High Wycombe, UK) operated by Merlin software. Dog bones (gauge length 26 mm, width 4 mm) were cut from the hot pressed plaques and analysed. Measurements were taken at 500 ms intervals using a 10 kN load cell. The sample was extended at a rate of 2 mm min^{-1} until the material failed. Three samples were analysed for each time point and the average calculated.

3. Results and Discussion

PHB-co-HV was mechanically blended with a range of PEG molecular weights in different mole ratios. The rheology, melting point, crystallinity and mechanical properties of each of the blends were analysed and the effects of PEG evaluated.

3.1. Viscosity

Rheological studies were performed on the blends to determine the effect of PEG on the viscosity of PHB-co-HV. Each of the blends displayed two distinct regions (Figure 1). A linear viscoelastic region exists at low strains rates (<50 %) in which the viscosity is independent of strain and therefore the polymer behaves as a Newtonian fluid. As the strain is increased above the critical strain, the viscosity begins to reduce, indicative of shear thinning. This observation is common with polymers as at high strains the long, entangled polymer chains become unravelled and drawn out in the direction of the shear, thereby reducing the overall viscosity [29].

A reduction in the viscosity of PHB-co-HV is observed on the addition of PEG, which is proportional to the amount of PEG within the blend (Figure 1a). On blending, PEG mixes with PHB-co-HV, weakening the intermolecular interactions, expanding the chains and thereby increasing the free volume in the system [30]. This increases the mobility of the polymer, lowering the viscosity. Although this has not been previously reported for PHB based polymers, the ability of PEG to reduce the viscosity of polymers, upon blending, has been previously reported for UHMWPE [31]. A similar trend was experienced across each of the molecular weights analysed.

The effect of PEG molecular weight on the viscosity of the blend was also investigated. The results (Figure 1b) show that although a significant viscosity reduction is observed on the addition of PEG, increasing the molecular weight from 200 to 400 Da displays no effect. However, increasing the molecular weight further to 600 Da reduces the viscosity by 50 %. Commonly an increase in the molecular weight of a blended material means fewer polymer chains for the same mass. This results in fewer interactions as it is the PEG end groups alone that will interact with PHB-co-HV. In this case the number of PEG chains remains consistent as the molecular weight is increased, due to the same mole fractions being used across each PEG grade, and therefore the effect of the chain ends can be omitted. The results therefore show that for PEG 200 and 400 increasing the size of the polymer chain has no impact on the viscosity of PHB-co-HV. As the molecular weight is increased to 600 Da the size of the PEG molecules becomes significant, separating the PHB-co-HV chains and increasing the free volume. This results in the viscosity reduction observed here. A similar trend was observed for each of the PEG : PHB-co-HV mole ratios analysed. A reduction in the viscosity is advantageous during processing as it allows lower temperatures to be used, protecting the polymer from degradation and reducing costs.

3.2. Infra-red spectroscopy

Previous work has shown that the formation of hydrogen bonds can be detected by the appearance of additional peaks in the infra-red spectra [32]. Guo reports the presence of three peaks associated with the carbonyl group of PHB when blended to poly(4-vinylphenol). These appear at 1742, 1724 and 1713 cm^{-1} and are attributed to the free amorphous carbonyl, intramolecularly bonded crystalline carbonyl and the carbonyl intermolecularly bonded to poly(4-vinylphenol).

A distinctive shift of the carbonyl peak to higher wavenumbers can be seen on the addition of PEG 400 which is proportional to concentration (Figure 2). This is created by the loss of intramolecular bonds within PHB-co-HV coupled with the increase in free carbonyls. No additional peak corresponding to the formation of intermolecular bonds with PEG can be seen however, this is believed to be due to the low concentration of PEG compared to PHB-co-HV. No trace of PEG can be found elsewhere in the spectra even at the highest concentrations. Whilst these results do not display the formation of hydrogen bonds they do show a disruption to the intramolecular bonding within PHB-co-HV on the addition of PEG indicative of miscibility. Similar effects were also found with PEG 200 and 600 (data not shown).

A peak shift was also observed on increasing the molecular weight of the PEG within the blend (Figure 3). As the number of chains remains consistent on changing the molecular weight this shows that the size of the polymer chain directly relates to the disruption of the intramolecular bonds.

3.3. Thermal properties of PHB-co-HV : PEG 600 blends

The variation of melting point with blend composition is shown in figure 4. It should be noted that the melting point of pure PHB-co-HV following the blending process was 170 °C which is approximately 5 °C less than that of unprocessed pellets. This indicates that partial degradation has taken place during processing [33] which is inevitable given the thermal instability associated with PHB-co-HV [9, 11]. It is apparent from figure 4 that the addition of PEG causes a reduction in the melting point of PHB-co-HV, proportional to concentration, showing that the PEG is retained in the inter-lamella regions. It is reported that the interaction of polymers can be assessed via such a reduction in the melting temperature [22, 34], so this

observation highlights the ability of PEG to interact successfully with the chains of PHB-co-HV within the amorphous phase and depress the observed melting temperature. During mixing with PHB-co-HV, PEG enters between the PHB-co-HV chains where infra-red analysis has shown it to weaken the intramolecular interactions and therefore increase the mobility of the chains. On cooling, the PEG chains will create steric hindrance during the crystallisation of PHB-co-HV limiting the growth of the spherulites. As a result smaller lamellae are formed leading to a reduced melting point [24]. It therefore follows that as more PEG is present within the blend the effects will be multiplied leading to a further reduction in the melting points. The glass transition temperature could not be observed in any of the DSC traces even when subjected to the higher heating rate of 50 °C/min used for the crystallinity analysis (refer to the supplementary information). This is as a result of the high crystallinity, and therefore low amorphous content, of PHB-co-HV and is commonly seen with PHB and its copolymers [23, 35, 36].

The reduction in the melting point has favourable implications in terms of processing. PHB-co-HV is said to have a narrow processing window and on heating to temperatures above the melting point (180 °C), degradation rapidly ensues [10]. The incorporation of PEG into the material reduces the melting point to below 170 °C, thereby offering a means of increasing the size of the (limited) processing window and reducing the amount of degradation that can occur.

The molecular weight of PEG was found to have a negligible effect on the melting point of PHB-co-HV in line with results reported by Requena *et al.*[21]. As this current investigation shows the molecular weight to have little effect on the melting point it is believed that the number of PEG chains is the dominating factor in melting point reduction.

The variation of degree of crystallinity with blend composition is also shown in figure 4. It is clear that there is no significant trend in terms of the effect of composition, however, there was a suggestion that decreasing the molecular weight of the PEG depressed the degree of crystallinity somewhat. Following extraction from the mechanical mixer, the blend cools and there is non-isothermal crystallisation of the PHB-co-HV. The PEG is rejected from the growth surface of the PHB-co-HV lamellae where it hinders the growth of the spherulites [24] slowing the primary crystallisation process, but clearly not the degree of crystallinity prior to subsequent storage.

3.4. Mechanical properties

Following hot pressing, the Young's modulus and ultimate tensile strength of each blend was determined. The Young's modulus was found to decrease as the concentration of PEG and/or the molecular weight increased (Figure 5). Small molecules, such as PEG, are often used in industry to improve the processability of polymers and enhance the properties of the final material. As observed in the rheology data and infra-red spectroscopy, on blending, PEG becomes intimately mixed with the PHB-co-HV chains which acts to separate the chains, thereby weakening their intramolecular interactions [23, 24]. This causes the chains to become more mobile leading to the reduction in the Young's modulus. It therefore follows that as the concentration of PEG increases these effects will be more pronounced leading to further reductions in the Young's modulus. A decrease was also observed as the molecular weight of PEG was increased. As the number of PEG chains, and therefore free ends, remains constant across the molecular weights analysed these results show that larger PEG molecules are more effective at plasticising PHB-co-HV. This is in contrast to work by Requena *et al.* in which the molecular weight was found to have no effect on the Young's

modulus [21]. The observed differences are possibly due to the reduction in the number of chains ends on increasing the molecular weight offsetting the increase in the size of the PEG molecules.

The ultimate tensile strength was also found to decrease as the molecular weight and concentration of PEG within the blend increased (Figure 5). This is likely to result from the rejection of a proportion of PEG to the interspherulitic regions which then facilitates chain mobility and in turn the progress of any cracks through the thickness of the specimens.

3.5. Hindrance of secondary crystallisation by blending with PEG

In general, no significant change in the degree of crystallinity was observed throughout the time study. A similar observation was reported during a 5 week storage study involving PHB-co-HV and 10 wt% PEG with molecular weights of 200, 1000 and 4000 Da [21].

As the main aim of this study is to extend the shelf life of processed PHB based polymers, an effective way to evaluate the effects of secondary crystallisation is to analyse the time dependence of the tensile properties of the blends. These results show secondary crystallisation and the resulting embrittlement of PHB-co-HV over time as evidenced by the increase in Young's modulus and UTS coupled with a decrease in the elongation to break (Figure 6). As the initial properties of the blends differed from that of pure PHB-co-HV, comparisons were made by plotting the change in each of the properties as compared to the original samples (Figure 6).

A 988 MPa increase in the Young's modulus was observed for PHB-co-HV over 84 days indicating stiffening of the amorphous phase and therefore the occurrence of secondary crystallisation (Figure 6a) [7, 9]. The addition of PEG was found to significantly limit the

process with an approximate 53 % reduction observed with PEG 600 with a mole ratio of 0.038. The reduction in the rate of increase of Young's modulus was found to be proportional to both PEG molecular weight and mole ratio.

The UTS also displayed a similar trend with smaller changes observed for the blends than pure PHB-co-HV (Figure 6b). Although an increase in UTS is generally favourable, indicating a stronger material, in this case it is a sign of embrittlement created by secondary crystallisation. In general, higher molecular weights and concentrations were found to be more effective in the retardation of the secondary crystallisation process.

Another sign of secondary crystallisation is a reduction in the elongation to break as the material becomes more brittle. With the exception of the low composition of PEG 200, each of the blends displayed reduced embrittlement compared to PHB-co-HV (Figure 6c). The rate of embrittlement was again found to be inversely proportional to the PEG molecular weight.

As discussed above, during the crystallisation of PHB-co-HV, PEG creates steric hindrance retarding the growth of the spherulites. It therefore follows that during storage the PEG chains will remain in the inter-lamella regions where they will also hinder the secondary crystallisation process. As the concentration of PEG within these blends increases a greater steric hindrance will be present and the rate of secondary crystallisation will decrease further leading to the observed reductions in the changes in Young's modulus, UTS and elongation to break. As the number of PEG chains remains constant on increasing the molecular weight these results suggest that the size of the PEG molecule is important in reducing the rate of secondary crystallisation with PEG 600 producing the greatest effects. As the size of the PEG chain increases it therefore follows that there will be greater steric hindrance in the

already constricted inter-lamella regions hindering the movement of the PHB-co-HV chains necessary for secondary crystallisation.

4. Conclusion

The ability of PEG to hinder the process of secondary crystallisation in PHB-co-HV has been evaluated. In the melt, PEG disperses into the PHB-co-HV and reduces the viscosity of the blend; there is a degree of miscibility. On cooling, the PHB-co-HV component crystallised, but some PEG was clearly retained in the inter-lamella regions as evidenced by the depression of the observed melting point. The melting point depression was proportional to the PEG content, with molecular weight displaying little impact on the melting point. The presence of PEG in the PHB-co-HV matrix reduced both the Young's modulus and tensile strength; these reductions were attributed to the further mobilisation of the amorphous phase in both the inter-lamella and inter-spherulitic regions.

The addition of PEG could not prevent secondary crystallisation and the resulting embrittlement, however, it did significantly limit the process over the timescale adopted in this study. PEG 600 in relatively high concentrations was found to be the most effective in this regard. This observation together with a melting point reduction that extends the processing window for PHB-co-HV makes PEG a worthwhile additive to an otherwise fundamentally brittle polymer.

5. Acknowledgements

This work was supported by EU Framework Programme 7 grant "ISA-PACK" (Grant number 289521).

6. References

- [1] Y. Doi, A. Segawa, M. Kunioka, Biosynthesis and characterization of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) in *Alcaligenes eutrophus*, *Int. J. Biol. Macromol.* 12(2) (1990) 106-111.10.1016/0141-8130(90)90061-E
- [2] A.C. Ward, B.I. Rowley, E.A. Dawes, Effect of Oxygen and Nitrogen limitation on poly-beta-hydroxybutyrate biosynthesis in ammonium-grown *azobacter-beijerinckii*, *Journal of General Microbiology* 102(SEP) (1977) 61-68.10.1099/00221287-102-1-61
- [3] Y. Doi, *Microbial Polyesters*, VCH Publishers, New York, 1990.
- [4] P.A. Holmes, Biologically produced (R)-3-hydroxalkanoate polymers and copolymers, in: D.C. Bassett (Ed.), *Developments in crystalline polymers -2*, Elsevier Applied Science Publishers, Essex, UK, 1988.
- [5] E. Bugnicourt, P. Cinelli, A. Lazzeri, V. Alvarez, Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging, *Express Polym. Lett.* 8(11) (2014) 791-808.10.3144/expresspolymlett.2014.82
- [6] O. Miguel, J.J. Iruin, Evaluation of the transport properties of poly(3-hydroxybutyrate) and its 3-hydroxyvalerate copolymers for packaging applications, *Macromol. Symp.* 144 (1999) 427-438.10.1002/masy.19991440140
- [7] F. Biddlestone, A. Harris, J.N. Hay, T. Hammond, The physical ageing of amorphous poly(hydroxybutyrate), *Polym. Int.* 39(3) (1996) 221-229.0959-8103/96/\$09.00
- [8] G.J.M. Dekoning, P.J. Lemstra, Crystallisation phenoma in bacterial poly(R)-3-hydroxybutyrate. 2. Embrittlement and rejuvenation *Polymer* 34(19) (1993) 4089-4094.10.1016/0032-3861(93)90671-v
- [9] M.J. Jenkins, K.E. Robbins, C.A. Kelly, Secondary crystallisation and degradation in PHB-co-HV: an assessment of long-term stability, *Accepted to Polymer Journal* (2017)
- [10] C. Vogel, S. Morita, H. Sato, I. Noda, Y. Ozaki, H.W. Siesler, Thermal degradation of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) in nitrogen and oxygen studied by thermogravimetric-Fourier transform infrared spectroscopy, *Applied Spectroscopy* 61(7) (2007) 755-764.10.1366/000370207781393370
- [11] I. Janigova, I. Lacik, I. Chodak, Thermal degradation of plasticized poly(3-hydroxybutyrate) investigated by DSC, *Polym. Degrad. Stabil.* 77(1) (2002) 35-41.10.1016/s0141-3910(02)00077-0
- [12] M. Kunioka, Y. Doi, Thermal degradation of microbial copolyesters - Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(3-hydroxybutyrate-co-4-hydroxybutyrate), *Macromolecules* 23(7) (1990) 1933-1936.10.1021/ma00209a009
- [13] W.D. Luzier, Materials derived from biomass/biodegradable materials, *Proceedings of the National Academy of Sciences* 89(3) (1992) 839-842.10.1073/pnas.89.3.839
- [14] P.X. Xing, L.S. Dong, Y.X. An, Z.L. Feng, M. Avella, E. Martuscelli, Miscibility and crystallization of poly(beta-hydroxybutyrate) and poly(p-vinylphenol) blends, *Macromolecules* 30(9) (1997) 2726-2733.10.1021/ma960615+
- [15] B. Fei, C. Chen, H. Wu, S.W. Peng, X.Y. Wang, L.S. Dong, J.H. Xin, Modified poly(3-hydroxybutyrate-co-3-hydroxyvalerate) using hydrogen bonding monomers, *Polymer* 45(18) (2004) 6275-6284.10.1016/j.polymer.2004.07.008
- [16] C. Chen, L.S. Dong, P.H.F. Yu, Characterization and properties of biodegradable poly(hydroxyalkanoates) and 4,4-dihydroxydiphenylpropane blends: Intermolecular hydrogen bonds, miscibility and crystallization, *Eur. Polym. J.* 42(10) (2006) 2838-2848.10.1016/j.eurpolymj.2006.07.005
- [17] Y. He, N. Asakawa, Y. Inoue, Blends of poly(3-hydroxybutyrate)/4,4'-thiodiphenol and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/4,4'-thiodiphenol: Specific interaction and properties, *J. Polym. Sci. Pt. B-Polym. Phys.* 38(22) (2000) 2891-2900.10.1002/1099-0488(20001115)38:22<2891::aid-polb40>3.0.co;2-v
- [18] B. Fei, C. Chen, H. Wu, S.W. Peng, X.Y. Wang, L.S. Dong, Comparative study of PHBV/TBP and PHBV/BPA blends, *Polym. Int.* 53(7) (2004) 903-910.10.1002/pi.1460

- [19] E.L. Fincher, W.J. Payne, Bacterial utilization of ether glycols *Applied Microbiology* 10(6) (1962) 542-547
- [20] J.R. Haines, M. Alexander, Microbial degradation of polyethylene glycols, *Applied Microbiology* 29(5) (1975) 621-625
- [21] R. Requena, A. Jimenez, M. Vargas, A. Chiralt, Effect of plasticizers on thermal and physical properties of compression-moulded poly (3-hydroxybutyrate)-co-(3-hydroxyvalerate) films, *Polym. Test* 56 (2016) 45-53.10.1016/j.polymertesting.2016.09.022
- [22] Y. Chen, Y. Park, I. Noda, Y.M. Jung, Influence of polyethylene glycol (PEG) chain length on the thermal behavior of spin-coated thin films of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)/PEG blends, *J. Mol. Struct.* 1124 (2016) 159-163.10.1016/j.molstruc.2016.02.059
- [23] S.E.M. Catoni, K.N. Trindade, C.A.T. Gomes, A.L.S. Schneider, A.P.T. Pezzin, V. Soldi, Influence of Poly(Ethylene Glycol)-(PEG) on the Properties of Influence of Poly(3-Hydroxybutyrate-CO-3-Hydroxyvalerate)-PHBV, *Polimeros* 23(3) (2013) 320-325.10.4322/polimeros.2013.037
- [24] D.F. Parra, J. Fusaro, F. Gaboardi, D.S. Rosa, Influence of poly (ethylene glycol) on the thermal, mechanical, morphological, physical-chemical and biodegradation properties of poly (3-hydroxybutyrate), *Polymer Degradation and Stability* 91(9) (2006) 1954-1959.<http://dx.doi.org/10.1016/j.polymdegradstab.2006.02.008>
- [25] V. Jost, H.C. Langowski, Effect of different plasticisers on the mechanical and barrier properties of extruded cast PHBV films, *Eur. Polym. J.* 68 (2015) 302-312.10.1016/j.eurpolymj.2015.04.012
- [26] F.J. Li, S.D. Zhang, J.Z. Liang, J.Z. Wang, Effect of polyethylene glycol on the crystallization and impact properties of polylactide-based blends, *Polym. Adv. Technol.* 26(5) (2015) 465-475.10.1002/pat.3475
- [27] C.A. Kelly, A. Naylor, L. Illum, K.M. Shakesheff, S.M. Howdle, Supercritical CO₂: A clean and low temperature approach to blending PDLLA and PEG, *Advanced Functional Materials* 22(8) (2012) 1684-1691.10.1002/adfm.201101889
- [28] M. Avella, G.L. Rota, E. Martuscelli, M. Raimo, P. Sadocco, G. Elegir, R. Riva, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fibre composites: thermal, mechanical properties and biodegradation behaviour, *J. Mater. Sci.* 35(4) (2000) 829-836.10.1023/a:1004773603516
- [29] L.I. Palade, H.J. Lehermeier, J.R. Dorgan, Melt rheology of high L-content poly(lactic acid), *Macromolecules* 34(5) (2001) 1384-1390.10.1021/ma001173b
- [30] D.F. Parra, J. Fusaro, F. Gaboardi, D.S. Rosa, Influence of poly (ethylene glycol) on the thermal, mechanical, morphological, physical-chemical and biodegradation properties of poly (3-hydroxybutyrate), *Polym. Degrad. Stabil.* 91(9) (2006) 1954-1959.10.1016/j.polymdegradstab.2006.02.008
- [31] M.J. Xie, H.L. Li, Viscosity reduction and disentanglement in ultrahigh molecular weight polyethylene melt: Effect of blending with polypropylene and poly(ethylene glycol), *European Polymer Journal* 43(8) (2007) 3480-3487
- [32] L.H. Guo, H. Sato, T. Hashimoto, Y. Ozaki, FTIR Study on Hydrogen-Bonding Interactions in Biodegradable Polymer Blends of Poly(3-hydroxybutyrate) and Poly(4-vinylphenol), *Macromolecules* 43(8) (2010) 3897-3902.10.1021/ma100307m
- [33] R. Renstad, S. Karlsson, A.C. Albertsson, P.E. Werner, M. Westdahl, Influence of processing parameters on the mass crystallinity of poly(3-hydroxybutyrate-co-3-hydroxyvalerate), *Polymer International* 43(3) (1997) 201-209.10.1002/(sici)1097-0126(199707)43:3<201::aid-pi761>3.3.co;2-z
- [34] A.J. Nijenhuis, E. Colstee, D.W. Grijpma, A.J. Pennings, High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: Thermal characterization and physical properties, *Polymer* 37(26) (1996) 5849-5857
- [35] Y.J. Phua, A. Pegoretti, T.M. Araujo, Z.A.M. Ishak, Mechanical and thermal properties of poly(butylene succinate)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) biodegradable blends, *Journal of Applied Polymer Science* 132(47) (2015) 10.10.1002/app.42815

[36] D. Garcia-Garcia, J.M. Ferri, T. Boronat, J. Lopez-Martinez, R. Balart, Processing and characterization of binary poly(hydroxybutyrate) (PHB) and poly(caprolactone) (PCL) blends with improved impact properties, Polym. Bull. 73(12) (2016) 3333-3350.10.1007/s00289-016-1659-6

ACCEPTED MANUSCRIPT

Figure captions

Figure 1: Viscosity analysis of PHB-co-HV : PEG blends with a) increasing concentration of PEG b) increasing PEG molecular weight

Figure 2: Infra-red spectra of PHB-co-HV on the addition different concentrations of PEG 400

Figure 3: Infra-red spectra of PHB-co-HV on the addition of medium concentrations of PEG with various molecular weights

Figure 4: The effect of PEG concentration and molecular weight on the melting point and crystallinity of PHB-co-HV

Figure 5: The effect of PEG concentration and molecular weight on the Young's modulus and ultimate tensile strength

Figure 6: Effect of the addition of PEG on the change in a) Young's modulus: b) UTS and c) elongation to break over time

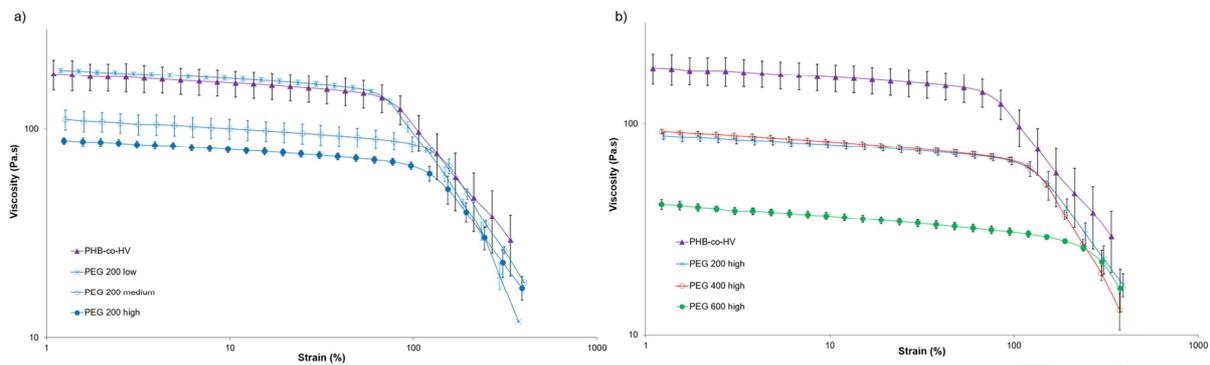
Tables

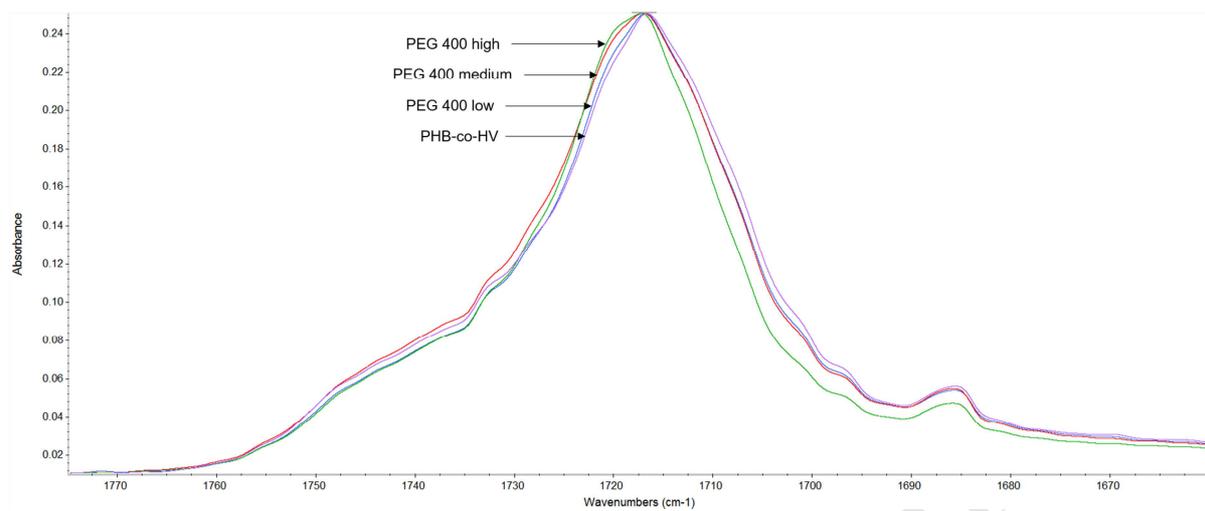
Table 1: Required mole PEG : PHB-co-HV repeat unit ratio for PEG 400 in various concentrations

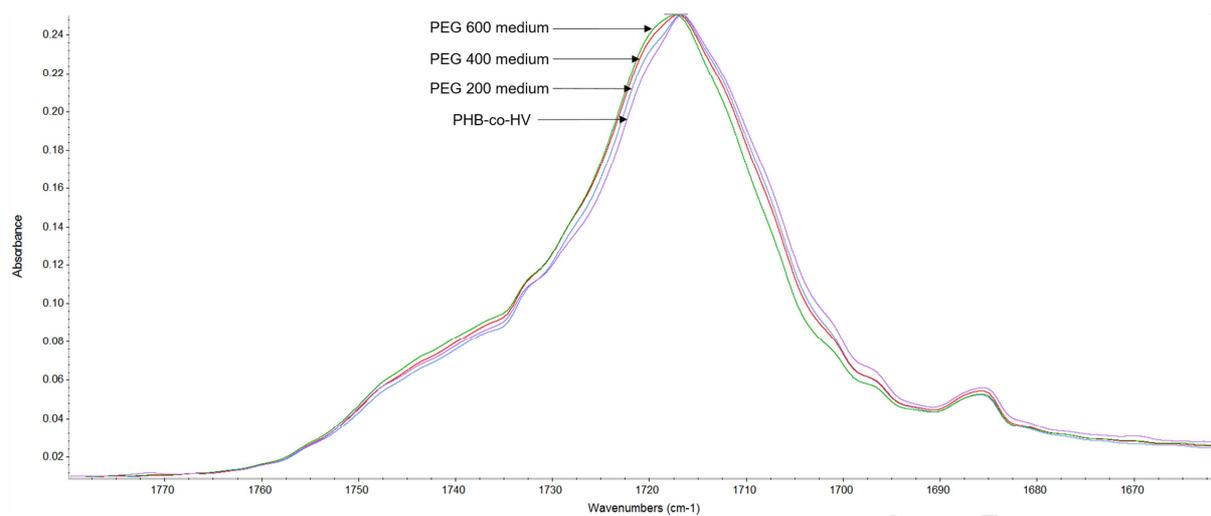
PEG content	PEG 400 (wt%)	Required PEG:PHB-co-HV mole ratio
Low	5	0.011
Medium	10	0.024
High	15	0.038

Table 2: Weight percent and mole PEG : PHB-co-HV repeat unit ratios used within this study

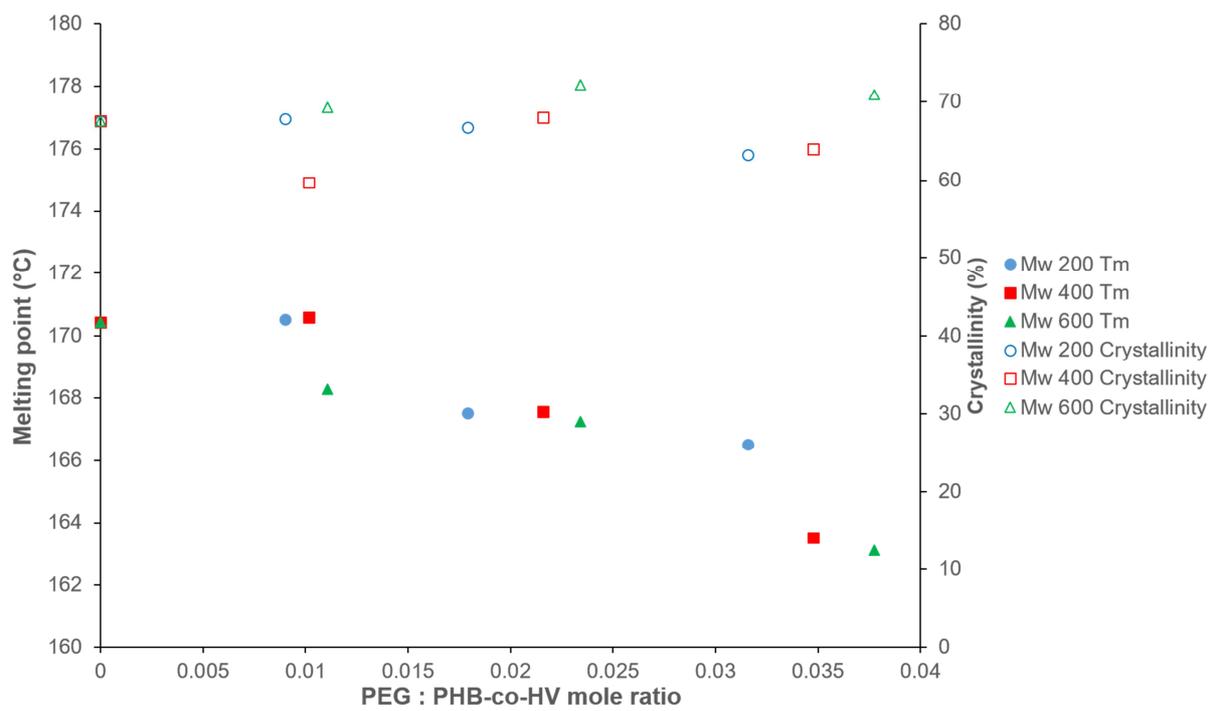
PEG (Molecular weight)	Content	PEG (wt%)	Actual PEG:PHB-co-HV mole ratio
200	Low	2.04	0.009
200	Medium	3.98	0.018
200	High	6.81	0.032
400	Low	4.49	0.010
400	Medium	9.09	0.022
400	High	13.86	0.035
600	Low	7.15	0.011
600	Medium	13.98	0.023
600	High	20.76	0.038

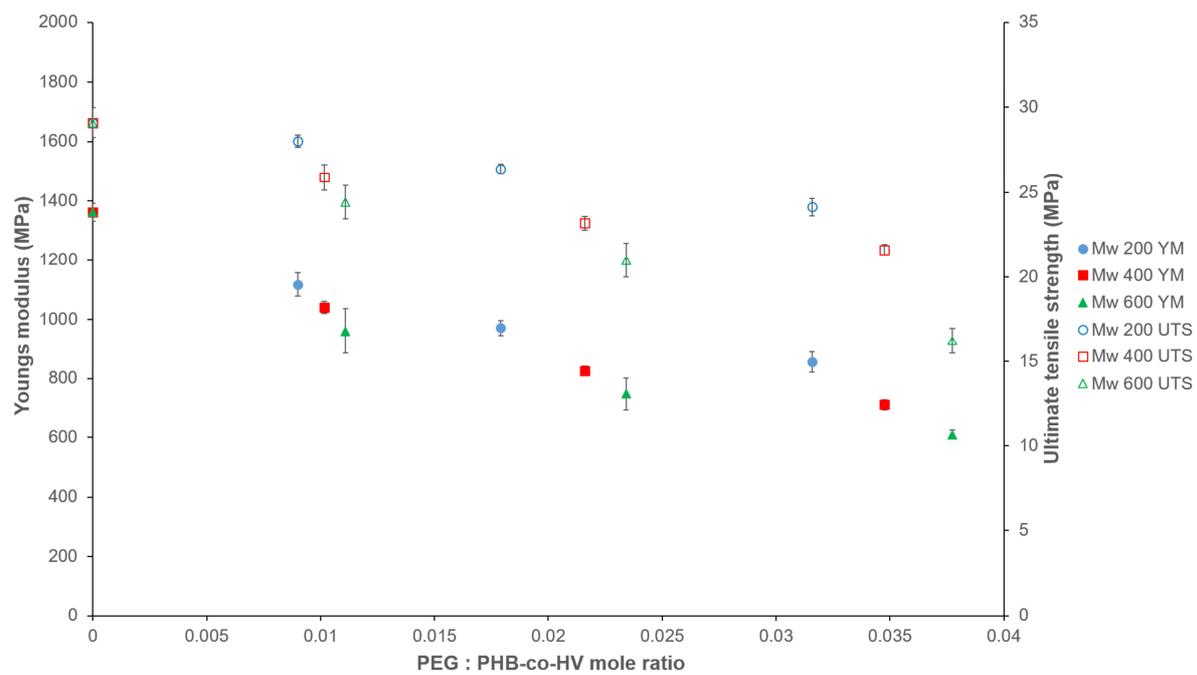


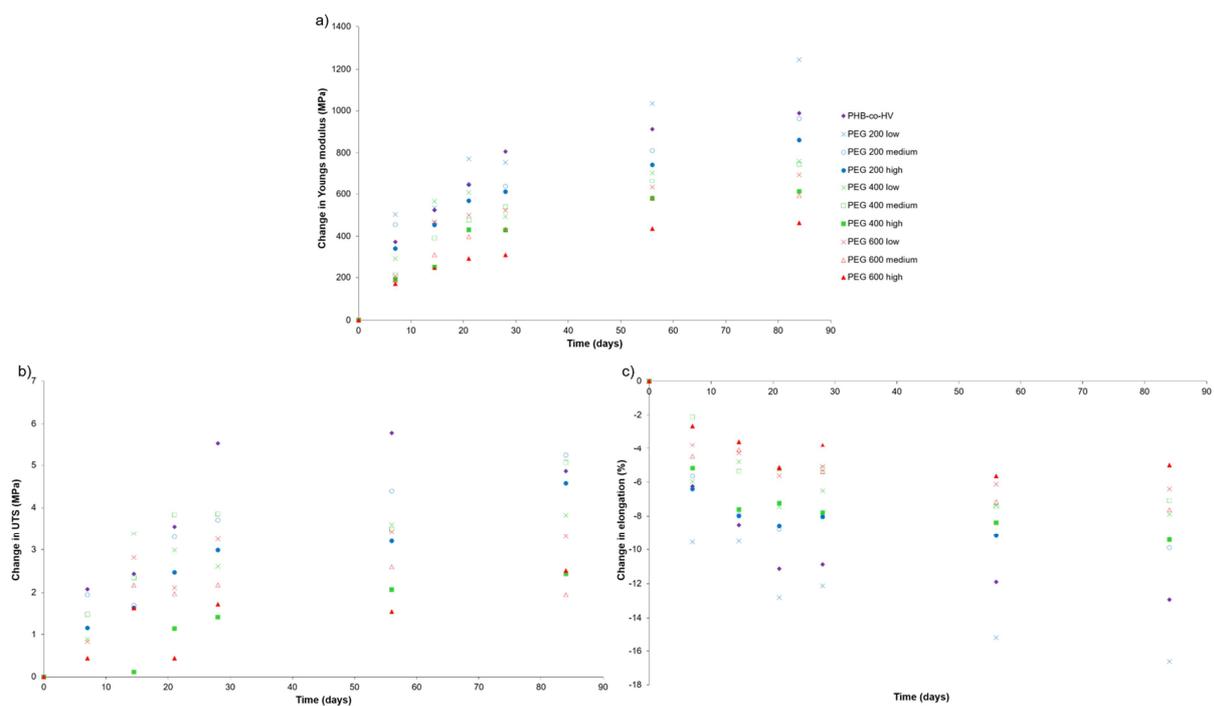




ACCEPTED MANUSCRIPT







Control of the secondary crystallisation process in poly(hydroxybutyrate-co-hydroxyvalerate) through the incorporation of poly(ethylene glycol)

Running head: Reducing the secondary crystallisation of PHB-co-HV with poly(ethylene glycol)

Catherine A. Kelly¹, Annabel V.L. Fitzgerald¹, Mike J. Jenkins^{1*}

¹School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, B15 2TT. UK

*to whom correspondence should be sent: email: m.j.jenkins@bham.ac.uk; tel: +44 (0)121 414 2841; fax - +44 (0)121 414 7468

- PHB-co-HV blended with PEG in a range of molecular weights and concentrations
- Reduction in melting point, viscosity, Young's modulus and tensile strength
- PEG reduces the rate of PHB-co-HV secondary crystallisation and embrittlement
- PEG 600 most effective at reducing the rate of secondary crystallisation