



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



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ARTICLE INFO

Keywords:

Poly(hydroxybutyrate-co-hydroxyvalerate)
Poly(ethylene glycol)
Secondary crystallisation
Blending
Stability

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.

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

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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 h 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

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

material (50 g) added to the Haake mixer. The system was left for 10 min 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):

Moles PEG : PHB – co – HV repeat unit ratio

$$= \left(\frac{\text{mass}_{\text{PEG400}}}{M_w\text{PEG400}} \times \frac{M_w\text{PHB-co-HV repeat unit}}{\text{mass}_{\text{PHB-co-HV}}} \right)$$

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:

PEG (%wt)

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

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.

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

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