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Rheological analysis of heat labile poly(3-hydroxybutyrate-co-3-hydroxyvalerate):poly(ethylene glycol) blends

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Abstract:

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-co-HV) has shown great promise as a sustainable and biodegradable packaging material, however, progressive embrittlement, caused by secondary crystallisation, and a poor thermal stability has limited widespread use. The addition of low molecular weight poly(ethylene glycol) (PEG) has previously been shown to reduce the rate of secondary crystallisation resulting in a more viable material. This paper aims to analyse the melt miscibility of these two polymers and to assess the effect of PEG on the thermal stability. As a result of the poor thermal stability of PHB-co-HV a modified rheological procedure is implemented to create Han plots and enable assessment of the miscibility. This approach showed PHB-co-HV and PEG to be miscible within the concentrations and molecular weights studied lending itself to the fine tuning of the properties of PHB-co-HV in order to produce the most suitable and stable packaging material. The presence of PEG was observed to increase the degradation rate of PHB-co-HV at 185 °C, however, the incorporation of PEG also enabled processing at lower temperatures

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significantly reducing the degradation rate and widening the narrow processing window commonly found with this polymer.

Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate); poly(ethylene glycol); rheology; miscibility; Han plot; degradation; blend

## 1. Introduction

Poly(3-hydroxybutyrate) (PHB) and its copolymers have generated interest from the packaging industry as a result of their sustainable and biodegradable properties.[1, 2] These polymers are formed as discrete granules by specific bacteria fed on a sugar source as a means of energy storage during periods of nutrient limitation.[3-5] They are extracted from the cells and processed into useable material with initial properties comparable to commercial polymers such as poly(propylene) (PP) and poly(ethylene terephthalate) (PET).[6, 7] The stereospecifity of biosynthesis results in an optically pure material generating crystallinities in excess of 50-80%[3], however, this also creates brittleness.[8, 9] To overcome this issue copolymers of PHB have been developed, most commonly poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-co-HV). The addition of hydroxyvalerate units into PHB have been shown to successfully improve the mechanical properties of the polymer in addition to widening the processing window and increasing biodegradability.[10, 11]

Another limitation surrounding the widespread use of PHB and its copolymers is a sub-ambient glass transition temperature which causes the polymer chains to be mobile at room temperature. As a result, further crystallisation occurs, leading to progressive embrittlement of the polymer in a process known as secondary crystallisation.[12, 13] Solutions to this

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problem include; incorporating bulkier units into the side chain of the copolymer or blending with other polymers or low molecular weight species.[14-16] Recently, the addition of low molecular weight poly(ethylene glycol) (PEG) has been shown to successfully reduce the rate of secondary crystallisation prolonging the effective lifetime of products made from these blends.[17, 18]

There have been numerous studies on the miscibility of PHB based copolymers with PEG, however, the majority of these have focussed on higher molecular weight grades (>5000 Da) and/or utilise solvent blending which is not conducive to the packaging manufacturing process.[19-21] Chen *et al.* have shown immiscibility when the PEG molecular weight exceeds 1500 Da[22], however, to date, little is known about the miscibility of PHB-co-HV with low molecular weight PEG. The high crystallinity of PHB-co-HV makes it difficult to assess the miscibility of the polymers by the conventional method of differential scanning calorimetry (DSC) as the glass transition temperature is often not visible.  One solution is to assess miscibility in the molten state using rheology and the Han plot.[23-25] Pure polymers generate a straight line on the log plot of storage modulus (G') against loss modulus (G'') for frequencies below the G' G'' crossover point with Han *et al.* reporting that any compositional deviation from this line indicates immiscibility of the blend.[26]

PHB-co-HV is thermally unstable above its melting point resulting in chain scission and a reduction in the molecular weight.[27] In addition, studies have shown that during prolonged exposure, degradation can occur at temperatures as low as 150 °C.[13] The reduction in the molecular weight causes a decrease in the storage modulus, loss modulus and complex viscosity with time and therefore the frequency sweeps needed for a Han plot cannot be accurately performed. A method has been devised to overcome this in which time sweeps are

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performed at specific frequencies and the data superposed to give a master curve.[28] Here, this method is utilised to enable a more accurate assessment of the miscibility of PHB-co-HV and PEG in the molten state in order to better understand how PEG is able to influence the previously seen reduction in secondary crystallisation and embrittlement of PHB-co-HV. In addition, the reduction in the rheological properties over time have enabled the thermal degradation of PHB-co-HV to be modelled and the effect of PEG on the thermal stability probed.

## 2. Materials and Methods

### 2.1 Materials

Tianan ENMAT Y1000P poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-co-HV) containing 3 wt.% 3-hydroxyvalerate was purchased from Helian Polymers (Venlo, Netherlands) and dried at 100 °C for 1 hour prior to use. Poly(ethylene glycol) (PEG) ($M_w$ 200, 400 and 600), were purchased from Sigma Aldrich (Dorset, UK) and used as received.

### 2.2 PHB-co-HV and PEG blending

A Rondol Rotomill (Stoke-on-Trent, UK) two roll mill was used to blend PHB-co-HV with various concentrations of PEG 200, 400 and 600. The front roller was heated to 165 °C and the back roller to 135 °C with a spacing of 0.45 mm set between the rollers. The required mass of PEG was hand mixed with PHB-co-HV pellets before being added to the two roll mill. The samples were blended for 5 minutes and then removed from the rollers, allowed to cool and stored in a freezer (-22 °C) to prevent phase separation and secondary crystallisation.[13]

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The initial basis of this study is to further examine the influence of PEG on the secondary crystallisation of PHB-co-HV, reported previously.[17] This work showed PEG to reduce the rate of PHB-co-HV secondary crystallisation believed to be as a result of being retained in the inter-lamella regions. In order to probe this further, the same PHB-co-HV/PEG blend compositions were produced to directly determine the miscibility of each formulation. These original formulations were chosen to ensure that the ratio of PEG chains to PHB-co-HV monomeric units, rather than the weight fraction, was kept consistent across the different molecular weights. As only the end groups of PEG can interact with PHB-co-HV this ensured that an equivalent number of theoretical interactions could occur between the two polymers as the size of the PEG molecules (i.e. molecular weight) increased This is discussed in more detail, along with the calculations used, in Kelly *et al*.[17] The exact PEG concentrations used are detailed in table 1 and these blends are designated as low, medium and high PEG contents throughout this article to directly match the previous work.[17]

| | | PEG concentration (wt%) | | |
| | | Low | Medium | High |
|---|---|---|---|---|
| **PEG molecular weight (Da)** | **200** | | 5.3 | |
| | **400** | 5.2 | 9.7 | 14.9 |
| | **600** | | 13.9 | |

**Table 1: Calculated PEG contents within the blends**

## 2.3  Rheological analysis

A Netzsch Kinexus Pro+ rotational rheometer (Wolverhampton, UK) with a 20 mm parallel plate geometry was used to analyse the rheological properties of the polymer blends. In a typical experiment the solid blended material (0.8 g) was placed onto the preheated (185 °C) lower plate. This temperature was chosen as the high melting point of PHB-co-HV prevented analysis of the pure material at lower temperatures. The top plate was lowered to a gap of 5

mm and the sample left to melt for 5 minutes. After this time the top plate was lowered further to generate a 1 mm measuring gap. Oscillation tests were performed at 185 °C, with a strain of 0.5 %, for 10 minutes. These experiments were repeated at a range of frequencies from 0.25 to 25 Hz. Three samples were analysed at each frequency and the average and standard deviation calculated.

## 3.  Results and Discussion

Miscibility of two polymers in the melt is generally assessed from rheological data through a Cole-Cole[29] or Han plot[26] (often called the modified Cole-Cole plot). This involves producing a frequency sweep with a degree of strain that falls within the linear viscoelastic region (LVER) of the polymer blend. A dynamic strain sweep was performed on pure PHB-co-HV at 185 °C, the lowest temperature that could be analysed due to the high melting point of the material, however, no LVER was observed. In addition, the shear storage modulus, loss modulus and complex viscosity were all found to decrease over time (Figure 1) indicative of polymer degradation. PHB-co-HV has been shown to be thermally unstable above its melting point of approximately 174 °C with others reporting that degradation can commence at temperatures significantly lower than this.[13, 27, 30] Following extrusion for approximately 12 minutes at 162 °C, Renstad *et al.* observed a 50 % reduction in the molecular weight of PHB-co-HV.[30] In addition, Jenkins *et al.* discovered degradation of PHB-co-HV at temperatures as low as 150 °C following prolonged exposure.[13] The thermal degradation of PHB-co-HV occurs via random chain scission of the ester groups, through the formation of an intermediate cyclic ring, and causes a reduction in the molecular weight.[27] As a result the viscosity and storage and loss moduli of the polymer decrease periodically.[28, 31, 32]

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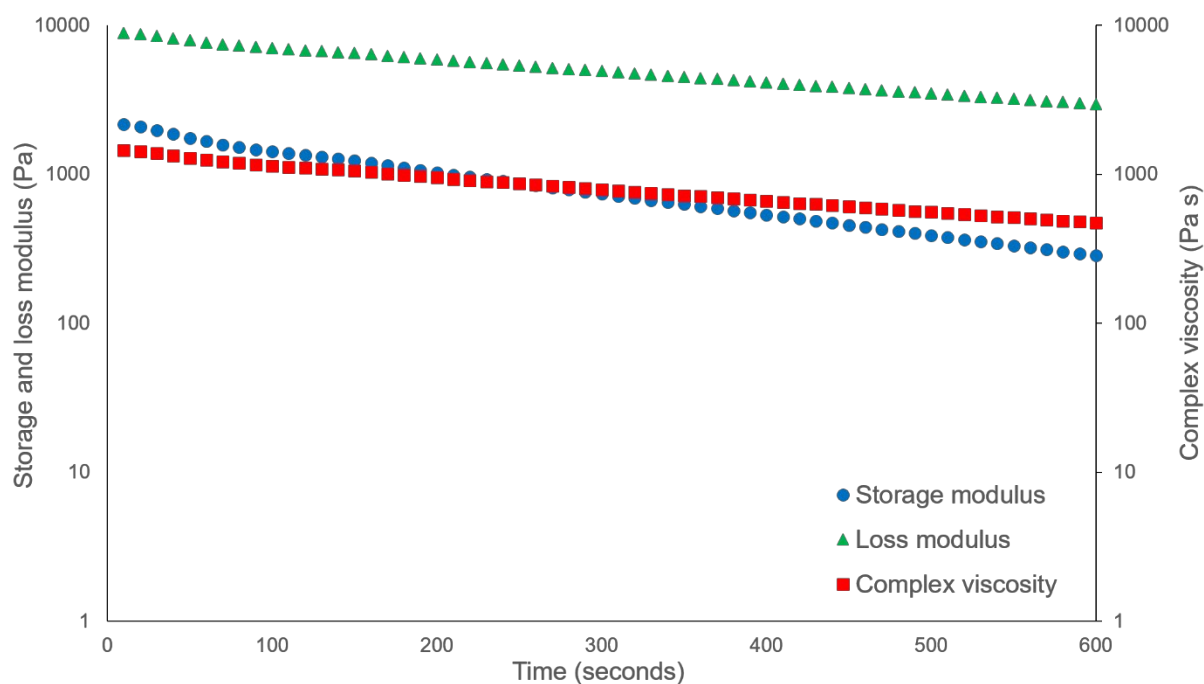
**Figure 1: Time sweep of PHB-co-HV at 185 °C. Degradation causes a continuous reduction in the storage modulus, loss modulus and viscosity.**

Thermal degradation not only prevents an accurate determination of the LVER, but also distort the results of frequency sweeps causing a progressive reduction in the viscoelastic properties throughout the analysis. To overcome this problem, Yamaguchi and Arakawa proposed performing time sweeps at set frequencies and superposing the results to form a master curve.[28] Figure 2 shows the time sweep curves for PHB-co-HV over a range of frequencies. It can be seen that in each case the storage modulus (G') decreases over time indicative of a reduction in molecular weight, and therefore thermal degradation as discussed above. The rate of reduction is observed to be higher at low frequencies showing the longer relaxation time scales to be more affected by degradation. A similar graph was also obtained for the loss modulus (G'') (data not shown).

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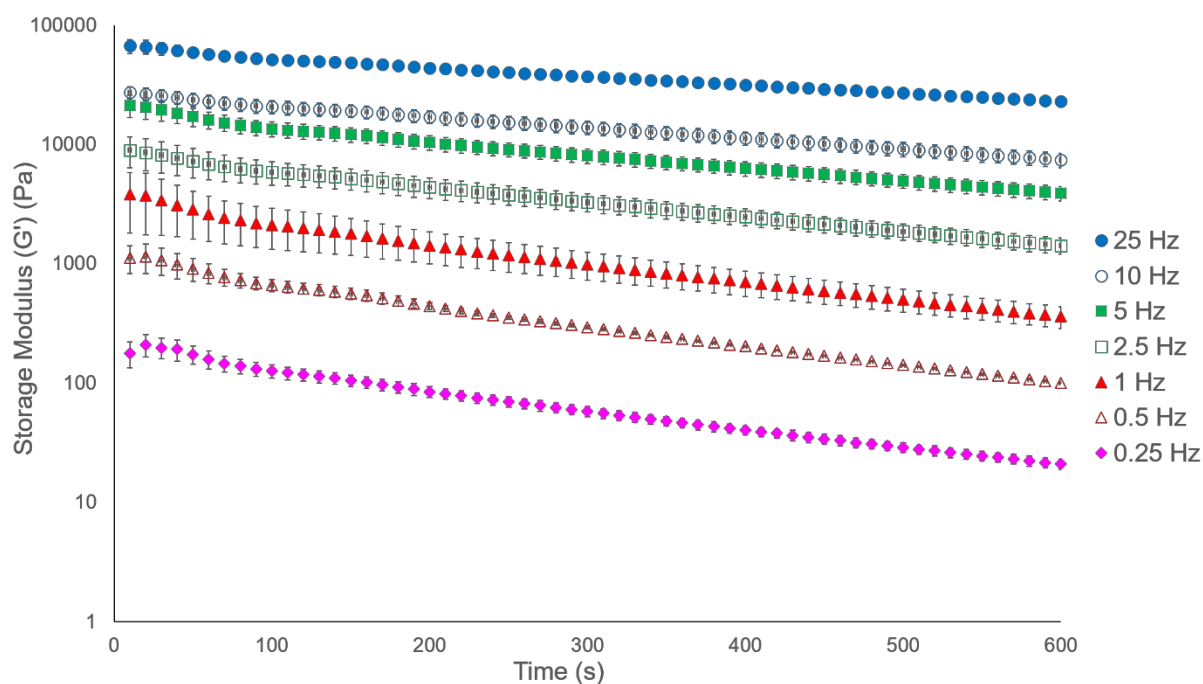
**Figure 2: Time sweeps of PHB-co-HV at 185 °C at various frequencies. A continuous reduction in the storage modulus is observed over time for each frequency indicative of thermal degradation. Error bars represent ±1 standard deviation from the mean**

In order to generate a graph comparable to a frequency sweep the storage moduli data from figure 2 were taken at 60 second intervals and plotted against the frequency (Figure 3 – Only the data points for every 120 seconds are shown for clarity). This time interval was chosen to provide enough data points to generate meaningful plots and aid superpositioning without over complication.
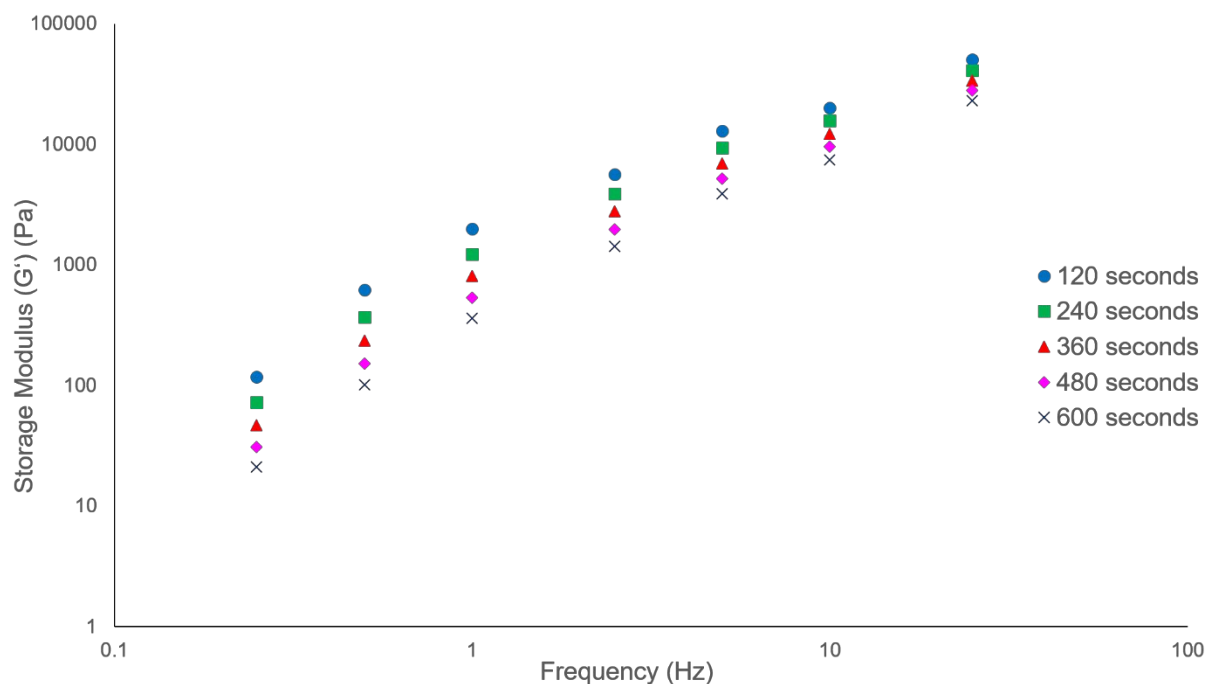
**Figure 3: Storage modulus versus frequency of PHB-co-HV at 185 °C for residence times of every 120 seconds.**

As detailed in the method reported by Yamaguchi *et al.*[28], these frequency-time curves were superposed by a horizontal shift to generate a master curve (Figure 4). A good fit between the data points was found upon shifting the curves showing this method to also be applicable to PHB-co-HV/PEG blends. In addition, the closeness of the fit indicates that thermal degradation does not affect the molecular weight distribution of the polymer.
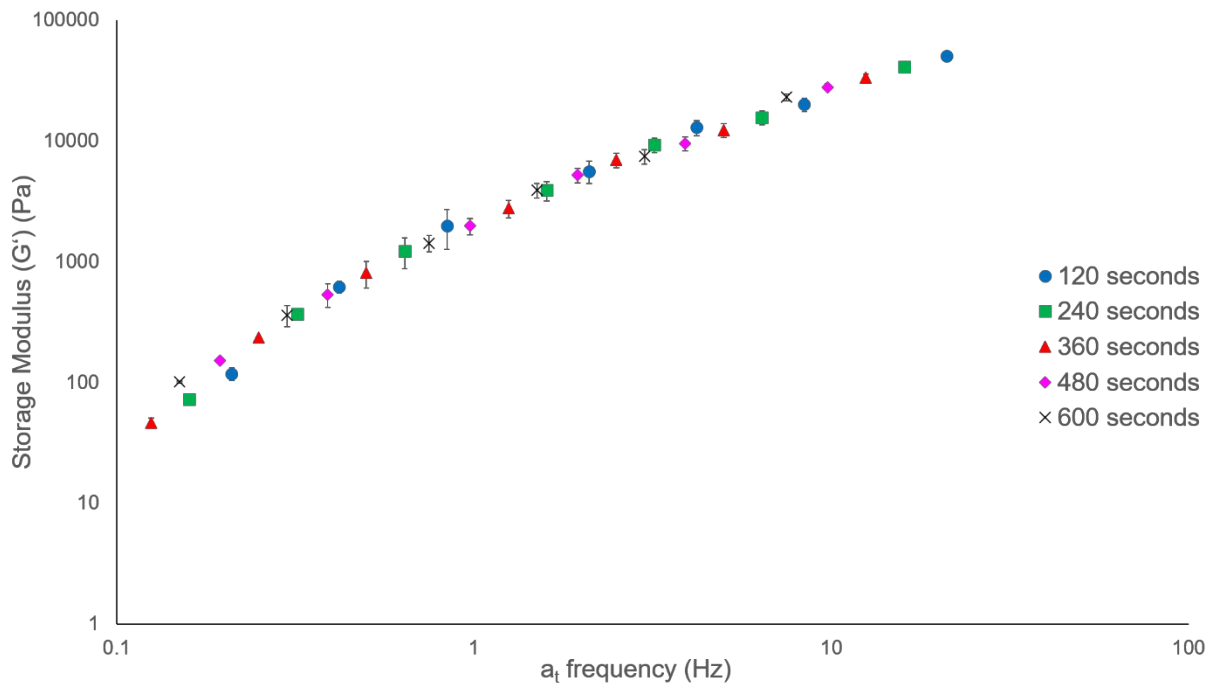
**Figure 4: Master curve of shear modulus versus frequency for PHB-co-HV at 185 °C. Only the data points for every 120 seconds are shown for clarity. The master curve was generated by superposing the results reported in Figure 3 via a horizontal shift. Error bars represent ±1 standard deviation from the mean**

Using the same method as generally applied to time-temperature superpositions, the shift factor required to produce the horizontal shift onto a master curve at 60 seconds was calculated for each time interval using the following equation:

$$Shift\ factor\ (a_t) = Frequency_t/Frequency_{60}$$ Equation 1

Where frequency$_t$ is the shifted angular frequency at time t and frequency$_{60}$ is the angular frequency at 60 seconds.

On plotting the log shift factor versus time a linear relationship was observed with a high $R^2$ value of 0.9996 (Figure 5). This enabled the shift factor to be calculated for any given time interval.

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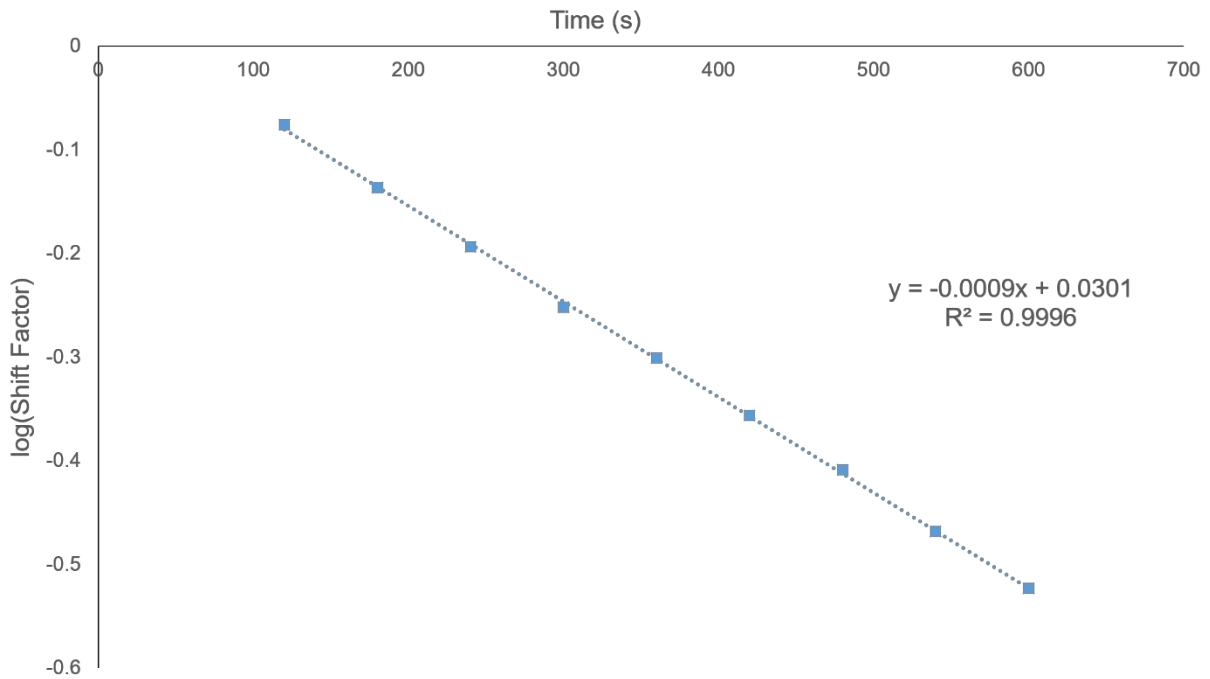
**Figure 5: A linear relationship was observed between the log of the shift factor required to generate the master curve and experimental time.**

At time zero the shift factor should be equivalent to 1 giving a log(shift factor) value of 0. In light of this, the shift factors required to produce a master curve at time zero can be calculated via transposing the above graph vertically to cross through the origin. This entire procedure can also be applied to the loss modulus in the same way. The resultant time zero storage and loss modulus master curves for PHB-co-HV are shown in figure 6.

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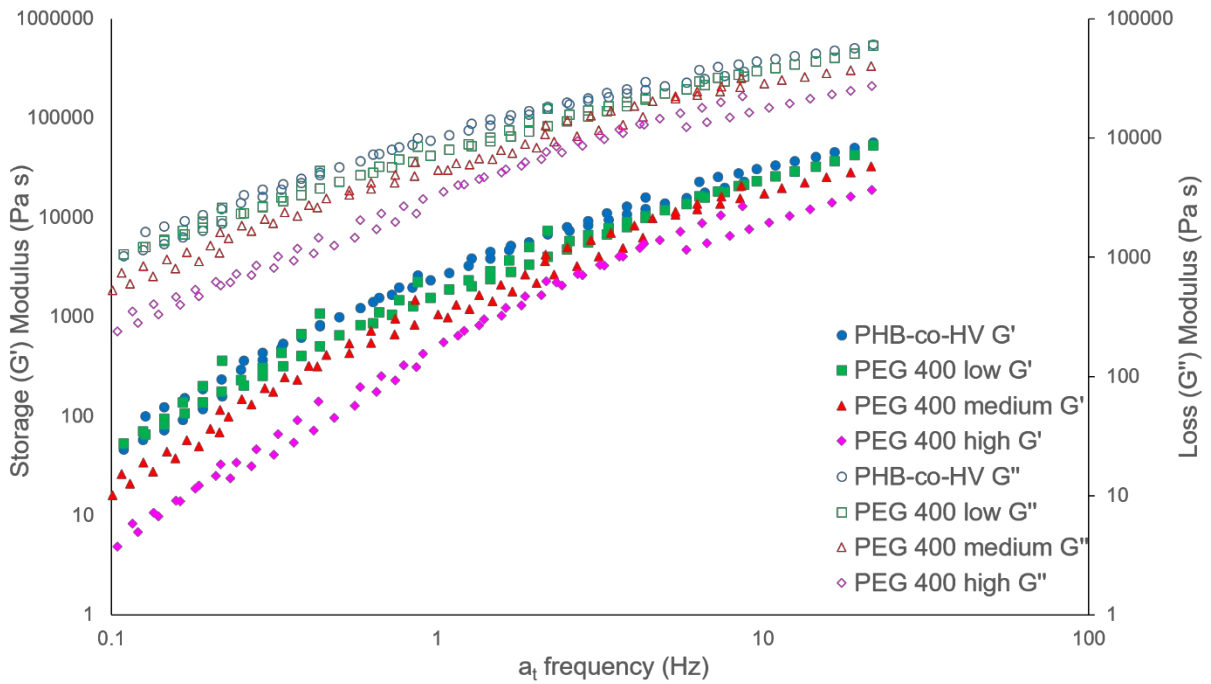
**Figure 6: Storage and loss moduli master curves of PHB-co-HV with varying concentrations of PEG 400 at 185 °C. The addition of PEG reduces the storage and loss moduli of PHB-co-HV.**

Analysis of the storage and loss moduli of the PHB-co-HV:PEG blends using this method allows the effect of PEG concentration and molecular weight on the rheological properties of PHB-co-HV to be assessed. Figure 6 shows the storage and loss modulus master curves for PHB-co-HV and blends containing various concentrations of PEG 400. On adding PEG to PHB-co-HV both the storage and loss moduli are reduced with this effect increasing as the concentration of PEG is raised. Park *et al.* attributed this reduction to a lowering of the crystallinity of PHB-co-HV,[23] however, we have previously shown that crystallinity remains consistent with changes in PEG concentration for this blend system.[17] In the study of polycaprolactone (PCL)/polylactic acid (PLA) blends, Nooroozi *et al.* reports a reduction in the storage and loss modulus of high molecular weight PLA as the content of PCL increased.[24] This was attributed to the lower viscosity of PCL. In contrast, an increase in

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the storage and loss modulus was observed with low molecular weight PLA when PCL had the greater viscosity. This is also thought to be the case here as PEG displays a significantly lower viscosity than PHB-co-HV.

The reptation time of polymers is given by the reciprocal of the frequency at the point where the storage and loss moduli equate. Although the crossover frequencies cannot be determined for these plots, as poor results were obtained at higher frequencies, the effect of the addition of PEG can be inferred from the proximity of the two plots at the maximum frequency analysed (Figure 7). The greater the concentration of PEG within the blend, the higher the crossover frequency and therefore the lower the reptation time. This highlights the increased mobility that the presence of PEG infers to the PHB-co-HV chains in the molten state.
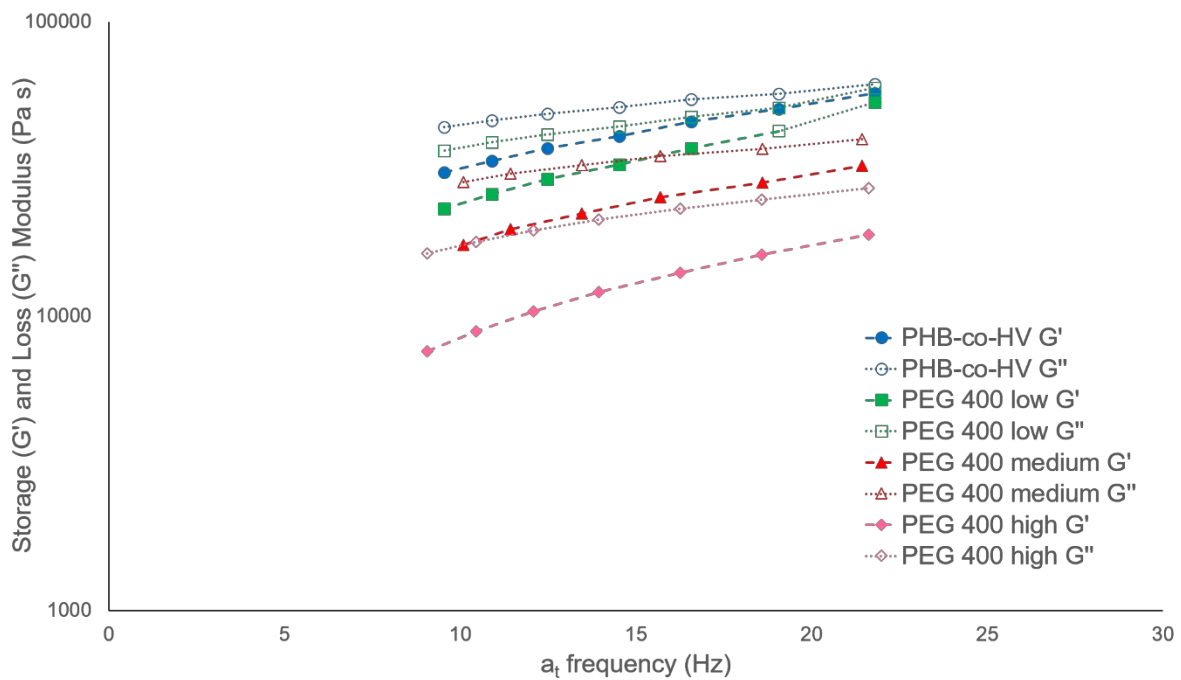


**Figure 7: Storage and loss moduli master curves of PHB-co-HV with varying concentrations of PEG 400 at 185 °C – crossover region only. The addition of PEG increases the crossover frequency and therefore reduces the reptation time of PHB-co-HV.**

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In the melt it is the concentration of PEG present, rather than the number of theoretical cross links, that is the dominant factor in PHB-co-HV blends. As such the effect of molecular weight is analysed by comparing blends of similar concentrations: PEG 400 (5.2 %) with PEG 200 (5.3 %) and PEG 400 (14.9 %) with PEG 600 (13.9 %). Figure 8 shows little difference to the storage and loss moduli of PHB-co-HV on varying the PEG molecular weight.
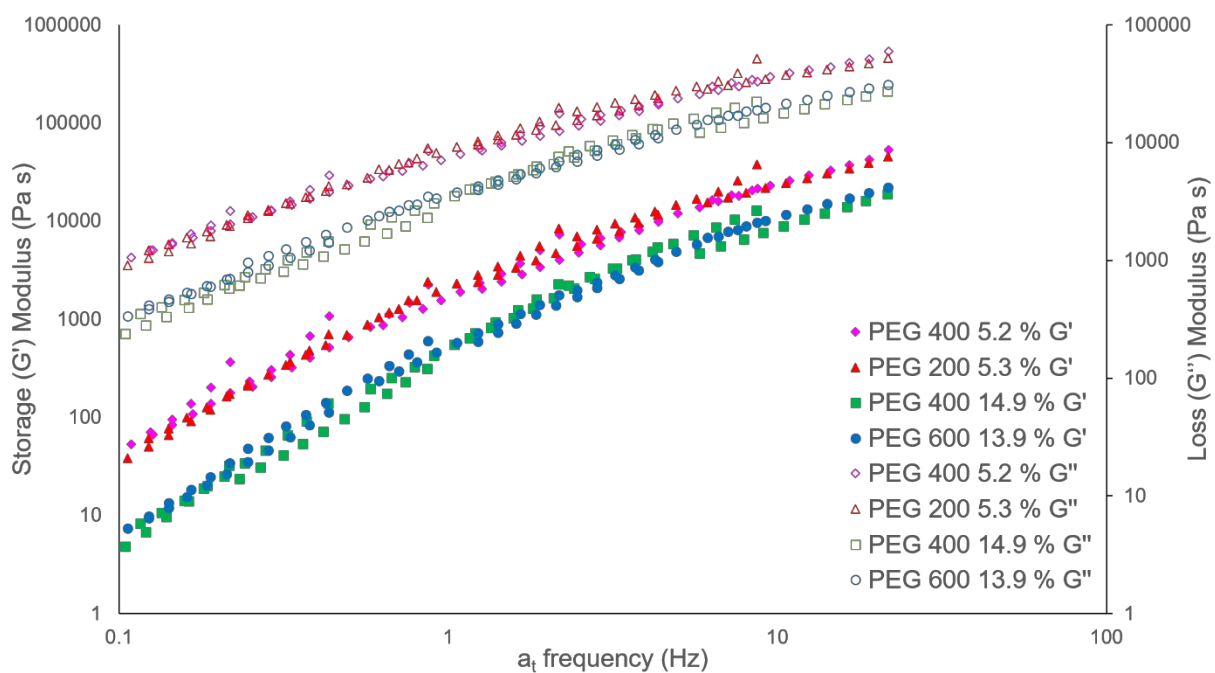


**Figure 8: Storage and loss moduli master curves of PHB-co-HV with various molecular weights of PEG at 185 °C. PEG molecular weight has no effect on the viscoelastic properties.**

The Han plot is commonly used to analyse the miscibility of polymers in the melt.[23-26, 33] Han and Chuang discovered that miscible blends showed no compositional deviation from the straight-line G' versus G'' log plot created by the pure polymer at low frequencies.[26] The

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results from the above master curves can be used to create Han plots for each of the blends (Figure 9). As can be seen from figure 8, the addition of PEG in various concentrations and molecular weights produces identical curves to that of PHB-co-HV showing miscibility of the two polymers under these processing conditions and compositions. In contrast, where immiscibility has been reported in the literature deviations of 1-2 decades have typically been observed.[24, 25]
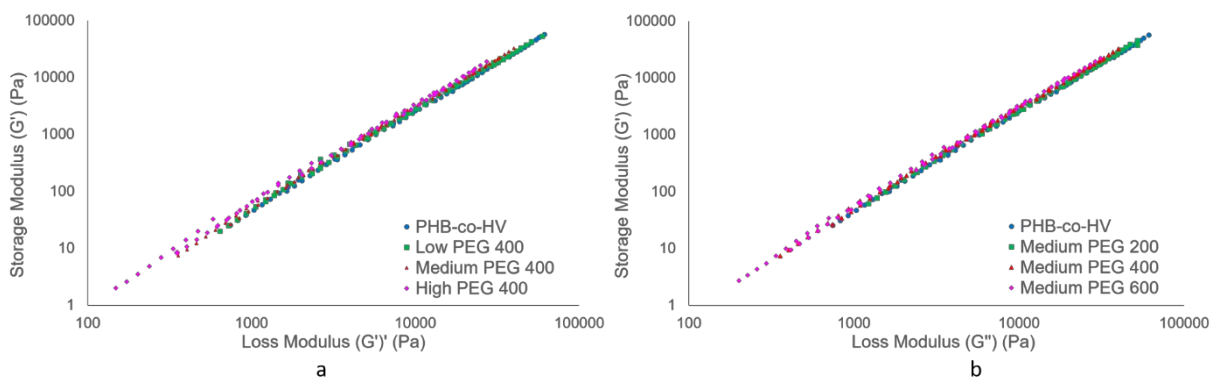


**Figure 9: Han plots for PHB-co-HV with a) various concentrations and b) PEG molecular weights at 185 ℃. The similarity of the curves produced by the blends to that of the pure polymer is indicative of miscibility.**

Deviation from the straight line of the pure polymer is caused by a higher value of the storage modulus at low frequencies. The viscoelastic behaviour of immiscible materials is influenced by the interfacial energy between non-compatible domains. At low frequencies, where the shape relaxation of the dispersed domain is probed, the contribution of this energy to the storage modulus is greater leading to a noticeable positive deviation.[24] This effect can also be analysed quantitatively by calculating the gradient of the log G' and log G'' versus log frequency plots below 1 Hz. For homogenous melts a relationship of $G' \alpha \omega^n$ and $G'' \alpha \omega^m$, where n and m are 2 and 1 respectively, is expected at low frequencies and any increases in these values signifies immiscibility.[25] The values for n and m where calculated as 1.9 and

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1.0, respectively, for pure PHB-co-HV with similar results also obtained for each of the blends again highlighting their miscibility (Table 2).

| PEG molecular weight | PEG concentration | n | m |
|---|---|---|---|
| PHB-co-HV | | 1.9 | 1.0 |
| 200 | Medium | 1.9 | 1.0 |
| 400 | Low | 1.7 | 0.9 |
| 400 | Medium | 1.9 | 1.1 |
| 400 | High | 2.0 | 1.1 |
| 600 | Medium | 2.0 | 1.1 |

**Table 2: Gradients of log G' and log G'' versus log frequency plots. Comparable n and m values to that of the pure polymer show miscibility of the two components.**

The results above highlight the miscibility of PHB-co-HV and PEG over these molecular weights and compositions. This demonstrates how, in the molten state, PEG is able to mix with PHB-co-HV to form an intimate mixture which remains following cooling; thus hindering the secondary crystallisation of PHB-co-HV reported previously.[17] The miscibility of the two materials over a wide range of concentrations and molecular weights leads to an ability to further tailor the properties of PHB-co-HV to meet the specifications required for packaging materials.

In addition to determining the miscibility of PHB-co-HV and PEG, the data obtained can be utilised to further probe the degradation of PHB-co-HV and its blends. Figure 1 showed a reduction in the storage modulus, loss modulus and complex viscosity of PHB-co-HV throughout the duration of the experiment indicative of degradation. Previous studies have shown the degradation of PHB and its copolymers to display first order kinetics[27, 34-36]

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and through this Daly *et al.* derived an equation, based on the zero shear complex viscosity, to model the degradation process:[34]

$$\frac{1}{\eta_t^\alpha} = \frac{1}{\eta_0^\alpha} + k_2 t$$

Equation 2

Where: $\eta_t$ and $\eta_0$ are the viscosity at time *t* and time zero; $\alpha$ equals 1/3.4; and $k_2$ is the observed degradation rate constant dependant on the polymer type, initial molecular weight and temperature.

Although the linear viscoelastic region could not be determine in the conventional way, as a result of high levels of degradation, extraction of data from the time sweeps enabled a plot of complex viscosity against frequency to be created which revealed a plateau below 1 Hz (data not shown). Therefore, the results at 0.5 Hz from the above studies were taken as an estimate of the zero shear complex viscosity to allow the degradation rates of the blends to be compared.

Based on equation 2, a system displaying first order kinetics will produce a linear relationship between $1/\eta_t^{1/3.4}$ and time with the gradient giving the degradation rate constant. PHB-co-HV and each of the blends generated straight lines with $R^2$ values greater than 0.99, and in the majority of cases greater than 0.999, (Figure 10) proving that even in the presence of PEG the degradation process follows first order kinetics.

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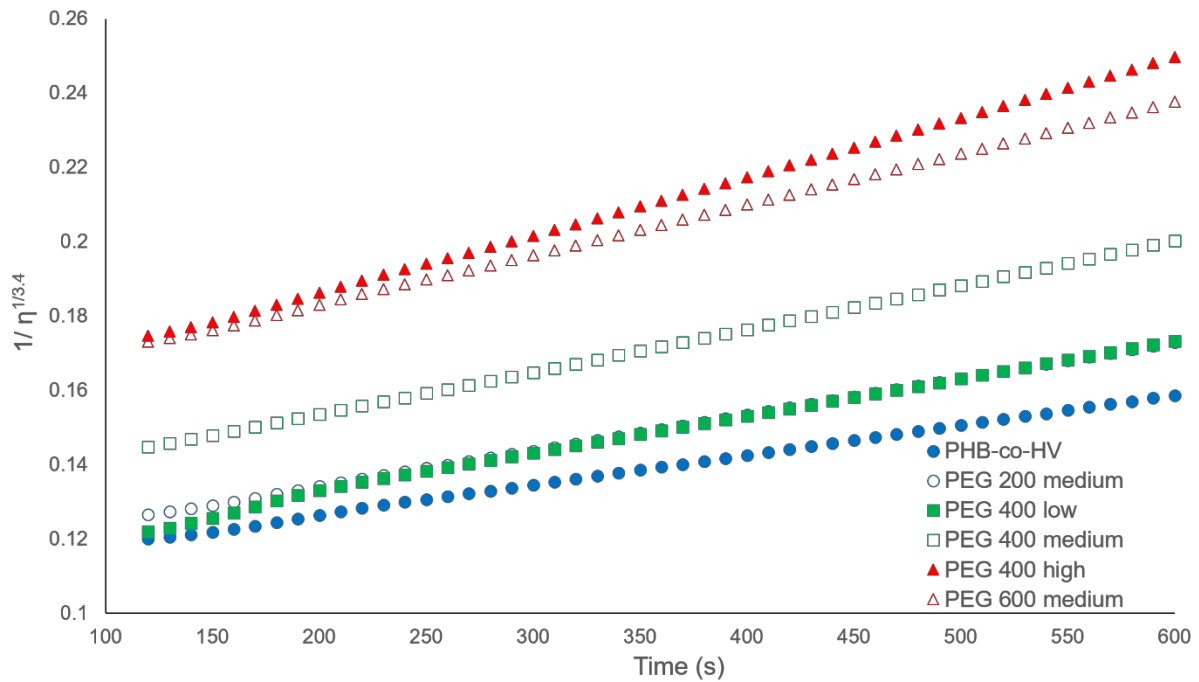
**Figure 10: First order kinetics plot of PHB-co-HV:PEG blends at 0.5 Hz. Linear trends, with high $R^2$ values, were found for each system showing the degradation of PHB-co-HV blends to obey first order kinetics. The degradation rate constant is given by the gradient of each plot.**

The degradation rate constant of a polymer is given by the gradient of these plots and was determined for pure PHB-co-HV and each of the blends (Table 3). The results show that the addition of PEG increases the rate constant, and therefore the rate of PHB-co-HV thermal degradation, with increasing the concentration further enhancing these effects. The reduction in the viscosity and viscoelastic properties of PHB-co-HV on the addition of PEG facilitates rearrangement of the polymer chain into the intermediate cyclic ring necessary for degradation and reduces the energy barrier. Increases in the degradation rate of PHB have been previously reported when copolymerised with either hydroxyvalerate or hydroxyhexanoate due to a similar increased chain mobility generated by the steric hindrance of the side chains.[36, 37]

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Previous studies on this blend system focussed on secondary crystallisation; thus molecular weight comparisons were made based on the number of possible crosslinks and therefore mole ratios. In the case of thermal degradation of the melt it is important to instead focus on the mass fraction of PEG within these blends. As a result comparisons between PEG 200 medium and PEG 400 low; and PEG 400 high and PEG 600 medium were made which showed no effect of molecular weight on the degradation rate constants.

| PEG molecular weight | PEG concentration | Degradation rate constant ($\times 10^{-5}$ Pa$^{-1}$s$^{-2}$) | Standard deviation ($\times 10^{-5}$) |
|---|---|---|---|
| PHB-co-HV | | 8.09 | 0.29 |
| 200 | Medium | 9.70 | 0.11 |
| 400 | Low | 10.30 | 0.44 |
| 400 | Medium | 11.60 | 0.10 |
| 400 | High | 15.90 | 2.00 |
| 600 | Medium | 13.57 | 0.49 |

**Table 3: Degradation rate constants of the PHB-co-HV blends. The addition of PEG was found to increase the rate constant and therefore degradation rate, with increasing the concentration enhancing the rate further. The results are given as the average and standard deviation of 3 repeats.**

However, the reduction in the melting point and viscosity generated by the addition of PEG also allows the blends to be processed at significantly lower temperatures than pure PHB-co-HV. The time sweep at 0.5 Hz was repeated on PHB-co-HV with the medium concentration of PEG 400 at 178 °C, a significantly lower temperature than pure PHB-co-HV could be analysed at. In this case the degradation rate was found to reduce to $6.16 \times 10^{-5}$ Pa$^{-1}$s$^{-2}$ which is significantly lower than observed with PHB-co-HV at 185 °C ($8.09 \times 10^{-5}$ Pa$^{-1}$s$^{-2}$). This shows that although for the same temperature the addition of PEG increases the rate of PHB-co-HV

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degradation it also enables it to be processed at lower temperatures. This reduction in temperature in turn reduces degradation to a rate below that of pure PHB-co-HV.

PHB-co-HV is known to be thermally labile and as a result has a very small processing window. As the most common processing methods used by the packaging industry are extrusion and thermoforming it is therefore important to understand the rate of thermal degradation and how this can be altered by the incorporation of additives. The ability of PEG to reduce the viscoelastic properties of PHB-co-HV, and in turn lower the processing temperature, leads to an overall reduction in the rate of degradation which is extremely beneficial to its processing capabilities.

## 4. Conclusions

Rheological analysis of PHB-co-HV and PEG blends have shown them to be miscible in the melt over the conditions and compositions analysed. Degradation of the blends was probed and the presence of PEG found to enhance the degradation rate of the polymer at 185 °C as a result of increased polymer chain mobility afforded by the lower viscosity PEG. However, this fall in viscosity also enabled processing at reduced temperatures, which, in turn significantly decreased the level of thermal degradation. A large reduction in the degradation rate constant from $8.09 \times 10^{-5}$ to $6.16 \times 10^{-5}$ $Pa^{-1}s^{-2}$ was observed when PHB-co-HV containing 9.7 wt% PEG 400 was analysed at 178 °C compared to pure PHB-co-HV at 185 °C.

The miscibility of PEG with PHB-co-HV, and its subsequent effects on the viscosity, viscoelastic properties and thermal degradation, is extremely beneficial when processing

PHB-co-HV into packaging materials as it can open up the narrow processing window. In addition, the miscibility of the materials not only hinders the secondary crystallisation process as reported previously but also allows for finer tuning of the processing parameters and properties of the final products.

## 5. CRediT author statement

**Catherine A. Kelly:** Conceptualisation, Methodology, Investigation, Writing- Original draft preparation. **Mike J. Jenkins:** Writing – Review & editing. **Shona H. Murphy:** Conceptualisation, Methodology, Writing – Review & editing.

## 6. Acknowledgements

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