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Melt viscoelasticity of biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) copolymers

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ABSTRACT

The rheological properties of a series of microbially synthesized poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)s (PHB-HHxs), with varying comonomer (HHx) content, were systematically investigated. Shear viscosities show dependence on the rate of deformation, temperature, molecular weight, and copolymer compositions. The zero-shear viscosity η_0 follows the classical $M_w^{3.4}$ power-law relationship with the weight average molecular weight M_w. The characteristic relaxation time λ, which indicates the onset of shear thinning, ranges from 0.02 to 0.2 s for different PHB-HHxs and is roughly linearly related to η_0. The temperature dependence of rheological properties follows an Arrhenius form. Activation energies for flow E_a are obtained from the slope of the natural logarithm of the shift factor α_T plotted against the inverse of temperature curve, and the values for PHB-HHxs are found to be in the range of 27–36 kJ/mol E_a decreases with HHx content in the copolymer, a trend that can be related to the difference in chemical structure between HHx and HB, according to the method of Vankrevelen and Hoftyzer. A Generalized Maxwell model models the viscoelastic behavior of the PHB-HHx melt well. The value of the plateau modulus G_N^0 obtained suggests a highly entangled configuration. The molecular weight between entanglements M_e decreases from 11,600 to 9400 as HHx content increases from 3.8 to 10.0 mol%. Our results suggest that the presence of propyl groups in HHx increases the steric hindrance of the PHB-HHx chains, thus resulting in increased segmental friction and entanglement density. As a result, viscoelastic parameters for PHB-HHx copolymers, such as η_0 and G_N^0, are readily tunable by varying the HHx content, making them attractive as "green" substitutes for non-degradable thermoplastics.

1. Introduction

Recently, concerns about the potentially harmful effects that non-degradable plastics may have on the environment and the increasing cost of petrochemical feedstocks have raised new challenges for the polymer industry. Interest is growing in developing biodegradable polymers to replace synthetic non-degradable materials. One class of biodegradable polymer that may help alleviate the plastic waste problem, poly(3-hydroxyalkanoate)s (PHAs), a class of aliphatic polyesters, has attracted much interest. PHAs are produced by bacteria as intracellular energy storage materials under growth conditions for which a critical nutrient is missing [1]. Besides being enzymatically degradable, PHAs possess good mechanical properties that are often compared favorably to petroleum-based thermoplastics. For instance, poly(3-hydroxybutyrate) (PHB), the first-introduced member in the PHA family, has similar degree of crystallinity, glass transition temperature, melting temperature, Young's modulus, and tensile strength as polypropylene (PP), a very tough, robust material [2].

However, the thermal processing of PHB homopolymer is difficult due to two inherent limitations: (1) low melt elasticity, and (2) a narrow thermal processing window [1]. The low melt elasticity stems from the lack of necessary chain entanglements. The narrow processing window arises from its high crystallinity and high melting temperature of the crystalline domains. A high processing temperature (close to or above T_m) is required at which the thermal degradation becomes significant. Such thermal degradation leads to random scission of polymer chains, resulting in a decrease in molecular weight and further reduction of the melt strength [3–5].

In response, Doi et al. [6] and Noda et al. [7,8] introduced poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHB-HHx), which consists of 3-hydroxybutyrate (HB) and a small amount of 3-hydroxyhexanoate (HHx) comonomers. The chemical structure of PHB-HHx is shown in Fig. 1. Thermal properties of PHB-HHxs,

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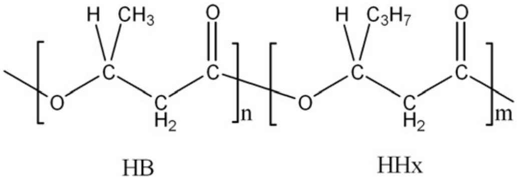

Fig. 1. Molecular structure of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHB-HHx). The comonomer units are distributed randomly.

including crystallization kinetics and melting behavior, have been studied by a number of groups [9–14]. Due to the propyl side group, HHx is excluded from being cocrystallized with HB. As a result, its presence lowers the melting temperature of the PHB-HHx as well as the degree of crystallinity. Hence, the PHB-HHx is expected to have a broader thermal processing window and less detrimental brittleness, which makes it attractive as a substitute for PHB.

Rheological information is very useful in screening polymers for certain processing operations [15]. Some rheological work has been presented earlier for PHB [5,16] as well as other types of PHAs, including poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [17], poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) [18], poly(3-hydroxybutyrate-*co*-5-hydroxyvalerate) and poly(3-hydroxybutyrate-*co*-6-hydroxyhexanoate) [19]. However, a systematic investigation on the rheology of PHB-HHx and its relationship to the copolymer composition is still missing. The aim of this paper is to present a systematic rheological characterization of four PHB-HHxs varying in the HHx content. The well-known difficulty for studying melt properties of PHB and its copolymer is the thermal instability of these polymers in the molten state. Random chain scission occurs in the backbone through the ester decomposition mechanism, which, although it does not change the chemical nature of these polymers, significantly reduces the molecular weight [20–22]. As a result, it is expected that there is some degree of molecular weight reduction during PHB-HHx sample preparation as well as during the rheological measurements; this is especially true for the former since it is conducted by melt pressing at higher temperature.

In this work, special attention has been given to obtaining the molecular weight of a rheological specimen immediately prior to the start of the rheological test; we believe that reflects the true molecular characteristic that may be related to the rheological results. Such molecular weights are herein referred to as time-zero weight average molecular weights ($M_{w,t0}$). We also note that since all rheological measurement temperatures are set to be at or below 150 °C, further change in molecular weight of the sample after the test has started is rather slow, as will be shown in the Results section and thus is not considered in this paper. Throughout the work, we use the time-zero weight average molecular weight for data analysis and discussion [4,5,20–25]. Dynamic shear viscosities were measured over a range of temperatures, spanning a range of time or frequency, along with the determination of molecular weight distributions that are known to affect the rheological behavior. The time-temperature superposition principle was applied to the modulus data to study the temperature dependence of the viscoelasticity. Relaxation behavior and melt mobilities of these materials were interpreted in terms of current models and were related to the molecular weight between entanglements and number of chains per unit volume.

2. Experiment

2.1. Materials

The biodegradable copolymers poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)s, PHB-HHx, used in this work were produced by the Procter & Gamble Company. There are four PHB-HHx copolymers with varying molar ratios of HHx as reported (Table 1). Samples that contained residual biomass were further purified by dissolution in hot chloroform followed by precipitation in ethanol. The white polymer powders were then filtered and dried in vacuum for at least 72 h prior to use.

2.2. Gel permeation chromatography (GPC)

The molecular weights of the PHB-HHxs were measured with a Viscotek GPCMax system equipped with a refractive index detector. Polystyrene standards purchased from the same company were used to create a 12-point calibration curve based on their refractive indices. Tetrahydrofuran was used as the solvent and all experiments were carried out at room temperature at a flow rate of 1 mL/min. The measured refractive index versus the elution volume was transformed to molecular weight data using polystyrene calibration standards.

2.3. Differential scanning calorimetry (DSC)

Thermal properties of the PHB-HHxs were measured with a TA Instruments Q100 differential scanning calorimeter using the temperature-modulated method. Samples were first equilibrated at −50 °C for 5 min and then heated to 185 °C at a rate of 3 °C/min; a temperature modulation for a period of 60 s and an amplitude of 1.00 °C was chosen based on instrument specification. Nitrogen was used as the purge gas at a flow rate of 50 mL/min. The melting temperatures were taken as the endothermic peak maxima on the non-reversible heat flow curves, and the glass transition temperatures were taken as the midpoints of the heat capacity changes.

2.4. Melt rheometry

An ARES rheometer (TA Instruments) was used to study the viscoelastic properties of the PHB-HHx samples. Prior to tests, all polymer samples were compression molded to make 1.5 mm thick and 25 mm diameter discs by a hydraulic hot press that was set to temperatures 15 °C above the respective melting temperatures. The ARES was equipped with a Forced Convection Oven (FCO), a platinum resistance thermometer sensor positioned at the center of the lower

Table 1
Sample notation, molecular weights, T_m and T_g of the PHAs (as received).

PHA Materials	Notation	M_n (10^3 g/mol)	M_w (10^3 g/mol)	PI	T_m (°C)	T_g (°C)
Poly(3-hydroxybutyrate-*co*-3.8 mol% 3-hydroxyhexanoate)	PHB-HHx3.8	220	659	2.99	151.6	2.03
Poly(3-hydroxybutyrate-*co*-4.6 mol% 3-hydroxyhexanoate)	PHB-HHx4.6	230	658	2.87	150.8	1.88
Poly(3-hydroxybutyrate-*co*-6.9 mol% 3-hydroxyhexanoate)	PHB-HHx6.9	284	723	2.55	145.8	1.53
Poly(3-hydroxybutyrate-*co*-10.0 mol% 3-hydroxyhexanoate)	PHB-HHx10.0	136	312	2.30	144.6	0.89

plate, and 25 mm diameter parallel plates. For each test, the FCO was pre-heated to 160 °C, and then the polymer disc was loaded in between two parallel plates. Temperature was maintained at 160 °C for 4 min to melt the polymers; then it was set to the respective test temperature and equilibrated for another 2 min prior to the rheological tests. During the last 20 s of this equilibration step, the oven was quickly opened and re-closed, during which a few mg of the melt PHB-HHx sample was quickly trimmed off from the edge of the parallel plates. This small amount of melt sample was then quenched to room temperature and used in a GPC test to determine the time-zero molecular weight ($M_{w,t0}$) of the respective rheological sample. Dynamic frequency sweep tests were carried out from 0.25 or 1 to 100 rad/s according to different experiment protocols. Dynamic time-sweep tests were done from time 0 s to 1200 s under a constant temperature and a constant frequency (1 rad/s). Tests were repeated three times to demonstrate reproducibility.

3. Results

3.1. PHB-HHx materials

Molecular compositions and sample notation of the four copolymers used in this paper are listed in Table 1. The molecular weights and polydispersity index (PI) of these materials, as received, are determined by GPC and melting and glass transition temperatures obtained by DSC are also summarized. Several observations are relevant: First, all the copolymers have polydispersity indices in the range of 2.3–3.0. Second, PHB-HHx3.8, PHB-HHx4.6 and PHB-HHx6.9 have similar molecular weights, while the PHB-HHx10.0 is roughly half the value. Finally, the melting temperature tends to decrease as the comonomer HHx content in the copolymer increases.

3.2. The influence of thermal degradation on rheological results

Like other polymers, PHA materials undergo thermal degradation at elevated temperature, and such phenomena are often more pronounced if accompanied by mechanical stress such as torque or shear [4,24]. For homopolymer PHB, substantial degradation was observed during the rheological measurement at temperatures near or above its T_m (around 175 °C) [5,23,26]. Such degradation of the polymers could result in a viscosity decrease that overlaps with the viscosity change due to the increasing shear rate, thus adding difficulty to the interpretation of rheological data.

Since the PHB-HHx copolymers have much lower T_m than PHB (>20 °C lower), we expected to be able to examine their melt rheology at much lower temperatures where the influence of the thermal degradation could be greatly reduced. In order to assess the degree of thermal degradation of the PHB-HHxs during the rheological experiments and how that influences the molecular weight, oscillatory dynamic time-sweep tests were conducted at three different temperatures (160 °C, 150 °C, and 140 °C), constant frequency (1 rad/s), and each for a duration of 10 min. The molecular weights of the PHB-HHx samples prior to and following each time-sweep test were measured using GPC.

Fig. 2 shows the continuous decrease in the complex shear viscosity of the PHB-HHx4.6 melt as the duration of oscillatory shear is increased. As the test temperature was decreased from 160 °C to 140 °C, the degradation process became slower. This phenomenon was similarly observed for other PHB-HHx samples. To mitigate the possible influence of thermal degradation on the rheological data, we kept the test temperatures at or below 150 °C throughout the work and programmed the measurements in such a way that no individual test exceeded 5 min. Under these conditions, as could be estimated from the time-sweep results, no more than 5% of the viscosity decrease should have occurred during each rheological test. Thus, in this paper, these influences will not be discussed further.

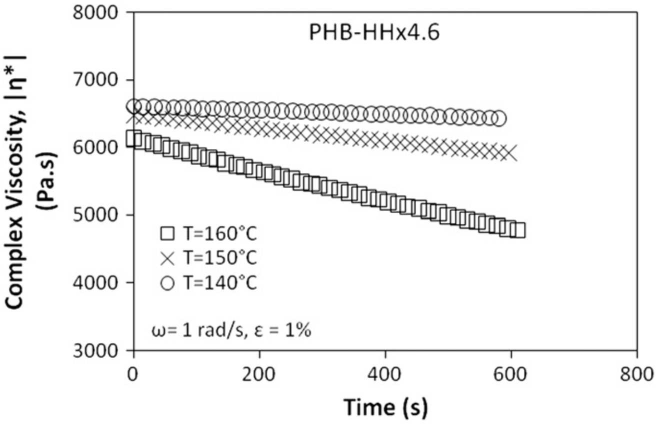

Fig. 2. Complex shear viscosities of PHB-HHx4.6 as a function of oscillatory shear time.

Since thermal history has a strong effect on the molecular weight of PHB-HHxs, and since rheological characteristics of materials are very sensitive to molecular weights, the specific weight average molecular weights immediate prior to ($M_{w,to}$) and following the rheological test ($M_{w,t}$) of every specimen tested by the rheometer were determined by GPC. Fig. 3 shows the relative molecular weight reduction caused by a time-sweep test, as an indication of its sensitivity to thermal history.

The normalized molecular weights decrease more or less linearly as a function of temperature, indicating that PHB-HHx samples undergo thermal degradation in the molten state under continuous oscillatory shear. Such degradation process is slower at lower temperature, suggesting that the decrease in apparent complex viscosity observed in the rheological measurements might be due to the decrease in molecular weight of the polymers caused by thermal degradation. In addition, the degradation rate seems to increase with HHx comonomer content when the temperature is constant, which is in agreement with some previous studies: the thermal degradation of homopolymer PHB is reported to be less severe compared to that of copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) [3,27].

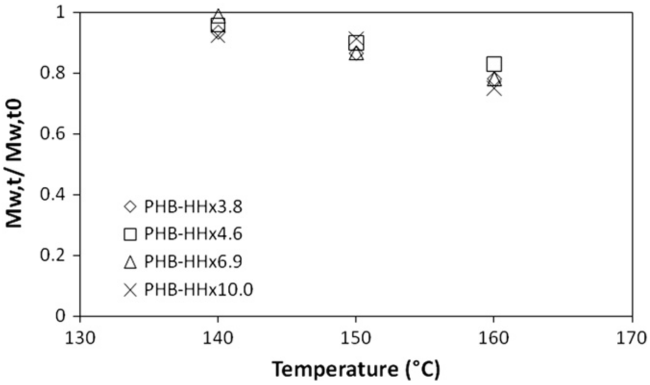

Fig. 3. Relative weight average molecular weight of copolymers after a time-sweep test at three different temperatures. (Shear frequency = 1 rad/s, strain = 1%, and test duration = 10 min).

3.3. Dynamic frequency sweep tests and non-Newtonian flow behavior of PHB-HHxs

In dynamic oscillatory frequency sweep measurements, complex viscosities were recorded over a range of different shear frequencies. Fig. 4 shows a representative set of complex viscosity curves as a function of frequency. Within a low-to-intermediate frequency range ($\omega = 0.25$–100 rad/s), all PHB-HHx samples exhibited shear thinning behavior typical for non-Newtonian fluids, such as polymer melts.

To assess the shear thinning behavior more quantitatively, non-Newtonian flow behavior (Fig. 4) observed for PHB-HHxs measured under dynamic shear was studied with the quantitative Cross model, which is known to describe well the dependence of viscosity on shear rate [28,29]. Since most of such models, including Cross, describe situations of steady shear, it is important to establish the "equivalence" between the dynamic shear viscosity that we measured and the steady-shear viscosity. According to the Cox-Merz rule [30], which applies to many polymer melts, the steady-shear viscosity $\eta(\dot{\gamma})$ is identical to the absolute value of complex shear viscosity:

$$\eta(\dot{\gamma}) = \left|\eta^{*}(\omega)\right| \quad \text{if} \ \dot{\gamma} = \omega \tag{1}$$

Both $\eta(\dot{\gamma})$ and $|\eta^{*}(\omega)|$ are known to approach the same constant value, the zero-shear viscosity η_0, at very low shear rate or frequency:

$$\eta_0 = \lim_{\dot{\gamma}\to 0}\eta(\dot{\gamma}) = \lim_{\omega\to 0}\left|\eta^{*}(\omega)\right| \tag{2}$$

The Cox-Merz rule has been previously proven to hold for PHB-HHx polymers [4].

By substituting the respective steady-shear terms with dynamic terms in the Cross model using Eqs. (1) and (2), we obtained a modified Cross model is obtained that has the form of:

$$\left|\eta^{*}(\omega)\right| = \frac{\eta_0}{1 + (\lambda\omega)^{m}} \tag{3}$$

The exponent m is known as the (Cross) power-law exponent, and λ is known as the (Cross) characteristic relaxation time. The m is a measure of the degree of dependence of viscosity on shear rate/frequency, with $-m$ being the slope of the curve in a double logarithm plot of η^{*} and ω in the shear thinning region. The m increases from zero to unity as the shear thinning effect becomes more important. The reciprocal of the characteristic relaxation time, $1/\lambda$, gives the critical shear rate/frequency that indicates the onset of shear thinning. The frequency sweep tests at 150 °C were conducted on three different samples for each of the four PHB-HHx copolymers. For each of these 12 samples, $M_{w,t0}$ and PI were obtained by GPC. Table 2 lists the average values and standard deviations of $M_{w,t0}$ and PI obtained on the three different rheological samples for each PHB-HHx composition. Note that all $M_{w,t0}$ are significantly smaller than M_w of the as-received materials, and $M_{w,t0}$ for a given PHB-HHx composition has a spread of values (roughly 30% variance). This is possibly due to the slight variance in temperature and pressure and thus the rate of melting for PHB-HHx powders during the hot-press step, which led to different degrees of thermal degradation of the samples. However, in Fig. 5, we plotted the obtained viscoelastic parameters η_0 and λ against $M_{w,t0}$ for each rheological sample and found no evidence of change in viscoelastic characteristics caused by different degrees of sample degradation. PI is also slightly reduced after thermal processing, but the reduction is not significant nor is there a large variance among samples (Table 2). A similar observation has been reported by Yamaguchi et al. for the homopolymer PHB.

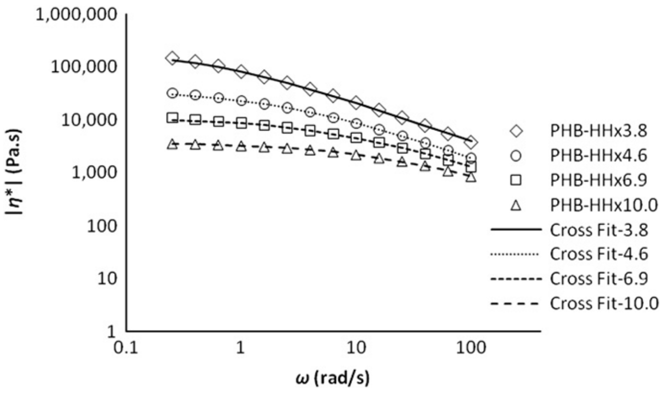

Fig. 4. Representative complex shear viscosity curves of various PHB-HHxs (Sample 1) (T = 150 °C) as a function of oscillatory shear frequency and the Cross model datafit curves.

Viscoelastic characteristic parameters η_0, λ, and m were obtained by fitting the dynamic shear viscosity curves using Eq. (3). These viscoelastic characteristics are plotted against the respective $M_{w,t0}$ in Fig. 5 or listed in Table 2. If η_0 is plotted against the weight average time-zero molecular weight $M_{w,t0}$, it is seen that the zero-shear viscosity of PHB-HHx falls on a master curve, where it follows the classical power-law relationship, $\eta_0 = KM_w^{\alpha}$, in which the power-law exponent α for PHB-HHx is 3.1. For homopolymer PHB, this value is reported to be 3.6 by Yamaguchi et al. [5], for a system similar to ours in which the PHB samples thermally degraded and had a polydispersity of roughly 2.0.

In addition, the characteristic relaxation time λ is seen to be closely related to the zero-shear viscosity. This is understandable if we consider the actual physical processes involved [31]. When a shearing force is applied to a polymer melt, the entangled polymer chains are stretched, viscous melts are observed because of the energy loss due to friction, and the viscous loss is closely related to the phase difference between the applied force and the retractive motion of the polymer chain (consider it to consist of a number of stiff springs). At a certain characteristic shearing frequency, the change in viscosity/energy loss due to friction is the most rapid, and this characteristic time is predicted to be the ratio of the viscous and elastic constants of the polymer system, e.g. for a simple Maxwell element, it is the ratio of the viscous constant of the dashpot and the elastic constant of the spring.

Moreover, these viscoelastic properties are dependent on the chemical composition. According to the Doi-Edwards theory of viscoelasticity, the ratio λ/η_0 is determined only by the polymer type and the bulk concentration, since the molecular weight dependence of λ and η_0 follow the same power-law relationship [32]. For PHB-HHxs, as shown in Fig. 5(c), the value of λ/η_0 is similar among PHB-HHxs, and seems to increase slightly with increasing HHx content.

With respect to the (Cross) power-law exponent m, we found that for PHB-HHxs the values of m range from 0.65 to 0.77. In

Table 2
M_w (as received), $M_{w,t0}$, polydispersity index (PI), and cross parameter m for PHB-HHxs.

Polymer	M_w (as received) (10^3 g/mol)	$M_{w,t0}$ (10^3 g/mol)	PI	m
PHB-HHx3.8	659	427 ± 155	2.79 ± 0.17	0.75 ± 0.02
PHB-HHx4.6	658	348 ± 100	2.76 ± 0.14	0.74 ± 0.02
PHB-HHx6.9	723	221 ± 93	2.48 ± 0.17	0.72 ± 0.03
PHB-HHx10.0	312	160 ± 33	2.07 ± 0.13	0.69 ± 0.04

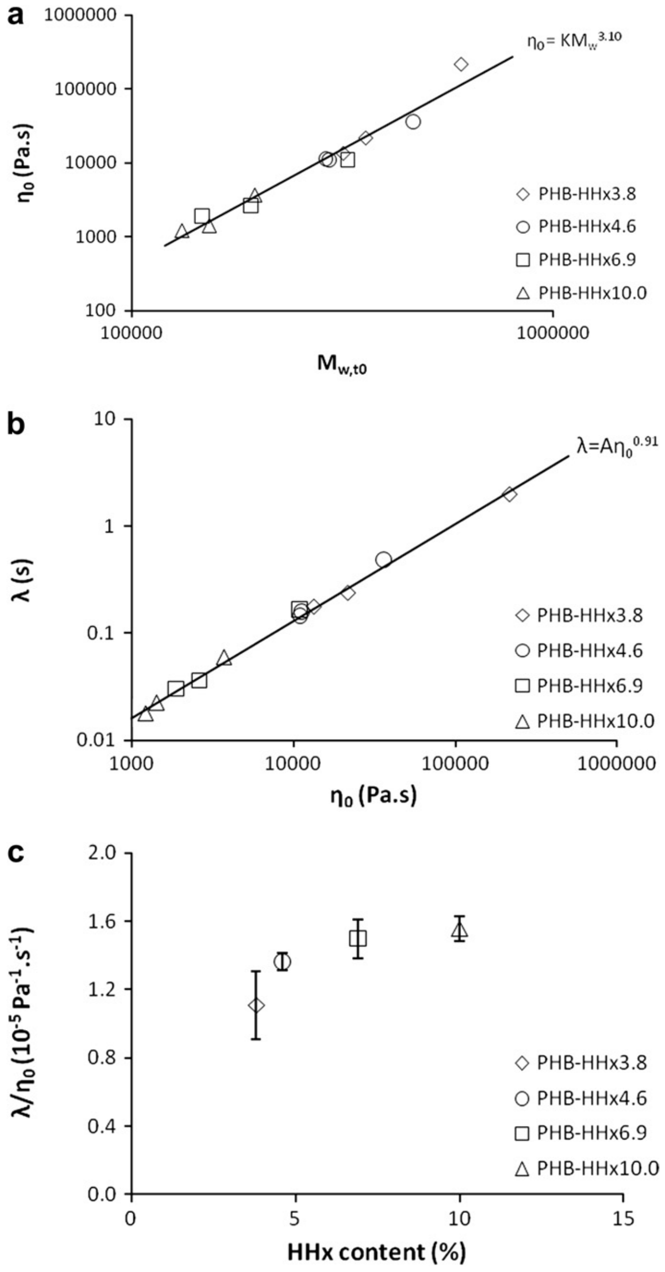

Fig. 5. Viscoelastic characteristic properties of PHB-HHxs obtained by Cross model data-fitting frequency sweep results and the relationship to molecular weight: (a) zero-shear viscosity η_0 versus weight average molecular weight M_w; (b) characteristic relaxation time λ versus η_0; (c) λ/η versus the HHx content in copolymer PHB-HHx.

comparison, previous work by Cross [28] showed that for polybutadiene (PBD) melt the exponent m was 0.67, and Bueche and Harding [33] had proposed an m of 0.75 for very concentrated polymer solutions, in good agreement with the PHB-HHx values.

3.4. *Dynamic frequency sweeps at varying temperatures and time-temperature superposition*

Dynamic moduli of PHB-HHx samples were measured at a series of temperatures, taken at every 10 °C interval starting from 150 °C down to roughly 120 °C, below which the polymer melt would start to crystallize during the test. The time-temperature superposition (TTS) principle was applied to shift all the rheological data to a reference temperature of 150 °C:

$$G'(\omega, T) = G'(\omega a_T, T_0) \tag{4}$$

$$G''(\omega, T) = G''(\omega a_T, T_0) \tag{5}$$

creating a master curve for that polymer at the reference temperature T_0 (Fig. 6).

The master curves for PHB-HHx show no deviation from time-temperature superposition. The shift factor α_T obtained from time-temperature superposition expresses the dependence of the zero-shear rate viscosity on temperature as follows:

$$a_T = \frac{\eta_0(T)}{\eta_0(T_0)} \tag{6}$$

The viscosity of polymeric melts, which describes the mobility of polymer chains in the molten state, is dependent, at short range, on the local packing density of the chain segments and, at long range, on the entangled network conformation. Near the glass transition temperature T_g, the barrier for polymer flow is mainly the free volume required to allow the necessary rotation of chain segments; thus, the viscosity is described by the Williams-Landel-Ferry (WLF) equation. For temperatures that are much higher ($\geq T_g + 100$ °C), the free volume is no longer the rate limiting factor, and the viscosity–temperature relationship follows an Arrhenius-like equation. The apparent activation energy is related to the energy required for a chain segment to jump from an occupied site to an unoccupied one [34].

Since all the rheological measurements in this work were conducted on polymer melts at temperatures much higher than T_g, the shift factor a_T is expected to follow the Arrhenius relationship with temperature, and this has been proven consistent with our results (Fig. 7(a)). The natural log of a_T is linearly proportional to the inverse of absolute temperature $1/T$. Following the Arrhenius equation,

$$\ln a_T = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{7}$$

the apparent activation energy of flow E_a was obtained from the slope of the $\ln a_T$ versus $1/T$ curves, and the results are plotted against the molar fraction of HHx monomer unit in the copolymer as is shown in Fig. 7(b). The E_a values for PHB-HHxs fall in the 29–34 kJ/mol range. Given that the E_a for homopolymer PHB was previously found to be 37.24 kJ/mol [24], the activation energy E_a is found to be linearly related to the comonomer content, decreasing with increasing HHx content.

4. Discussion

4.1. *Relaxation behavior of PHB-HHx chains*

The measured dynamic modulus data could be used to obtain more information on PHB-HHx melt characteristics. First, it is straightforward to obtain a crossover frequency ω_c (see Table 4), which is basically the x-axis value for the “crossover point” where G' and G'' are equal (Fig. 6). If the whole polymer system were considered as a single Maxwell mechanical element, $1/\omega_c$ would provide the characteristic relaxation time of such an element, which is modeled as the ratio of the viscous constant of the dashpot and the elastic constant of the spring [35–37].

As is well known, however, the actual relaxation of a polymer chain has a large spectrum of relaxation times, and it is better to describe its behavior using models involving multiple characteristic relaxation times instead of a single one. Hence, we have used the Generalized Maxwell model to represent our PHB-HHx systems, and the dynamic functions are:

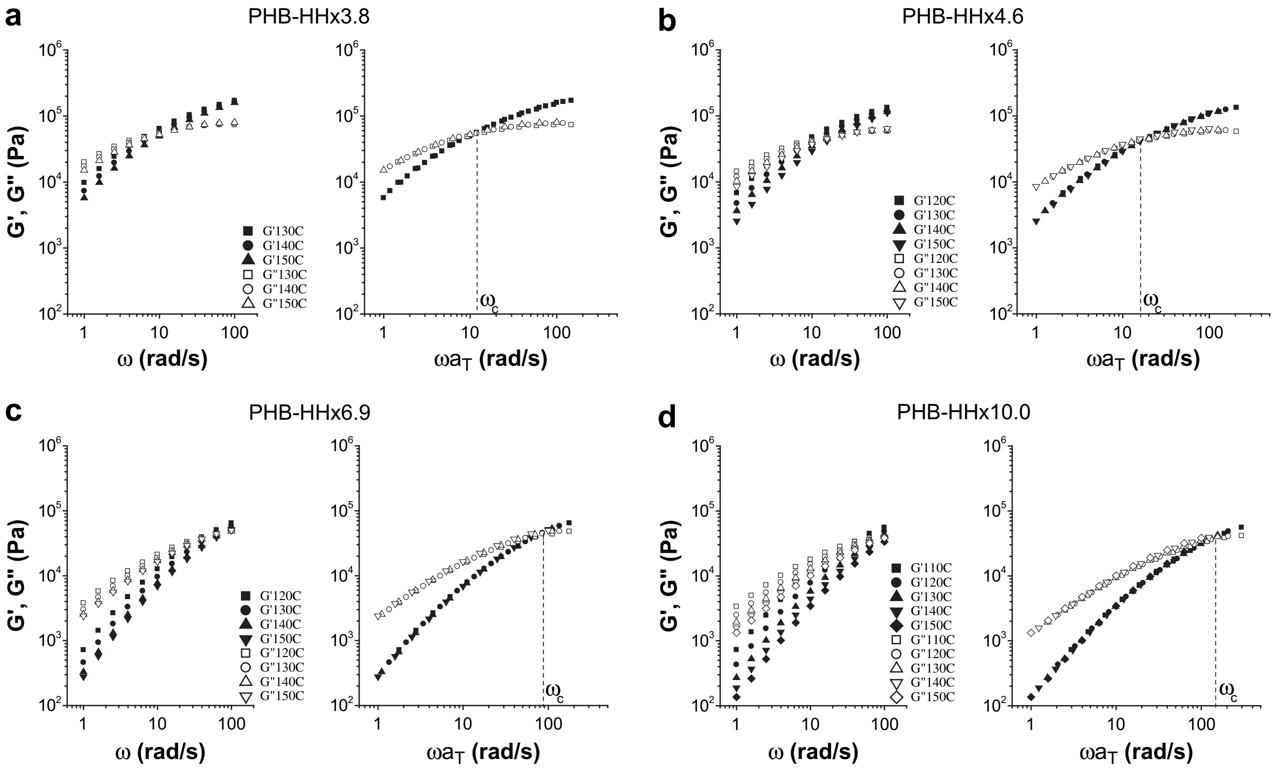

Fig. 6. Dynamic moduli as a function of frequency for PHB-HHxs at different temperatures and the master curves by shifting to a reference temperature of 150 °C.

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)^2}{\left[1+(\omega\lambda_i)^2\right]} \tag{8}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i(\omega\lambda_i)}{\left[1+(\omega\lambda_i)^2\right]} \tag{9}$$

where G_i and λ_i are the initial modulus and relaxation time corresponding to the ith Maxwell element in the Generalized Maxwell model.

The relaxation spectra for the PHB-HHx materials were computed from the master G' and G'' curves (Fig. 8) by selecting a reasonable set of relaxation times λ_i on the time scale of $1/\omega_c$ and then fitting the linear regression model on the coefficients G_i. The parameters used to fit curves in Fig. 8 are listed in Table 3. Note that five elements can fit the curves reasonably well.

The relaxation times of elements span three decades or more, indicating the relaxation of PHB-HHx polymer is complex. Although the individual parameters have no physical significance, the resulting sets of G_i and λ_i allow evaluation of some important overall viscoelastic characteristics of PHB-HHxs:

Zero-shear viscosity

$$\eta_0 = \sum \lambda_i G_i \tag{10}$$

Mean relaxation time

$$\overline{\lambda} = \frac{\sum \lambda_i^2 G_i}{\sum \lambda_i G_i} \tag{11}$$

Plateau modulus

$$G_N^0 = \sum G_i \tag{12}$$

Molecular weight between entanglements [38]:

$$M_e = \frac{\rho RT}{G_N^0} \tag{13}$$

where ρ is the melt density, R is the ideal gas constant, and T is the absolute temperature. The calculated values for PHB-HHxs are listed in Table 4.

It is clear that excellent agreement is obtained between the two zero-shear viscosities η_0 estimated by the generalized Maxwell model and by the Cross model discussed earlier. By contrast, the two mean relaxation times, $\overline{\lambda}$ and λ, the former from the Maxwell model calculation and the latter from datafit of the dynamic viscosity curves with the Cross model, tend to have different values, although both decrease with HHx content. The difference could stem from the polydispersity of the PHB-HHx copolymers, given that many viscoelastic properties are sensitive to molecular weight distributions (MWD) [39].

As Wissbrun proposed [40], the relaxation time scale for a polydisperse polymer differs from the relaxation time for the respective monodisperse polymer of the same η_0 by a fitting parameter λ_f. It was found that λ_f is extremely sensitive to MWD, decreasing as M_w/M_n decreases. Later, it was discovered that the behavior of a polydisperse system could be described by integrating over the stress response of all individual chains whose length distribution properly follows the MWD with a double reptation

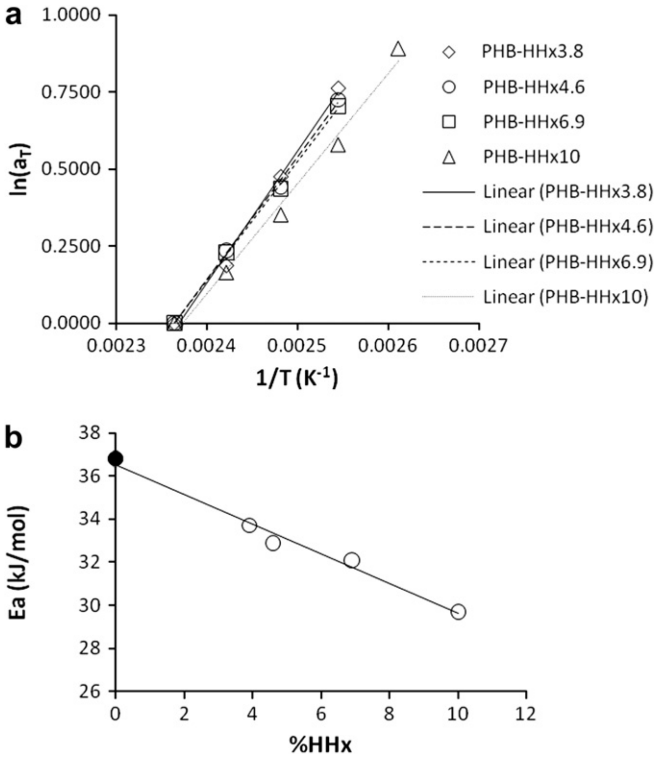

Fig. 7. (a) $\mathrm{Ln}(a_T)$ versus $1/T$ for different PHB-HHxs (symbols) and their linear fits (lines). The reference temperature T_0 is 150 °C. (b) Activation energy for flow (E_a) versus the mole ratio of HHx units in the polymer (%HHx) at the reference temperature of 150 °C. (Solid symbol: data from Ref. [20]).

model, known as the mixing rule [41]. An extensive review on the effect of MWD on the linear viscoelasticity can be found in the work by Wasserman and Graessley [42]. It is worth noting that Wasserman and Graessley also found surprisingly good agreement between the results calculated with the mixing rule compared to those obtained simply by using M_w in the 3.4 power-law equation, indicating the possible non-sensitivity of η_0 to MWD. This also explains the good agreement we observed for the two η_0 as mentioned above. Furthermore, it has been recognized that the generalized Maxwell model can be used suitably for polydisperse systems: since the G' and G'' are modeled by summing up multiple Maxwell elements with a range of different relaxation times, the effect of MWD has been properly incorporated into the relaxation spectrum [43–45]. Hence, our results and later discussion, which are all based on data obtained from the generalized Maxwell model, are not expected to be influenced by the slight variance in the MWD among different PHB-HHx samples. The estimated relaxation times λ_c obtained by taking the inverse of ω_c in Fig. 6 are also listed in Table 4. λ_c is smaller than $\overline{\lambda}$ for each copolymer, but it appears to approximate well the median value of the groups of λ_i used in the datafit.

The estimated plateau modulus G_N^0 is found to be insensitive to the molecular weight, given that the value of G_N^0 is very close among the four samples tested which have very different M_w. This finding is consistent with what has been suggested by other researchers [15]. However, as the HHx comonomer content increases, G_N^0 increases slightly, which results in the decreasing M_e.

Fetters et al. summarized several molecular relationships by which the viscoelastic properties can be related to the size of the random coil and to the degree of entanglement in the melt [46]. At 413 K, the relationships are:

$$G_N^0 = 12.16\ \mathrm{MPa}\left(\mathring{A}\right)^3\left(\frac{r^2}{M}\rho N_a\right)^3 \tag{14}$$

$$M_e = 225.8\frac{\mathrm{cm}^3}{\left(\mathring{A}\right)^3\mathrm{mol}}\left(\frac{r^2}{M}\right)^{-3}\rho^{-2}N_a^{-3} \tag{15}$$

where r represents the end-to-end distance of the unperturbed chain, M is the molecular weight, and N_a is Avogadro's number. The end-to-end distance is related to the chain molecular weight and the Kuhn step length as follows:

$$\frac{r^2}{M} = \frac{l^2}{m_0} \tag{16}$$

where l is the Kuhn step length and m_0 is the molecular weight of the Kuhn segment. If l is large, the polymer chain tends to have high bending rigidity. From Eqs. (13)–(16), it is seen that G_N^0 increases while M_e decreases with l. Since the value of m_0 is very close for all PHB-HHxs, the decrease in M_e with increasing HHx content (Table 4) could stem from the increase in Kuhn step length l, presumably due to the increase in steric hindrance from the propyl side group in the HHx. A similar observation was reported by Harrison et al. [24], where a PHB-HHx copolymer with 6 mol.% HHx has a lower M_e than poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB-HV) with 10.5 mol.% HV. Our results on PHB-HHx suggest that such a decrease originates with the increase in the side group length on HHx relative to HV, rather than, as suggested previously [24], being attributed to the difference in comonomer concentration and the isotacticity of the PHB-HV.

4.2. *Melt viscosities of PHB-HHxs*

Similar to many other polymer melts, the shear viscosity of the PHB-HHx melt is rather complex. The viscosity not only depends on temperature and pressure, but also varies with the rate of deformation. At low rates of shear, the polymer melt flow is Newtonian. The Newtonian viscosity (η_0) follows the empirical relationship of $\eta_0 = KM_w^\alpha$. At high shear rate, the elastic effects that accompany the flow of polymer chains become significant, which is usually observed as shear thinning. Both the Newtonian viscosity and the characteristic time for shear thinning are found to be related to polymer species, concentration, and molecular weight distribution.

With his theoretical work, Graessley proposed that, for a bulk polymer or a concentrated polymer solution with high molecular weight, the shear viscosity is controlled by the entangled network structure, and the decrease in viscosity with increasing shear rate is caused by the shear-induced change to the network [39]. Thus, the zero-shear viscosity η_0 can be related to polymer chain characteristics as:

$$\eta_0 = K\zeta_0\phi^{3.5}\overline{n}^{3.5} \tag{17}$$

where K is a constant that depends on the polymer species, ζ_0 is the polymer segmental friction coefficient, ϕ is the volume fraction of polymer, and $\overline{n}$ is the average number of segments in a polymer chain, which is slightly greater than the weight average [39]. Since ϕ is unity for a bulk polymer, and K is assumed to be the same among four PHB-HHx copolymers, Eq. (17) is reduced to a simple relationship between ζ_0, η_0, and $\overline{n}$:

$$(\mathrm{const.})\times\zeta_0 = \eta_0\overline{n}^{-3.5} \tag{18}$$

Hence, the relative value of the segmental friction coefficient can be estimated from the η_0, M_w and the average molecular weight of monomer. The value of $\eta_0\overline{n}^{-3.5}$ is listed for each PHB-HHx in Table 4.

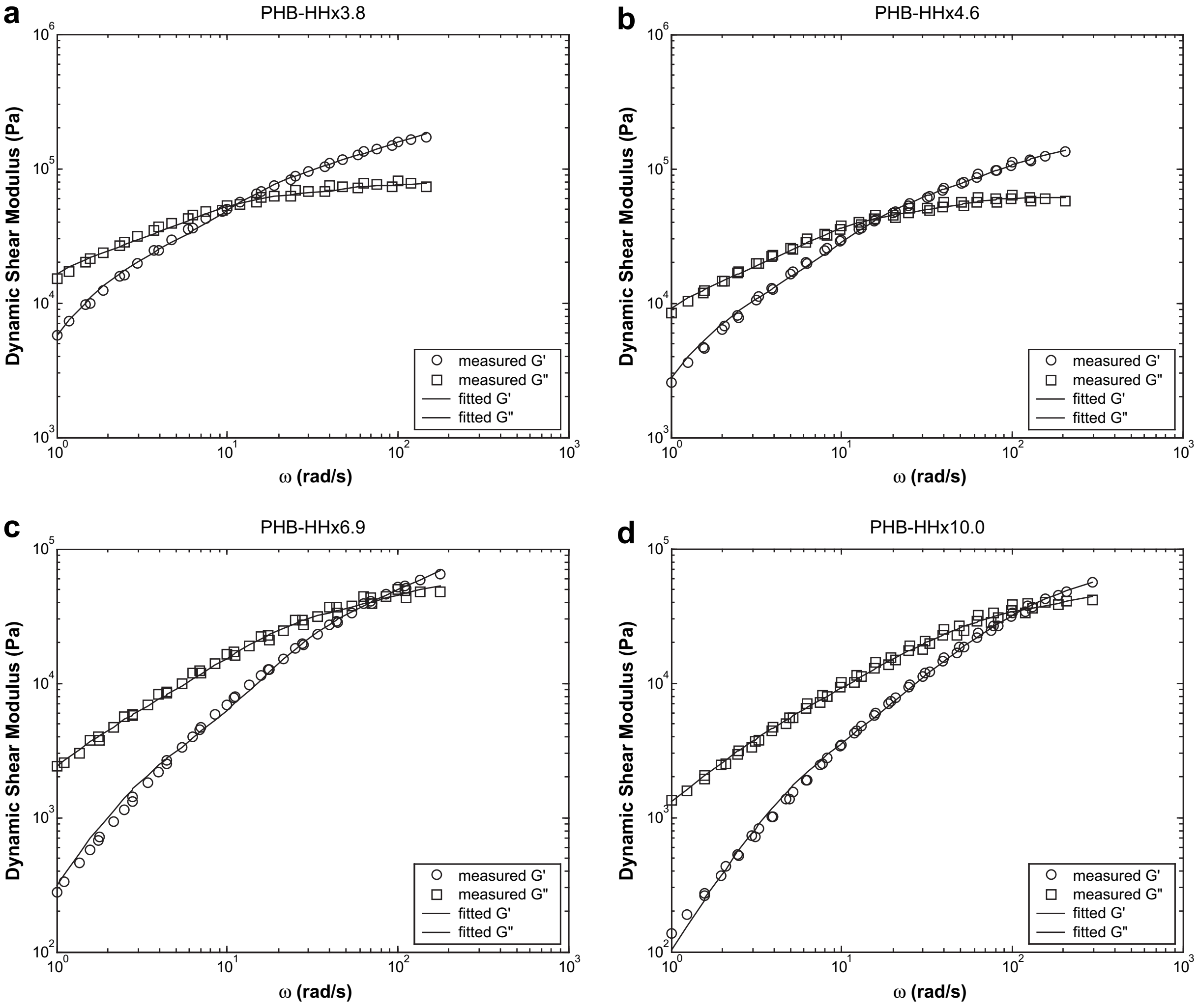

Fig. 8. Dynamic shear modulus of PHB-HHxs fitted with Generalized Maxwell model.

Similarly, the value of $\eta_0\overline{n}^{-3.5}$ for the homopolymer PHB can be calculated from data reported previously by Yanaguchi et al. ($\eta_0 = 1140$ Pa s, $M_w = 302.000$) [5], and is found to be 0.22×10^{-9} Pa s. As these data suggest, the friction coefficient ζ_0 increases with increasing HHx content, which is expected since the propyl side group on HHx possibly increases the steric hindrance to the chain motions.

The side group not only affects the zero-shear viscosity η_0 but also affects the shear thinning behavior. Bueche [31] introduced a molecular relaxation time that predicts that the viscosity begins to decrease with increasing shear rate in the range where the product of this relaxation time and the shear rate is of the order of unity. This time constant λ_b is approximated to be on the order of the Rouse relaxation time and is related to the zero-shear viscosity η_0 in the form of:

$$\lambda_b = \frac{12\eta_0}{\pi^2 \nu kT} \tag{19}$$

where ν is the number of molecules per unit volume, k is Boltzmann's constant and T is the absolute temperature. Based on the characteristic relaxation time $\overline{\lambda}$ obtained earlier to substitute for the λ_b in eq. (19), the number of molecules per unit volume ν may be calculated and the results are summarized in Table 4.

Similarly, the value of ν for the homopolymer PHB can also be calculated from the η_0 and λ values that were reported previously [5], and the value obtained is 16.2×10^{-6} mol cm^{-3}. Clearly, the number of polymer chains per unit volume decreases progressively as the HHx content increases. In other words, the polymer chains

Table 3
Parameters used in Generalized Maxwell models for Fig. 8.

PHB-HHx3.8		PHB-HHx4.6		PHB-HHx6.9		PHB-HHx10.0	
G_i	λ_i	G_i	λ_i	G_i	λ_i	G_i	λ_i
6.1E + 04	0.00562	1.2E + 05	0.001	1.7E + 05	0.000562	2.4E + 05	0.000316
7.6E + 04	0.01	8.0E + 04	0.01	6.1E + 04	0.00562	2.2E + 04	0.00316
5.9E + 04	0.0562	4.1E + 04	0.0562	3.4E + 04	0.0316	3.4E + 04	0.01
2.5E + 04	0.1	1.5E + 04	0.1	6.1E + 02	0.1	1.1E + 04	0.0316
2.2E + 04	0.562	1.0E + 04	0.562	3.0E + 03	0.316	2.9E + 03	0.178

Table 4
Viscoelastic characteristics of PHB-HHxs.

Polymer	η_0 (10^3 Pa s)	η_0[a] (10^3 Pa s)	$\bar{\lambda}$ (s)	λ[a] (s)	λ_c[b] (s)	G_N^0 (10^5 Pa)	M_e (10^3 g mol^{-1})	$\eta_0 \bar{n}^{-3.5}$ (10^{-9} Pa s)	ν (10^{-6} mol cm^{-2})
PHB-HHx3.8	19.3	21.6	0.39	0.24	0.084	2.43	11.6	1.7	10.8
PHB-HHx4.6	10.6	11.0	0.34	0.15	0.051	2.63	10.7	2.3	6.4
PHB-HHx6.9	2.50	2.63	0.14	0.036	0.012	2.64	10.6	2.7	5.9
PHB-HHx10.0	1.34	1.43	0.079	0.023	0.006	3.05	9.4	4.2	0.79

[a] Zero-shear viscosity η_0 and relaxation time λ obtained with Cross model.
[b] Relaxation time λ_c obtained from the inverse of crossover frequency $1/\omega_c$ in Fig. 6.

pack more closely for PHB-HHx with fewer HHx segments. This is expected since HHx has a propyl side group instead of the methyl group on HB, and the steric hindrance would prohibit the tight packing of polymer chains. Additional evidence of such steric effect from the propyl side group is the increase in the free volume with increasing HHx. The glass transition temperature T_g data obtained with DSC (Table 1) show that the T_g decreases with HHx content, suggesting an increase in free volume with increasing propyl side groups. Hence, the observed results on various rheological properties of PHB-HHx are consistent with each other and with the thermal properties, all of which originate in the chemical structures of the copolymer components.

4.3. Temperature dependence of rheological properties

Besides the effect of molecular weight, the rheological properties of polymer melts are also governed by the molecular structure of the polymer and the temperature. In order for a polymer to flow, long range coordinated chain motion of the polymer must be allowed. This requires that there be enough space between the chains, and that the thermal energy in the system be sufficiently high for polymer chains to overcome the energy barriers for their motion, e.g. energy required for a rotation involving a few covalent bonds to take place.

Since E_a is the energy of activation of viscous flow, it is not only a function of temperature but also of the entropy of polymer rearrangement. It is thus possible to correlate E_a with the chemical structure of the polymer. One empirical group additivity method of doing so has been proposed by Vankrevelen and Hoftyzer [47] in which they defined a molar viscosity–temperature function:

$$\chi = M_u (E_a(\infty))^{1/3} \tag{20}$$

where $E_a(\infty)$ is the activation energy of flow at high temperature and M_u is the molecular weight of the structural polymer unit. They found χ to be additive so that for a polymer with known chemical structure, the value of χ can be calculated by adding up the values for its chemical groups.

Hence,

$$\chi(\text{PHB}) = \chi(-\text{CH}(\text{CH}_3)-) + \chi(-\text{CH}_2-) + \chi(-\text{COO}-) = 2930$$

$$M_u(\text{PHB}) = 86$$

$$E_a(\text{PHB}) = \left(\frac{\chi}{M_u}\right)^3 = 3.95 \times 10^3 (\text{J/mol})$$

For the other comonomer HHx

$$\chi(\text{HHx}) = 3430$$

$$M_u(\text{HHx}) = 114$$

Here we assume that, for copolymers, χ and M_u are the sums of the respective χ and M_u values of each comonomer component, weighted by its molar percentage in the copolymer. Hence,

$$\chi(\text{PHB} - a\%\text{HHx}) = a\% \times 3430 + (1 - a\%) \times 2930$$

$$M_u(\text{PHB} - a\%\text{HHx}) = a\% \times 114 + (1 - a\%) \times 86$$

The activation energy is then

$$E_a(\text{PHB} - a\%\text{HHx}) = \left(\frac{\chi(\text{PHB} - a\%\text{HHx})}{M_u(\text{PHB} - a\%\text{HHx})}\right)^3$$

It is seen from Table 5 that the calculation supports the trend we see in the actual measurement, that E_a decreases with HHx content. However, the actual E_a decreases faster than the estimate (Fig. 8). The experimental E_a of PHB-HHx10.0 has a value of 29.7 kJ/mol, which, if we use the calculation method stated above, would correspond to a theoretical PHB-HHx with 73 mol% HHx. This suggests that the thermal-rheological properties of PHB-HHx change more rapidly with the fraction of the comonomers HHx than a linear relationship would predict, and that a small fraction of HHx has significantly lowered the energy barrier for the viscous flow of PHB-HHx polymer melts due to its propyl side group.

In addition, according to Vankrevelen and Hoftyzer, most unbranched linear polymers have low E_a values (about 25 kJ/mol for polyethylene, polybutadiene and poly(ethylene oxide). The value of PHB-HHx is close to that of Nylon (36 kJ/mol) and is slightly smaller than that of polypropylene (43 kJ/mol). The energy barrier for flow for biodegradable PHB-HHx falls right in the range of that for flexible thermoplastics.

5. Summary

Rheological properties of biodegradable poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) copolymers have been studied, and the viscoelastic properties were related to the molecular structure.

Rheological behavior, such as the shear viscosity of PHB-HHx, depends on the rate of deformation, temperature, molecular weight distribution, and copolymer composition. The viscosity approaches a Newtonian plateau at low shear frequency and begins to decrease as frequency increases. The zero-shear viscosity η_0 approximately follows the classical $M^{3.4}$ relationship to the weight average molecular weight. A slight dependence of η_0 on the PHB-HHx copolymer composition is also observed, which was found to stem from the

Table 5
Activation energy for flow (calculated from molar viscosity–temperature function).

Polymer	E_a (kJ/mol)
PHB-HHx3.8	38.9
PHB-HHx4.6	38.7
PHB-HHx6.9	38.3
PHB-HHx10.0	37.8

increase in the segmental friction coefficient ζ_0 since the presence of the propyl side group in the HHx monomer increases the steric hindrance for polymer rotation. The characteristic relaxation time λ, which reflects the onset of shear thinning, can be obtained by fitting the viscosity curves with the Cross model, and is shown to be proportional to the zero-shear viscosity and is sensitive to the molecular weight distribution.

The temperature dependence of rheological properties follows the Arrhenius form. Activation energies E_a for flow are obtained from the slope of $\ln a_T$ versus $1/T$ curve and the values for PHB-HHxs are found to be larger than for linear polymers such as polyethylene and smaller than stiffer polymers such as polystyrene. As predicted by the method of Vankrevelen and Hoftyzer, E_a decreases as HHx content increases. The actual values decrease more rapidly than predictions, indicating that HHx has a significant effect on lowering the energy barrier for flow that is not proportional to its small molar fraction.

The time-dependent elastic response of PHB-HHx melts to shear deformations can be described using a Generalized Maxwell model, and the plateau modulus G_N^0 and the molecular weight between entanglements M_e are thus obtained. G_N^0 has a predicted value of $2 \sim 3 \times 10^5$ Pa for all PHB-HHxs, which is independent of molecular weight as generally suggested for highly entangled polymer systems. M_e decreases as HHx content increases. The result suggests that the co-existence of HHx influences the conformational characteristics of the PHB-HHx chains and networks: increasing HHx content decreases the mesh size of the network. Since the melt strength of a polymer often stems from the high densities of the physical entanglements, this has led to the possibilities for biodegradable PHB-HHx polymers to be used in conventional thermoplastic applications that require a certain degree of melt strength. Hence, our results suggest that the presence of propyl groups in HHx increases the segmental friction coefficient as well as the entanglement density of the PHB-HHx chains. Thus, viscoelastic characteristics such as η_0 and G_N^0 are readily tunable by varying the HHx content. This indicates that these polymers have the potential to be designed for a variety of applications, e.g. as green substitutes for non-degradable thermoplastics.

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