

# Enhancement of Melt Elasticity for Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by Addition of Weak Gel

Keiichi Arakawa, Tadashi Yokohara, Masayuki Yamaguchi

School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan

Received 11 February 2007; accepted 2 April 2007

DOI 10.1002/app.26631

Published online 10 October 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Rheological properties in a molten state are studied extensively for poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHB-HV, with a small amount of crosslinked poly(epichlorohydrin), PECH, having low density of crosslink points. It is found that adding 2 wt % of xPECH greatly enhances the melt elasticity of PHB-HV, one of the serious defects of microbial PHB, whereas it has

no effect on the shear viscosity. As a result, viscoelastic nature, and thus processability, of PHB-HV can be controlled by blending the crosslinked PECH. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1320–1324, 2008

**Key words:** biodegradable; polyester; blends; rheology; viscoelastic properties

## INTRODUCTION

Biomass-based polyesters, such as poly(lactic acid) and poly(butylene succinate), have been used extensively in recent years because of a global interest in environment. Poly(3-hydroxybutyrate) (PHB) and its copolymers, one of the most important biomass-based polyesters, will be also employed in various applications in near future because of their attractive properties, such as heat-resistance and rigidity,<sup>1–4</sup> which are comparable to those of isotactic polypropylene (PP). Further, the excellent biodegradability, which occurs even in an anaerobic condition, is significantly attractive property from the viewpoints of the application to biological nitrogen removal at water-purification process.<sup>5–7</sup> Currently however, mechanical brittleness and poor processability prohibit the replacement from conventional plastics and the application to the biological denitrification process. Therefore, further investigation to modify the mechanical and rheological properties is required.<sup>8</sup>

Although the thermal degradation, which occurs around at 170°C, i.e., lower temperature than melting point of PHB, is one of the most serious problems and responsible for the poor processability of PHB,<sup>9–11</sup> recent study enables to predict the rheologi-

cal change during processing quantitatively. This would be an useful information on operating condition at processing.<sup>11</sup> According to this article, viscosity drop is more than 50% when the residence time is over 5 min at 180°C. Further, copolymerization technology, which leads to lower melting point, is quite important to avoid the thermal degradation during processing.<sup>2–4</sup> Because the melting point of poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHB-HV, with 7 wt % of 3-hydroxyvalerate is ~160°C,<sup>2</sup> processing could be performed without the thermal degradation.

Low level of melt elasticity is another reason for the poor processability. Since microbial PHB and its copolymers have narrow molecular weight distribution and have no long-chain branches, elastic properties in a molten state are quite depressed.

Meanwhile, Yamaguchi and Miyata have found that melt elasticity of PP, such as extrudates swell and strain-hardening behavior in elongational viscosity, is greatly enhanced by mixing a weak gel whose molecular segments are miscible with PP chains, even though the amount of the weak gel is less than 3 wt %.<sup>12,13</sup> Furthermore, the addition of the weak gel has little or no effect on the steady-state shear viscosity. Similar results were found in a blend system composed of polyethylene and crosslinked polyethylene with low density of crosslink points.<sup>14–16</sup> Moreover, the blend is found to be applicable for various processing techniques, such as foaming and thermoforming.<sup>13–16</sup> The marked elastic properties are ascribed to the chain stretching of a weak gel in the blend via trapped entanglements between matrix polymer chains and dangling chains in the weak

Correspondence to: M. Yamaguchi (m\_yama@jaist.ac.jp).

Contract grant sponsor: JFE 21st Century Foundation, Ogasawara Foundation for the Promotion of Science and Engineering, Japan Education Center of Environmental Sanitation.

gel.<sup>17</sup> Although, the technology has been applied only to polyolefins, it would be available for biomass-based plastics with poor melt elasticity.

The purpose of this study is to enhance the melt elasticity of microbial PHB-HV by addition of a weak gel.

## EXPERIMENTAL

### Materials

The polymers employed in this study were microbial poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHB-HV, purchased from Aldrich, and poly(epichlorohydrin), PECH, kindly supplied by Daiso. The content of 3-hydroxyvalerate in PHB-HV is 12 wt %. Molecular weight and its distribution were evaluated by a gel permeation chromatograph, GPC, (Tosoh, HLC-8020) with TSK-GEL GMHXL, as a polystyrene standard. Chloroform was employed as eluant at a flow rate of 1.0 mL/min and the sample concentration was 1.0 mg/mL. The number- and weight-average molecular weights of PHB-HV are  $M_n = 1.38 \times 10^5$  and  $M_w = 3.81 \times 10^5$ , respectively. Further, those of PECH are  $M_n = 1.04 \times 10^5$  and  $M_w = 1.06 \times 10^6$ .

### Blend preparation

PECH was crosslinked by the following procedure; 0.189 wt % of a crosslink accelerator (Daiso, P-152) and 0.560 wt % of a chlorine catcher (Kyowa Chemical Industry, DHT-4A) were mixed together with PECH at 130°C for 5 min in an internal batch mixer (Toyoseiki, Labo-plastmil). The blade rotation speed was 15 rpm. After cooling down the compound to 60°C, 0.319 wt % of a crosslinking agent (Daiso, Daisonet XL-21S) and 0.189 wt % of a retardant (Kanto Chemical, Santogard PVI) were added into the compound and mixed again for 1 h at 15 rpm. The obtained blend was crosslinked at 170°C for 15 min and at 150°C for 2 h using a laboratory compression-molding machine (Tester Sangyo, Table-type-test-press SA-303-I-S). The crosslinked PECH, xPECH, was used as a processing modifier of PHB-HV.

Two types of blends were prepared in this study: One is PHB-HV/xPECH (98/2) and the other is PHB-HV/PECH (80/20). Both blends were mixed in the internal mixer at 160°C for 2 min at a blade rotation rate of 40 rpm. Further, as a comparison, PHB-HV was put into the mixer and processed without xPECH at the same condition.

The obtained blends were compressed into a film sheet by the laboratory compression-molding machine at 160°C and at 10 MPa for 2 min. Then they were quenched at 40°C for 5 min. The thickness of the sample films was adjusted to suitable thickness for measurements.

### Measurements

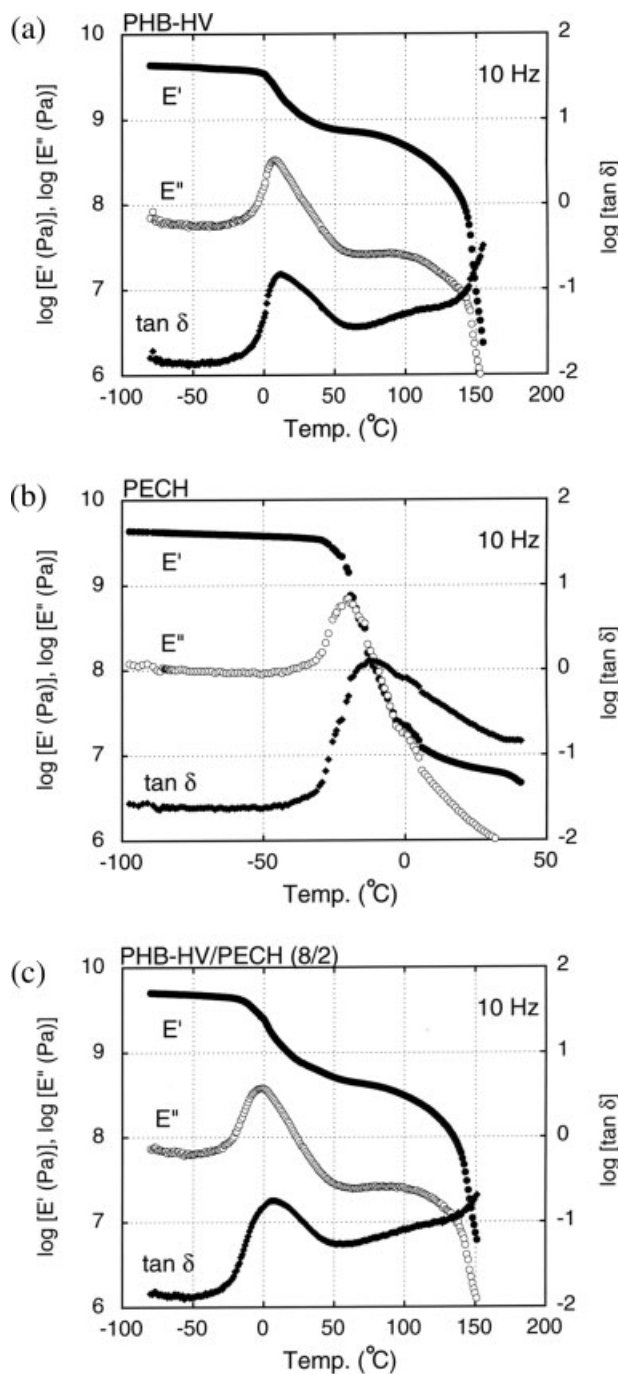
Temperature dependence of oscillatory tensile moduli in the solid state was measured employing a rectangular specimen, in which the width is 3 mm, the thickness is 0.7 mm, and the length is 20 mm, using a dynamic mechanical spectrometer (UBM, E4000). The applied frequency was 10 Hz and the heating rate was 2°C/min.

Steady-state shear viscosity was measured at various shear rates at 160°C by a capillary rheometer (Yasudaseiki, 140 SAS-2002) having a cylinder of 9.55 mm in diameter. The capillary die used was 20 mm in length and 1.0 mm in diameter and had an entrance angle of  $\pi$ . Neither Bagley nor Rabinowitsch correction was carried out for the calculation of the shear stress and the shear rate. Furthermore, the swell ratio of extruded strands and the draw-down force were measured using another circular die having the following dimension; 8 mm in length, 2.095 mm in diameter, and an entrance angle of  $\pi/2$ . The temperature in the capillary reservoir cylinder and the die was kept at 160°C, and the down speed of the plunger was 100 mm/min, yielding a  $6.28 \text{ s}^{-1}$  shear rate. Furthermore, the drawdown force was collected by a tension detector (Nidec-Shimpo, Tension-meter PLS). An extruded strand was vertically pulled through the tension detector by a set of rotating wheels at a rate of 2.6 m/min; this corresponds to a draw ratio of about 25.

## RESULTS AND DISCUSSION

### Miscibility between PHB-HV and PECH

Temperature dependence of oscillatory tensile moduli, such as storage modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$ , for PHB-HV, PECH, and PHB-HV/PECH (80/20) are shown in Figure 1. As seen in Figure 1(a), PHB-HV exhibits typical dynamic mechanical properties of a crystalline polymer. The storage modulus decreases rapidly at room temperature attributed to the glass transition, and falls off sharply at 150°C because of melting of crystals. Further, a broad and weak peak in  $E''$  and  $\tan \delta$  is detected between 60 and 130°C, which is ascribed to  $\alpha$  dispersion. The sharp peak located around 5°C is due to the glass transition of amorphous region, i.e.,  $\beta$  relaxation peak. These dynamic mechanical spectra are quite similar to those of isotactic polypropylene. On the other hand, PECH shows typical dynamic mechanical properties of a rubbery material. The peak temperature in the  $E''$  curve due to the glass transition is about -20°C. In the case of the blend, the  $\beta$  relaxation peak is located between those of the individual pure components as a single peak. The result demonstrates that PECH is dissolved into



**Figure 1** Temperature dependence of oscillatory tensile moduli, such as storage modulus  $E'$  (●), loss modulus  $E''$  (○), and loss tangent  $\tan \delta$  (◆), at 10 Hz for (a) PHB-HV, (b) PECH, and (c) PHB-HV/PECH (80/20).

the amorphous region of PHB-HV. In other words, PECH is miscible with PHB-HV in the amorphous phase. Consequently, blending PECH will lower the brittle-ductile transition temperature. Blending PECH into PHB-HV, however, has little effect on the crystallization of PHB-HV. Therefore,  $E'$  for the blend drops off sharply at the same temperature as that for the pure PHB-HV, which is different from

the phenomenon observed in the blends composed of PHB and cellulose-ester.<sup>8</sup>

### Characteristics of xPECH

Degree of swelling  $q$  and gel fraction  $\phi_{g'}$ , defined as the following relations, were measured to characterize xPECH.

$$q = \frac{w_s}{w_g} \quad (1)$$

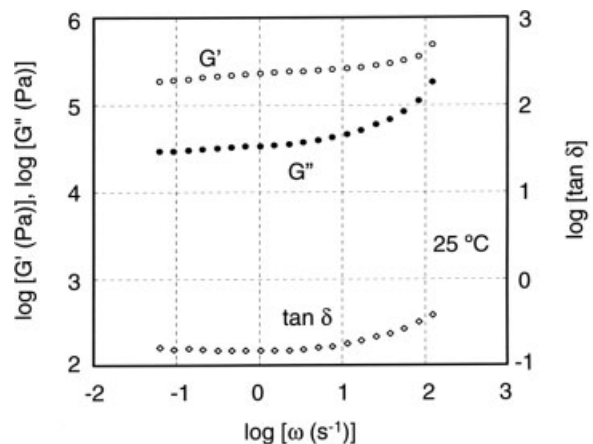
$$\phi_{g'} = \frac{w_g}{w_w} \quad (2)$$

where  $w_s$ ,  $w_{g'}$ , and  $w_w$  are the weights of swollen gel, dry gel, and sum of the dry gel and sol, respectively. Chloroform was used as a solvent. It is found that the gel fraction of xPECH is 80.5 wt % and the degree of swelling is 40.2. The high level of swelling indicates low density of crosslink points in xPECH.

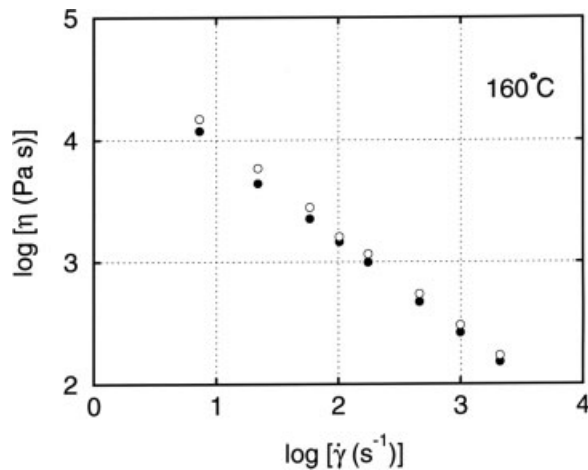
Figure 2 shows the angular frequency dependence of oscillatory shear moduli, such as storage modulus  $G'$ , loss modulus  $G''$ , and loss tangent  $\tan \delta$ , at room temperature for xPECH. As seen in the figure, both  $G'$  and  $G''$  decrease slightly with decreasing the frequency. The figure indicates that xPECH is a weak gel as compared with a conventional vulcanized rubber, because  $G'$  depends on the frequency even in the low frequency region.

### Rheological properties of PHB-HV/xPECH blend

Steady-state shear viscosity  $\eta$  ( $\dot{\gamma}$ ) at various shear rates is evaluated by a capillary rheometer at 160°C for pure PHB-HV and PHB-HV/xPECH (98/2) blend. As illustrated in Figure 3, both samples show



**Figure 2** Frequency dependence of oscillatory shear moduli, such as storage modulus  $G'$  (○), loss modulus  $G''$  (●), and loss tangent  $\tan \delta$  (◇), at room temperature for xPECH.



**Figure 3** Steady-state shear viscosity as a function of shear rate at 160°C for (○) PHB-HV and (●) PHB-HV/xPECH (98/2).

typical shear-thinning, i.e., non-Newtonian, behavior in the experimental region. Further, it is clarified that the addition of xPECH slightly depresses the shear viscosity of PHB-HV. Considering that rheological properties of PHB and the copolymer are greatly affected by the thermal degradation,<sup>11</sup> the slight depression of the shear viscosity would be attributed to the acceleration of the thermal degradation by blending xPECH.

Oscillatory shear moduli at 160°C for PHB-HV and PHB-HV/xPECH are plotted against the angular frequency in Figure 4. As seen in Figure 4(a),  $G'$  is proportional to  $\omega^2$  and  $G''$  is to  $\omega$  in the low frequency region. The results demonstrate that the rheological terminal parameters, such as zero-shear viscosity  $\eta_0$ , steady-state compliance  $J_e^0$ , and weight-average relaxation time  $\tau_w$ , can be determined as follows:

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (3)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (4)$$

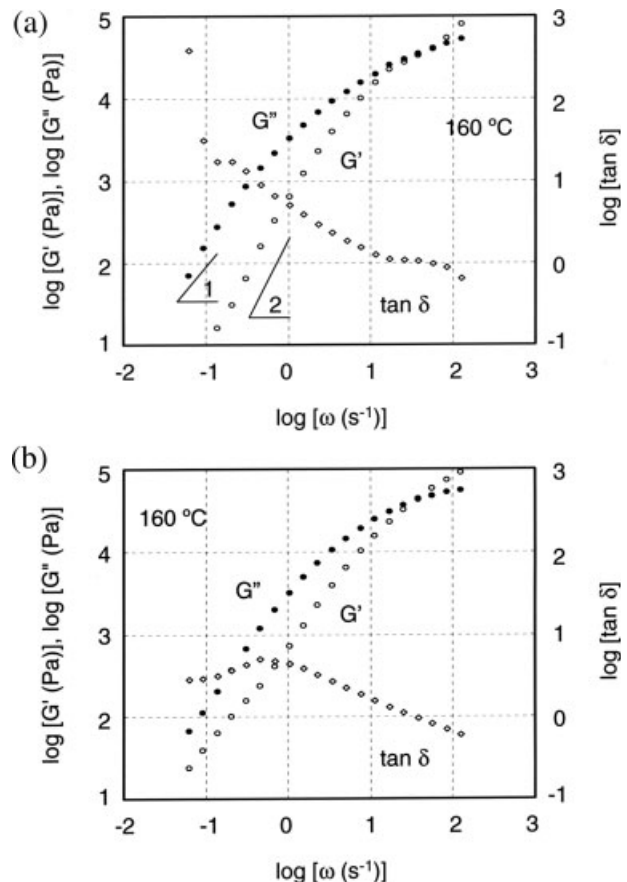
$$\tau_w = \eta_0 J_e^0 \quad (5)$$

PHB-HV used in this study shows the following values at 160°C:  $\eta_0 = 3.2 \times 10^3$  [Pa/s],  $J_e^0 = 1.1 \times 10^{-4}$  [Pa<sup>-1</sup>], and  $\tau_w = 0.35$  [s]. Furthermore, the rheological properties strongly suggest that the distribution of relaxation time is significantly narrow, leading to the poor processability because of the lack of melt elasticity. This is reasonable because microbial PHB-HV has narrow molecular weight distribution ( $M_w/M_n = 2.76$ ) with no long-chain branches.

Furthermore, the magnitude of  $G''$  for PHB-HV/xPECH (98/2) is a slightly lower than that for PHB-

HV. This result corresponds with Figure 3. It can be concluded from Figures 3 and 4 that the shear viscosity is hardly changed by adding 2 wt % of xPECH. Further, it should be notified that  $G'$  in the lower frequency region is considerably enhanced by the addition of xPECH, which is attributed to the long-time relaxation mechanism.

Yamaguchi and Miyata have studied the rheological properties for the blend composed of PP and crosslinked ethylene-hexene-ethylidene norbornene whose chains are miscible with PP molecules in a molten state (xEHDM).<sup>12,15</sup> According to them, blending 1–3 wt % of xEHDM with low density of crosslink points, i.e., the gel just beyond the sol–gel transition point, leads to a long-time relaxation mechanism attributed to the topological interaction between dangling chains in xEHDM and PP chains. On the other hand, a gel with high density of crosslink points or a sol does not show the topological interaction with PP. This is plausible because both the gel with high density of crosslink points and the sol have quite few dangling chains. Further, they have found that the long-time relaxation associated



**Figure 4** Frequency dependence of oscillatory shear moduli, such as storage modulus  $G'$  (○), loss modulus  $G''$  (●), and loss tangent  $\tan \delta$  (◇), at 160°C for (a) PHB-HV and (b) PHB-HV/xPECH (98/2).

**TABLE I**  
**Extrudate Swell Ratio and Drawdown Force**

Sample	Swell ratio	Drawdown force (mN)
PHB-HV	1.26	too low to detect
PHB-HV/xPECH	1.77	500

with the topological interaction is responsible for anomalous elastic properties in a molten state, such as marked strain-hardening in elongational viscosity and enhanced extruded swell, whereas the shear viscosity is hardly changed. Their study indicates that it is significantly important to check the elastic properties of PHB-HV/xPECH.

Table I shows the swell ratio, i.e., the ratio of the diameter of an extruded strand to that of the die, at  $6.28 \text{ s}^{-1}$  for PHB-HV and PHB-HV/xPECH. It is well known that the swelling behavior, so-called Barus effect, is related to the primary normal stress difference, one of the most important elastic properties as investigated by Vlachopoulos<sup>18</sup> and Tanner.<sup>19,20</sup> As demonstrated in the table, the swell ratio is greatly enhanced by blending xPECH.

Furthermore, the drawdown force is also listed in the table. The drawdown force, which is often employed in industries because of its convenience, is a measure of elastic response under uniaxial flow.<sup>21–23</sup> In the case of PHB-HV, however, the measurement cannot be carried out because the tension required to pull the strand is too low to detect. On the other hand, the drawdown force of PHB-HV/xPECH is considerably high. The result directly demonstrates that adding a small amount of xPECH will greatly reduce the heat-sagging, one of the serious problems at various processing techniques, such as blow-molding, extrusion, and thermoforming.<sup>14</sup> It is well known that the drawdown force closely relates to the elongational viscosity and processability. Moreover, the growth curve of transient uniaxial elongational viscosity in the linear region is three times as high as that of the shear viscosity. Considering that the blend shows slightly lower shear viscosity than the pure PHB-HV, a large part of the drawdown force for PHB-HV/xPECH is attributed to the enhanced strain-hardening behavior in elongational viscosity. The stretching of the chain sections between the crosslink points of the crosslinked polymer is responsible for the marked melt elasticity as reported for the polyolefin blend.<sup>12–17</sup>

The enhanced elastic property as shown in this study will improve the processability of PHB-HV at various processing techniques.

## CONCLUSION

Rheological properties were studied for the blends of PHB-HV and xPECH having low density of crosslink points. It is found that adding a small amount of xPECH greatly enhances the melt elasticity, such as Barus effect and drawdown force. Steady-state shear viscosity is, however, unchanged by blending xPECH. The anomalous rheological properties will be attributed to the trapped entanglements between dangling chains in the xPECH and PHB-HV molecules. The xPECH employed in this study can be used as a rheological modifier for microbial PHB and its copolymers, which will widen the application of the biomass-based polyester.

The authors thank Daiso Corporation for their valuable suggestions about the crosslink method of PECH.

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