

***GPEC 2006 Paper Abstract #2B***

**Title: The Rheology and Degradation of Renewable Resource Polymers**

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**ABSTRACT**

In recent years there has been a growing interest in the development of alternatives to petroleum based products. Bio-derived polymers have been shown to demonstrate similar mechanical properties as well as superior degradation properties to existing commercial products. One family of biodegradable polyesters of particular interest are polyhydroxyalkanoate (PHA) co-polymers. In this work, we investigate the flow behavior of both a pure PHA co-polymer, namely poly (3-hydroxybutyrate-co-3-hydroxyhexanoate), and blends of this PHA with PLA. We report on the shear and extensional flow behavior of these materials. Extensional tests of the materials are performed over a range of temperatures (155°C to 175°C) and strain rates (0.01 to 10 s<sup>-1</sup>) typically encountered in processing applications.

Transient dynamic rheological experiments, coupled with GPC analysis, were employed to determine the degradation kinetics of the materials. A random chain scission model was used to determine the degradation rate constant over a range of temperatures. Results will be presented for both the pure PHA samples as well as the PLA/PHA blends.

# **The Shear, Extensional and Degradation Rheology of Renewable Resource Polymers**

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## **Abstract**

In this work, a rheological study of a series of polymers derived from renewable resources is presented. Two poly(hydroxyalkanoate) (PHA) copolymers, PLA, and PLA-PHA blends were investigated. Dynamic oscillatory, transient, and extensional rheological tests were used to characterize the flow behavior and degradation of these materials at elevated temperatures typically encountered in processing. Steady-state values of the extensional viscosity were obtained for the two pure PHA samples, while a strain hardening behavior was observed for PLA and the two blends. Transient experiments indicate that increasing the C6 comonomer concentration increases the rate at which the PHA copolymer degrades. Likewise, an increase in the concentration of PHA in the blends also results in an increase to the degradation rate.

## **1. Introduction**

Bio-derived polymers offer an alternative to existing commercially available petroleum-based polymers. It has been shown that these materials can have similar properties to such conventional polymers as PET, polyethylene, and polypropylene [1]. Unlike most petroleum-based polymers, renewable resource materials also appear to offer potential environmental and degradation benefits. Bio-derived polymers are frequently synthesized by fermentation [2], and commonly undergo degradation far easier than petroleum-based polymers [3]. As concern surrounding waste generation continues to grow, bio-derived polymers that can degrade after use may offer a viable alternative in many applications. Conversely, potential degradation at typical processing conditions presents challenges in industrial acceptance of these materials.

We investigate the thermal and rheological properties of a series of renewable resource polymers and their blends. Dynamic rheological testing is employed to quantify the effects that temperature, co-monomer concentration, as well as blend composition have on the rheological response and degradation of these polymers. In addition to shear rheology, transient extensional testing is also performed.

## 2. Experimental

In this work, polyhydroxyalkanoates (PHA) and poly(lactic acid) were employed in the rheological testing. Two PHA copolymers were supplied by Procter & Gamble, and PLA (4032D grade) was provided by Natureworks®. The PHAs used in this study are random copolymers composed of 3-hydroxybutyrate and 3-hydroxyhexanoate monomers. The samples varied in both the molecular weight and the comonomer (3-hydroxyhexanoate) concentration. The structures of the PHA and PLA investigated are shown in Figures 1a and 1b, respectively.

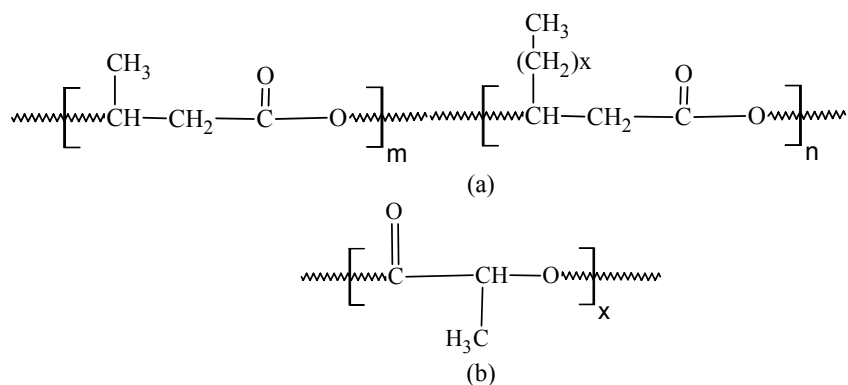


Figure 1: General structure of (a) a polyhydroxyalkanoate copolymer with m hydroxybutyrate units and n units of hydroxyhexanoate ( $x=2$ ); (b) poly-lactic acid.

Table 1 shows the properties of the two PHA samples, the PLA, and the two PLA-PHA blends studied in this work. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters 2690 Alliance system with HPLC grade chloroform and refractive index detection at 35°C. Thermal characteristics were obtained using a Perkin-Elmer DSC instrument.

*Table 1:* Properties of the materials employed in this work.

Sample	Mol % C6	MW (g/mol)	T <sub>m</sub> (°C)
PHA I	6.9	633,000	139
PHA II	12.1	871,000	102
PLA 4032D	---		175
Blend A (10% PHA I)	---		170
Blend B (20% PHA I)	---		170

All rheological testing was performed using a TA Instruments ARES rotational rheometer with an inert (nitrogen) atmosphere. The procedures used to obtain the shear and degradation rheology of PHA are discussed in greater detail in the literature [4,5]. In addition to shear rheology, the extensional viscosity was measured using the TA Instruments Extensional Viscosity Fixture (EVF) attached to the ARES rotational rheometer. The EVF fixture enables the investigator to probe the transient evolution of the extensional viscosity as a function of temperature and strain rate. Tests with a Dow Affinity Linear Low Density Polyethylene (LLDPE) (PL1880) confirm that results from the EVF were consistent with literature results [6] obtained using the established Rheometric Scientific RME instrument. Procedures for sample preparation as well as running the EVF are similar to those discussed previously [5].

### 3. Results and Discussion

#### 3.1 Dynamic Shear Rheology of PHA and PLA

Figures 2a and 2b show the dynamic frequency results of PHA Sample I at 155°C and PLA at 180°C, respectively. Rheological testing of PLA is done at higher temperatures than PHA because of the differences in melt temperature. Comparing PLA with PHA Sample I we observe that PHA is more strongly shear thinning over the shear rates probed.

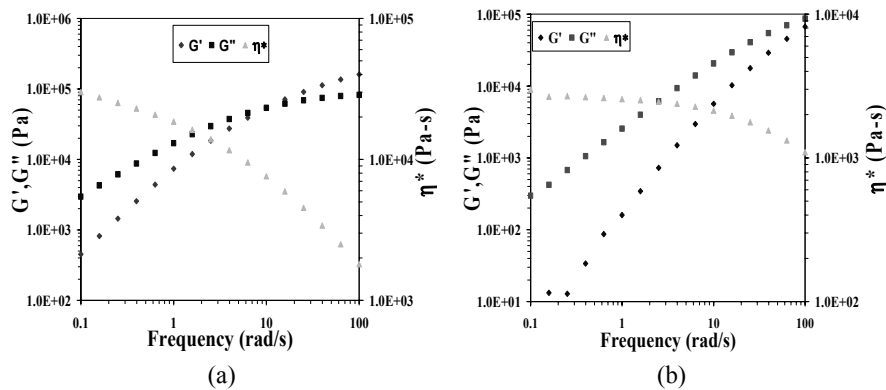


Figure 2: Dynamic properties of (a) PHA Sample I at 155°C; (b) PLA at 180°C.

#### 3.2 Extensional Rheology of PHA and PLA

Figures 3a and 3b show the transient startup extensional viscosity curves for Sample I (155°C) and PLA (185°C), respectively. Looking at the extensional viscosity of PHA Sample I, a steady-state value is achieved for all strain rates presented. Likewise, a decrease in extensional viscosity with increasing strain rate, a phenomena known as strain-rate thinning, is observed. Similar behavior is observed for PHA Sample II. However, a different trend occurs in the PLA results. For PLA, the extensional viscosity appears to plateau out to a

steady state value at short times; however, as time increases the extensional viscosity again increases. This behavior has been observed by materials such as polystyrene [7] and low-density polyethylene [8], and is known as strain hardening.

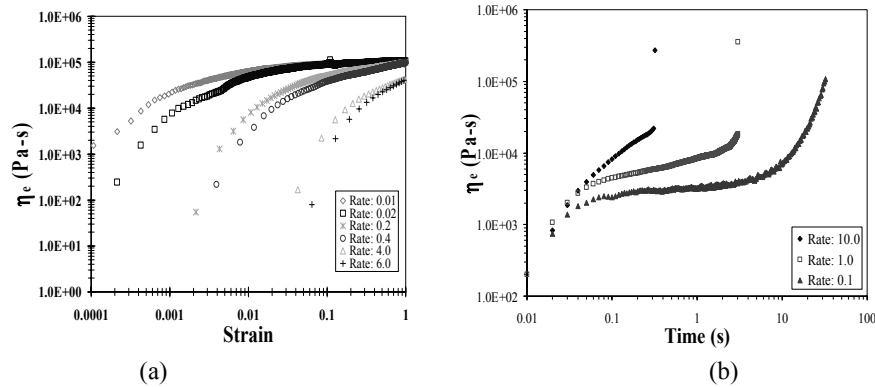


Figure 3: Extensional viscosity ( $\eta_e$ ) of PHA Samples I as a function of strain (a) and PLA as a function of time (b).

Trouton's Ratio  $T_R$  may be used to compare the extensional properties of a material to the shear properties, and is written in the following form [9]:

$$T_R = \frac{\eta_e}{\eta_o^*}. \quad (1)$$

For a Newtonian material, the Trouton Ratio is equal to 3. For the PHA samples,  $T_R$  is approximately equal to three, which may be expected a low strain rates where a steady value of the extensional viscosity is achieved. However, in the case of PLA the Trouton ratio exceeds three due to the strain hardening characteristics of the material.

### 3.3 Transient Dynamic Rheology of PHA

At elevated temperatures, it is well-known that many polymers derived from renewable resources degrade. Figures 4a and 4b show the scaled complex

viscosity as a function of both time and temperature for PHA Samples I and II, respectively. The complex viscosity decreases more rapidly in PHA Sample II, reflecting a higher rate of degradation due to a higher 3-hydroxyhexanoate comonomer concentration. We also observe that with increasing temperature the polymer degrades more rapidly.

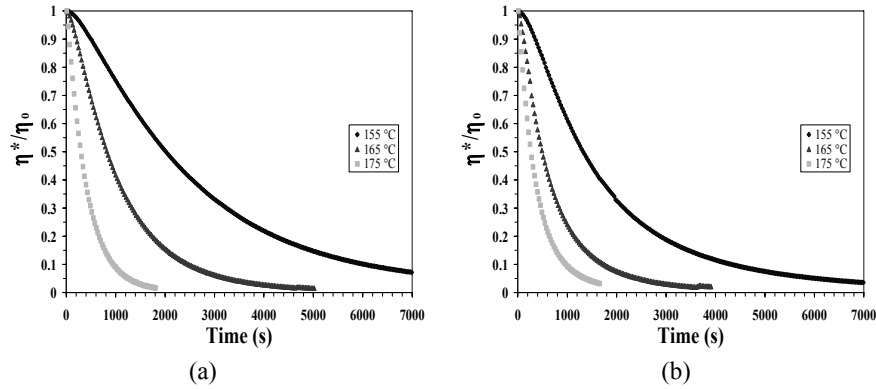


Figure 4: Dynamic Time Sweeps of PHA (a) Sample I; (b) Sample II.

### 3.4 Kinetics of Degradation of PHA

The transformation of rheological data to degradation kinetics for PHA is discussed by Daly et al. [4] in more detail. The rate constant,  $k_2$ , may be determined from the following expression [10]:

$$\frac{1}{\eta^\alpha} = \frac{1}{\eta_o^\alpha} + k_2 t \quad (2)$$

where  $\eta$  is the viscosity at time  $t$ ,  $\eta_o$  is the initial shear viscosity prior to degradation, and  $\alpha$  is 1/3.4, where 3.4 represent the molecular weight dependence of the zero-shear viscosity. Applying Equation (2) to the rheological data of Figure 4, we are able to obtain  $k_2$  at varying temperatures

from the slope of the curves shown in Figure 5. The linearization of the data confirms the form of Equation 2.

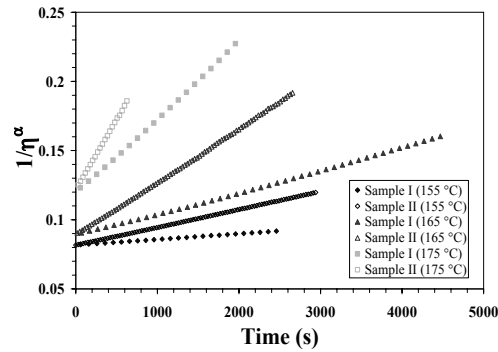


Figure 5: Linearization of the rheological data according to Equation (2) of PHA copolymers at varying temperatures.

### 3.5 Degradation Effects on the Extensional Rheology of PHA

Given the results presented above, we chose to investigate the effects of polymer degradation in the extensional viscosity measurements. A major obstacle in this goal is that at very low strain rates ( $< 0.001 \text{ s}^{-1}$ ) and elevated temperatures, sagging becomes a major issue in the EVF experiments. In addition, the EVF experiments may only be performed for a finite time due to experimental limitations. To overcome these complications, samples were pressed at the desired temperature ( $155^\circ\text{C}$ ) and held for various lengths of time (30 and 60 minutes) before being cooled down and tested using the EVF. During the pressing, degradation is expected to occur due to the elevated temperature.

Figures 6a and 6b show results for the extensional viscosity, at a strain rate of  $1.0 \text{ s}^{-1}$  and after pressing the samples for a fixed interval, for PHA Samples I



and II, respectively. A steady state value is achieved or approached for both samples even after degradation. The extensional viscosity decreases with increasing pressing time for both materials, indicating that the polymer has degraded during the pressing. When comparing the shear viscosity and the extensional viscosity after degradation of 30 and 60 minutes, it is observed that the Trouton ratio continues to hold for both samples.

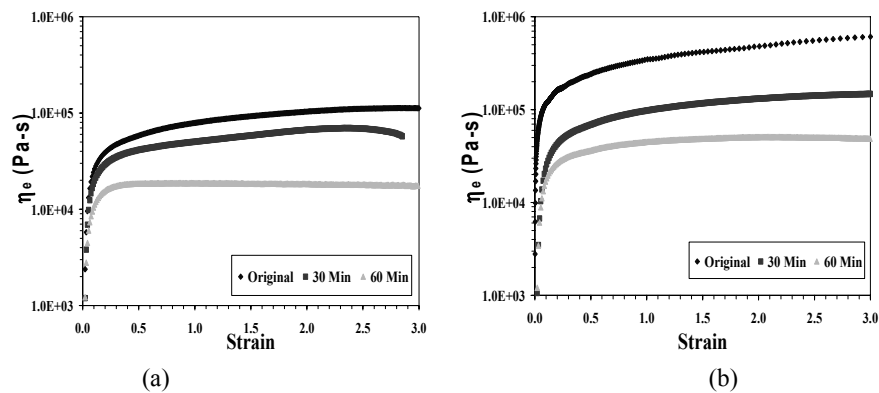


Figure 6: Effects of Degradation on  $\eta_e$  of PHA Samples I (a) and II (b) at 155°C.

### 3.6 Dynamic Rheology of PLA-PHA Blends

PLA was blended with 10% PHA Sample I (Blend A) and 20% PHA Sample I (Blend B) using a twin-screw extruder. A rheological characterization was then performed on both of these blends at 165°C.

Increasing the mass concentration of PHA shows an increase degree of shear thinning of the blend as seen in Figure 7. Observing trends in the shear-thinning region, we see that Blend A and pure PLA appear to have similar slopes. However, Blend B demonstrates much stronger shear thinning, similar to that of Sample I in Figure 2a, and reflecting the influence of the PHA content on the rheological properties.

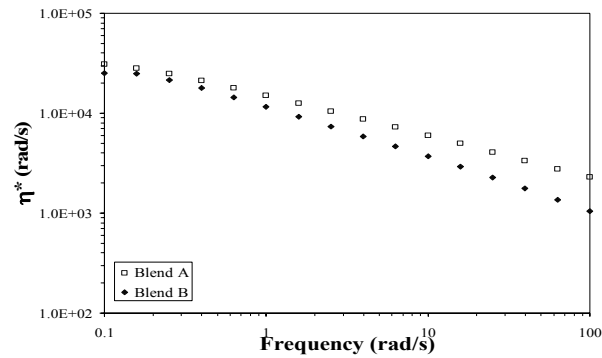


Figure 7: Comparison of Complex Viscosity Blends at 165°C.

### 3.7 Extensional Rheology of PHA-PLA Blends

Figures 8a and 8b illustrate the evolution of extensional viscosity of the blends as a function of time for a range of strain rates. By increasing the mass concentration of PHA a decrease in extensional viscosity is observed due to the elevated temperatures at which the measurements were performed. The extensional viscosity of both blends is also observed to increase over time, rather than reach a steady state. This result is consistent with the strain hardening behavior of pure PLA.

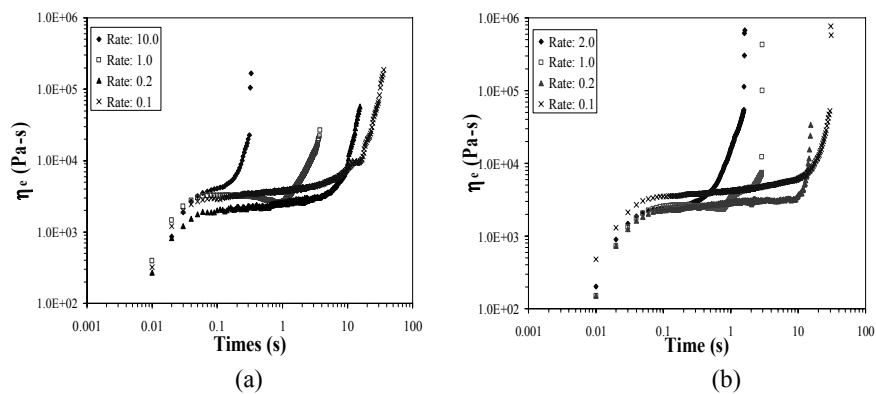


Figure 8: Start up of  $\eta_e$  at varying strain rates and at 185°C for (a) Blend A (a); (b) Blend B.

### 3.8 Degradation of PHA-PLA Blends

Finally, we turn to the degradation behavior of the PHA-PLA blends. Figure 9 shows the dynamic time sweep results for pure PLA, pure PHA Sample I, Blend A, and Blend B at 175°C. It is known that PHA degrades more rapidly than PLA. Since the two blends are low mass concentrations of PHA, they are less likely than pure PHA to degrade at elevated temperatures. As expected, the blends fall midway between the pure PLA and the pure PHA degradation behavior. Efforts are underway to determine the degradation kinetics of the blend materials.

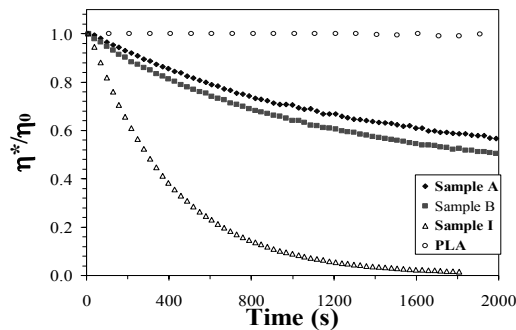


Figure 9: Comparison of Degradation of PLA, PHA I, Blend A, and Blend B at 175°C.

## 4. Summary

The rheological and degradation behavior of a series of renewable resource polymers were investigated. Steady-state values for extensional viscosity of the two PHA samples were observed, as well as a strain rate thinning behavior. However, the extensional viscosity of PLA and the two blends demonstrated a strain hardening behavior. Transient testing was performed to investigate the effect that PHA concentration has on the PHA-PLA blend rheology.

## 5. References

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