

Thermal Degradation Kinetics of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

Patricia A. Daly,¹ David A. Bruce,¹ David H. Melik,² Graham M. Harrison¹

¹Department of Chemical Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634

²The Procter & Gamble Company, Corporate Research and Development, 8611 Beckett Road, West Chester, Ohio 45069

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ABSTRACT: The degradation kinetics of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), a member of the Nodax family of polymers, were investigated using transient constant shear rate and dynamic time sweep rheological tests. The rate of chain scission at several times and temperatures was correlated with viscosity data and verified using molecular weight determination of the degraded samples. The experimental results show that the molecular weight and the viscosity of Nodax decrease with time over the range of temperatures that were studied (155–175°C). The degrada-

tion kinetics, which exhibited first-order behavior, were determined as a function of the flow history and thermal history. An apparent activation energy of 189 ± 5 kJ/mol for thermal degradation was found by modeling variations in the rate with temperature using an Arrhenius law model. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 66–74, 2005

Key words: polymer degradation; kinetics; rheology; polyhydroxyalkanoate

INTRODUCTION

Bioderived polymers, such as polylactide (PLA), continue to gain acceptance in commodity polymer applications as well as high value-added specialty applications such as biomedical implants.¹ Initially, PLA and related materials were limited to biomedical applications because of the high price of the polymer (>\$5/lb in 1995); however, significant improvements in production methods^{2,3} have made some of these materials cost competitive with existing petroleum-based commodity polymers such as polyethylene and related polyesters. For example, PLA fibers are being used in many consumer products, including blankets, clothing, and pillow fibers; and molded PLA films are being used for one time use consumer items, such as cold food containers.

The driving forces behind much of the development of new low cost bioderived polymers (e.g., Nodax, Sorona, Eastar, etc.) stem from environmental concerns and government incentives aimed at reducing green house gas emissions, oil dependency, and waste generation. The primary goal of these new polymers is

to have mechanical properties similar to commercially successful petroleum-based polymers, but in today's business environment bioderived polymers will only become competitive with existing commercial polymers when they can be interchanged with no loss of properties or profits.

As the disposal of polymer waste becomes an increasingly significant environmental and political issue, the ability to undergo biodegradation on a relatively short time scale is an attractive attribute for many single-use commodity thermoplastics. However, for bioderived polymers to achieve widespread acceptance in the manufacturing arena, they must be sufficiently stable to undergo processing at elevated temperatures. Polyhydroxyalkanoates (PHAs) are a well-established class of bioderived biodegradable polymers that have been proposed for a variety of commercial applications.⁴ Of particular interest is a class of PHAs that are copolymers of polyhydroxybutyrate and other hydroxyalkanoates. The structure of a copolymer of hydroxybutyrate and a generic hydroxyalkanoate is shown in Figure 1.

The first commercial PHA, Biopol, is a copolymer of hydroxybutyrate and hydroxyvalerate. Researchers at Procter & Gamble have recently developed a series of PHAs known as Nodax, which are currently synthesized biologically and extracted from fermentation products. The difference between Biopol and the Nodax family of PHAs is the length of the alkyl branches that are present along the polymer backbone (i.e., the value of x in Fig. 1). For Biopol the value of x

Correspondence to: G. M. Harrison (graham.harrison@ces.clemson.edu).

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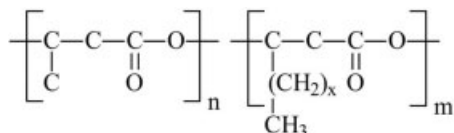


Figure 1 The general structure of a polyhydroxyalkanoate with n hydroxybutyrate units and m units of a branched hydroxyalkanoate.

is 1, whereas for the Nodax family of polymers the value of x ranges from 2 to 18. The difference in the properties of Biopol and the Nodax family of polymers is due in large part to the effect that the branch length has on the crystallization behavior of the material. Specifically, PHAs having extended alkyl chain branches are less brittle and more amenable to a wider range of processing conditions and end-use applications.⁵ For brevity, the PHA copolymer used in this study, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate), will be referred to as Nodax for the remainder of the article.

Studies of the thermal degradation of polymers have typically been carried out using thermogravimetric analysis (TGA) and pyrolysis. TGA is a technique in which the change in mass of a polymer sample is measured while the sample is heated at a constant rate in either an inert or oxidizing atmosphere. The data from TGA experiments can be used directly or in the form of differential TG curves to determine the kinetic parameters, such as the apparent activation energy (E_a), rate constant (k), and order of reaction (n).⁶ In a pyrolysis experiment, the sample is quickly heated to a high temperature [much greater than the melting temperature (T_m)] for a short period and the gas products are captured and analyzed using gas chromatography coupled with mass spectrometry.^{6,7} Through this technique, the identity and the relative amounts of products are identified and the degradation kinetic parameters for the system under investigation may be elicited.

A less common approach for determining the degradation kinetics of polymers involves the use of transient flow experiments.^{8–10} In these experiments, the viscosity and molecular weight of a polymer are monitored with time as the material undergoes constant shearing or deformation. The advantage of this technique is that the experimental conditions used to observe polymer degradation resemble the environment seen by a polymer during normal processing. One such study used a flow cell incorporating a torque meter to determine the degradation kinetics of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate).⁸ By monitoring the molecular weight and torque with time at varying temperatures, the authors were able to ascertain the polymer degradation kinetic parameters. Seo and Cloyd⁹ used a rotational rheometer to measure

the polymer viscosity directly as a function of temperature and time. The results were then used to determine the degradation kinetics for polyester. These types of kinetic studies offer the advantage of accurately accounting for the effect of both mechanically and thermally induced degradation as compared to pyrolysis or TGA studies that monitor only the effect of thermal degradation. Although the same general information can be obtained from both the torque meter and the rotational rheometer, experiments performed in a rotational rheometer have the advantage of having a well-defined flow field as well as tighter temperature control.

In this work, we examined the degradation of Nodax as a function of temperature and flow history through a comprehensive rheological investigation. Based upon the rheological results, we also report on the degradation kinetics of the material.

EXPERIMENTAL

Materials and methods

Nodax was provided by Procter & Gamble. The as-delivered weight-average molecular weight (M_w) was 670,000 with a polydispersity index (PDI) of 1.9. Nodax exhibited two melt temperatures: 134 and 148°C.

Rheological testing was performed on a TA Instruments ARES rotational rheometer using a 25-mm cone and plate geometry with a cone angle of 0.1 rad. The Nodax polymer pellets were compression molded into disks with a diameter of 25 mm before the rheological tests. To minimize the possibility of degradation prior to the beginning of a rheological experiment, fresh samples were used for each experiment.

The samples were loaded into the rheometer after a nitrogen atmosphere was used to bring the oven to the experimental temperature. Initially, the gap between the cone and the plate was set to 0.1 mm and the excess polymer was wiped away. Then, the gap was set to the experimental separation of 0.056 mm. Both dynamic and transient experiments were performed. Prior to the dynamic oscillatory frequency sweeps, the linear viscoelastic regime was determined using a strain sweep at a constant frequency. In addition to standard dynamic oscillatory frequency sweeps, two types of transient tests were performed: a dynamic time sweep test and a transient constant shear rate test. For the dynamic time sweep experiments, the sample was subjected to a repeated oscillatory deformation (of a constant frequency and maximum strain) for a specific time interval. The storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) were measured as a function of time. For the transient constant shear rate test, the sample was subjected to a constant shear rate for the specified time, and the

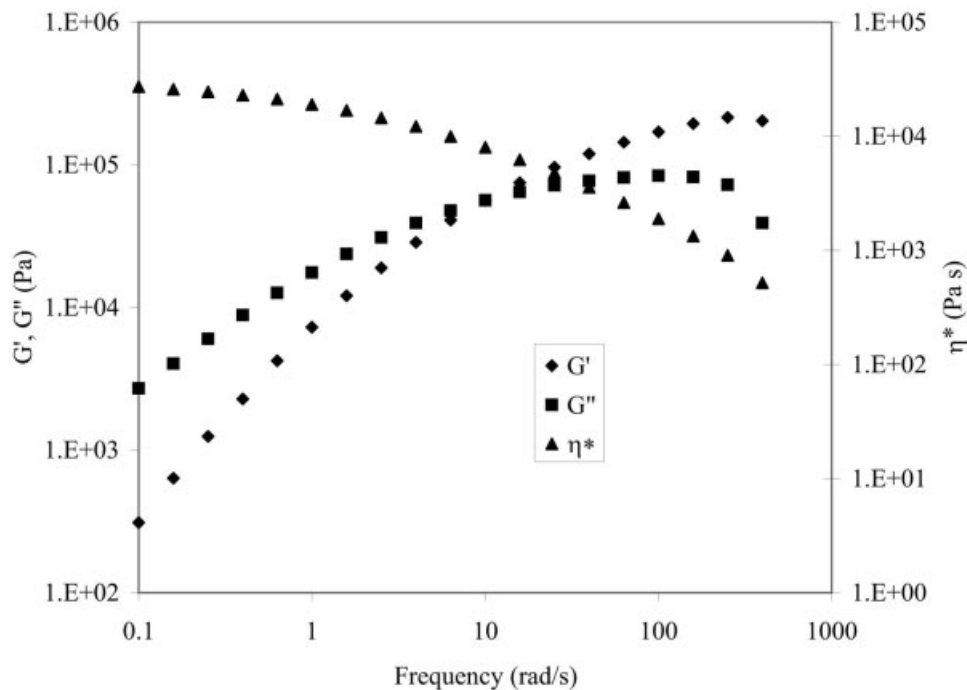


Figure 2 The linear viscoelastic spectra of Nodax at 155°C.

viscosity was measured as a function of time. Except as noted, all experiments were conducted under a nitrogen atmosphere.

The dynamic time sweep tests were designed to probe polymer degradation in the absence of significant deformation of the polymer. A small oscillatory motion (10 rad/s) was applied, and the dynamic response (G' and G'') was measured. From the dynamic moduli, the η^* value was calculated. The transient constant shear rate tests measured the evolution of the viscosity as a function of time at a constant shear rate of 0.1 s^{-1} . Both types of test were conducted for times ranging from 30 to 90 min. At the conclusion of each rheological test, the samples were rapidly cooled and removed from the rheometer for molecular weight analysis.

To investigate the effects of temperature on the degradation kinetics, the rheological tests were run at 155, 160, 165, 170, and 175°C.

Molecular weights were determined from gel permeation chromatography (GPC), using a Waters 2690 Alliance system with HPLC grade chloroform and refractive index detection at 35°C with two consecutive Polymer Laboratories PLgel 5- μm mixed-D and mixed-E columns. Polymer Laboratories EasiCal PS-2 polystyrene standards were used for calibration.

RESULTS

Rheology

A dynamic frequency sweep of Nodax at 155°C is shown in Figure 2. Because Nodax degrades with time

at elevated temperatures, the range of frequencies that were investigated was limited. Multiple sweeps with both increasing frequency and decreasing frequency were performed to ensure reproducibility and to demonstrate that there is minimal degradation occurring during the time required for the experiment ($<5 \text{ min}$). From the linear viscoelastic spectrum of Nodax, the zero-shear η^* was determined to be 30,000 Pa s. This viscosity value was consistent with the zero-shear η^* value of 40,000 Pa s reported by Satkowski et al.⁵ for a similar PHA containing a slightly higher comonomer content and greater molecular weight that was measured at 150°C.

Figure 3 shows both the shear viscosity (η) and η^* as a function of the rate of deformation at 155°C. As with the dynamic frequency sweep, the viscosity values were obtained before significant degradation occurred. The onset of shear thinning occurs at approximately 2 s^{-1} . At low shear rates, it is apparent that Nodax follows the Cox–Merz rule, allowing us to infer the shear viscosity from complex viscosity data in subsequent experiments.

The time dependent dynamic rheological behavior of Nodax was observed over temperatures ranging from 155 to 175°C. Dynamic time sweeps, performed using a frequency of 10 rad/s, are shown in Figure 4. The reduced η^* [i.e., the value of the η^* at time t (η^*_t) scaled with the initial value of the η^* (η^*_0)] is plotted as a function of time. Looking first at the effect of time on the complex viscosity, it is apparent that the viscosity decreases with increasing time. At 155°C, there was a gradual decrease in

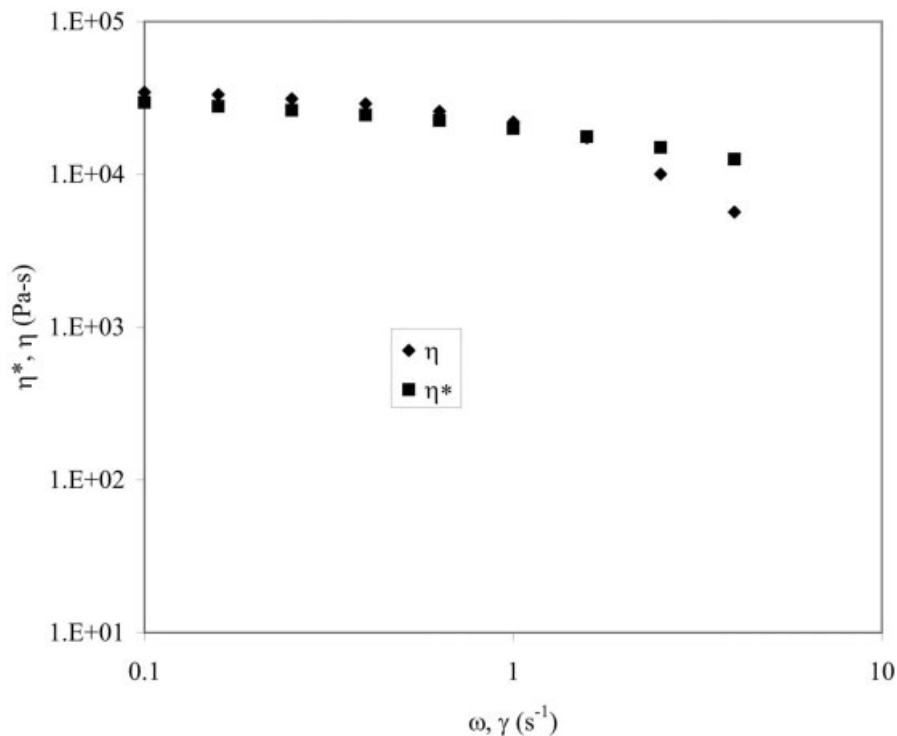


Figure 3 The complex and shear viscosity of Nodax as a function of the deformation rate at 155°C.

the viscosity over the entire length of the experiment, reflecting the thermal degradation of the polymer. As the temperature was raised above 165°C, there was an accelerated decrease in the vis-

cosity followed by a more gradual decay at times greater than 2000 s. For example, at 175°C the complex viscosity decreased by 96% within 50 min of testing; however, the viscosity only decreased an-

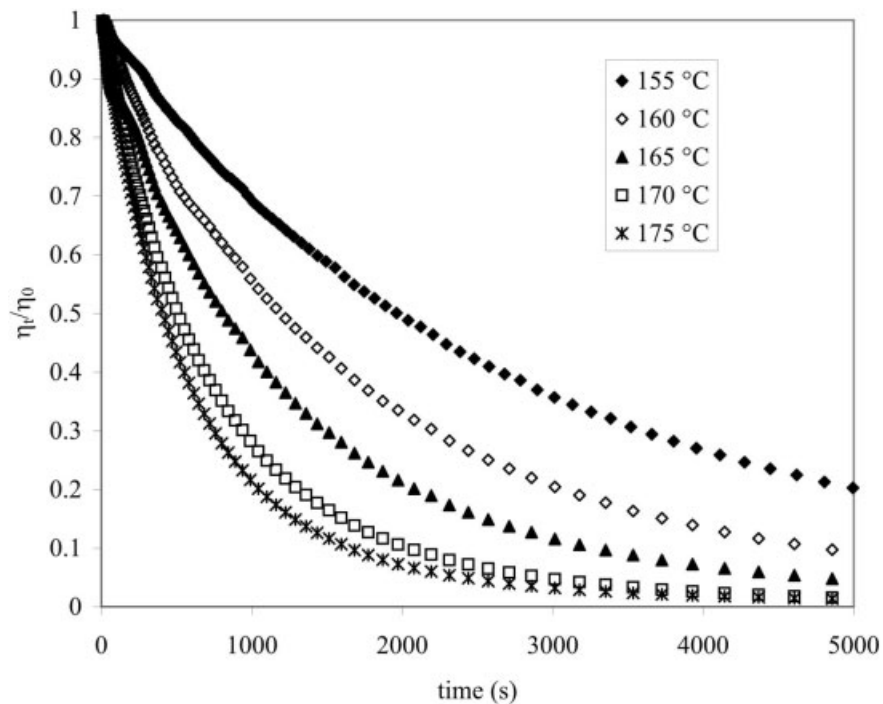


Figure 4 The reduced complex viscosity (10 rad/s frequency) of Nodax as a function of the time and temperature.

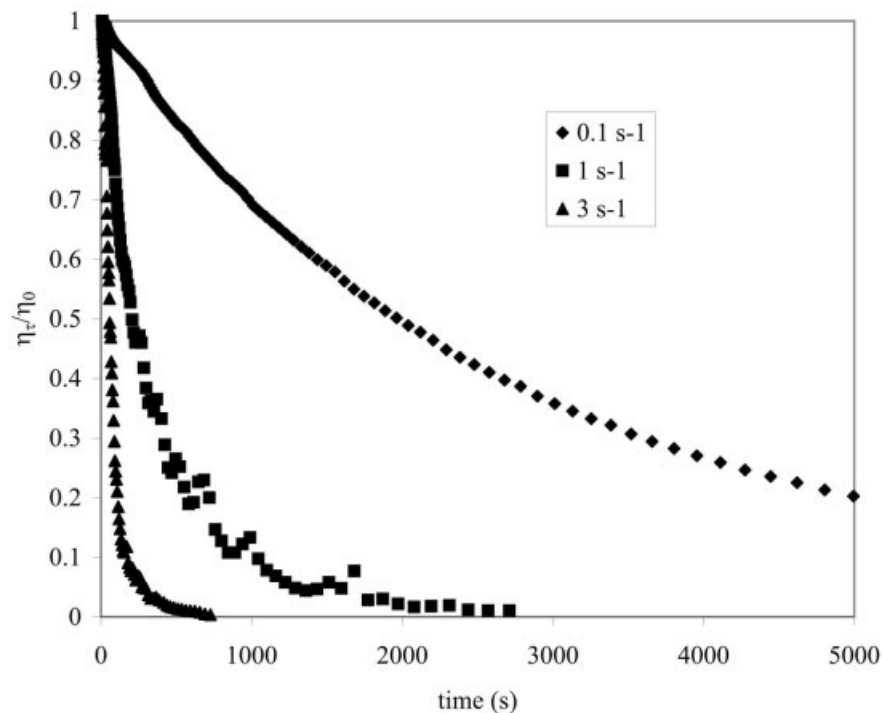


Figure 5 The variations in the reduced shear viscosity of Nodax at 155°C from the thermal and mechanical degradation.

other 3% during the last 40 min of testing. The behavior exhibited by Nodax is consistent with a first-order decay process.

During rheological testing it is possible that mechanical degradation is occurring in addition to thermal degradation. In order to track the effects of mechanical degradation, transient shear tests were performed at 155°C using constant shear rates ($\dot{\gamma}$) of 0.1, 1.0, and 3 s⁻¹. The results of these transient shear experiments are shown in Figure 5. As the shear rate is increased, the viscosity decreases more rapidly with time, reflecting an increase in the effect of mechanical degradation with higher deformation rates. Specifically, the η of Nodax was decreased by 20% following 90 min of shearing at $\dot{\gamma} = 0.1$ s⁻¹ whereas it was decreased by 99% after 45 min of shearing at $\dot{\gamma} = 1$ s⁻¹. Further, at $\dot{\gamma} = 3$ s⁻¹, shear viscosity η decreased by 99% in less than 10 min. It should be noted that mechanical degradation was most pronounced at temperatures just above the melting temperature. The effects of mechanical degradation appeared to be less significant as the temperature was increased and appeared to have essentially no effect at 175°C because of the rapid thermal degradation occurring at these elevated temperatures.

Because it is well known that many biodegradable polymers, such as PLA, undergo hydrolytic degradation in the presence of low concentrations of water,⁴ it was important to determine if the degradation of Nodax was significantly affected by the moisture in the atmosphere surrounding the polymer melt during

rheological studies. To investigate the effect of moisture present during testing on the degradation process, dynamic time sweeps were performed at 175°C with and without a nitrogen environment. (All other experiments in this article are conducted in a nitrogen atmosphere.) As can be seen from Figure 6, the decrease of η^* with time was not significantly affected by the heating medium (atmosphere) employed. In addition, the results obtained using samples dried overnight at 55°C in a vacuum oven prior to the experiments were indistinguishable from those that were not dried before experiments were conducted. This implies that Nodax undergoes thermal and mechanical degradation in the absence of hydrolytic degradation because the rate of hydrolytic degradation depends on the moisture content of the system.

Molecular weight determination

Polymer samples were collected after transient dynamic tests lasting 30, 60, and 90 min. After the rheological experiment, the molecular weight of the samples was determined by GPC. The M_w data as a function of the transient dynamic test time for all test temperatures are presented in Figure 7. In general, the M_w decreased with an increase in test time and temperature. This was the expected result for polymer degradation via chain scission because the length of polymer chains should decrease with time. It is also reasonable to assume that the number of chain

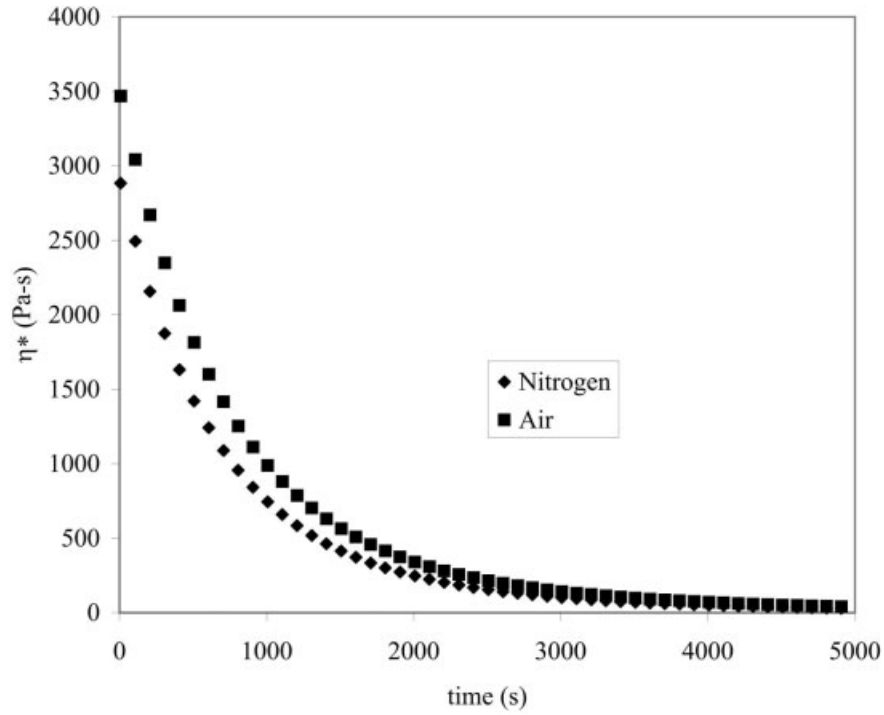


Figure 6 The effect of the oven environment on the evolution of the complex viscosity of Nodax as a function of time at 175°C.

scissions will be more rapid at elevated temperatures because thermal degradation is more pronounced. The PDI of all samples, when available, was between 1.7

and 1.9. The initial PDI was 1.9, which tended to decrease slightly during rheological testing, although no clear trend was observed.

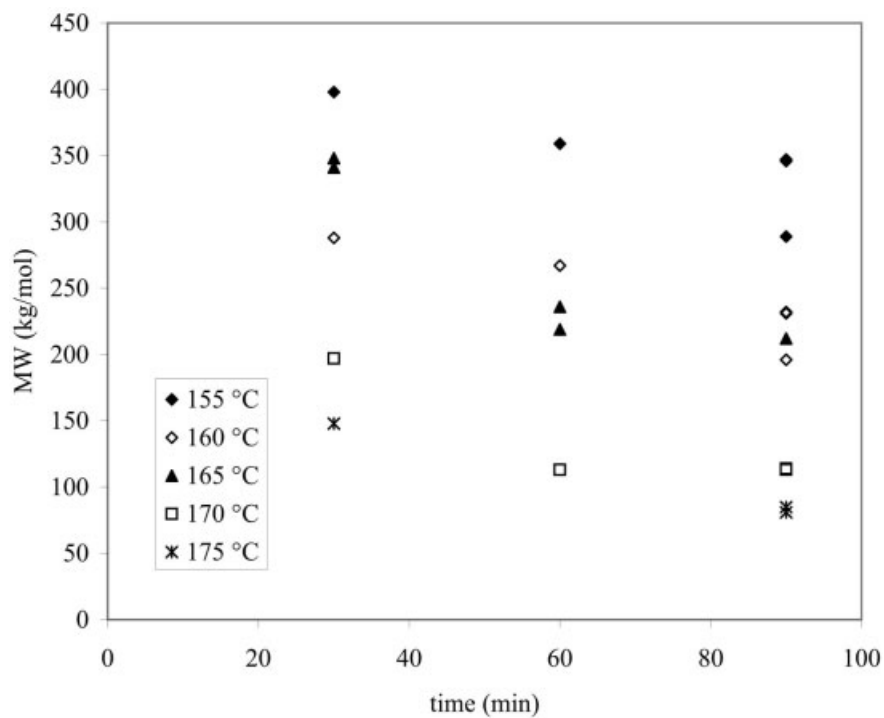


Figure 7 The weight-average molecular weight of Nodax samples as a function of the transient dynamic shear test time and temperature.

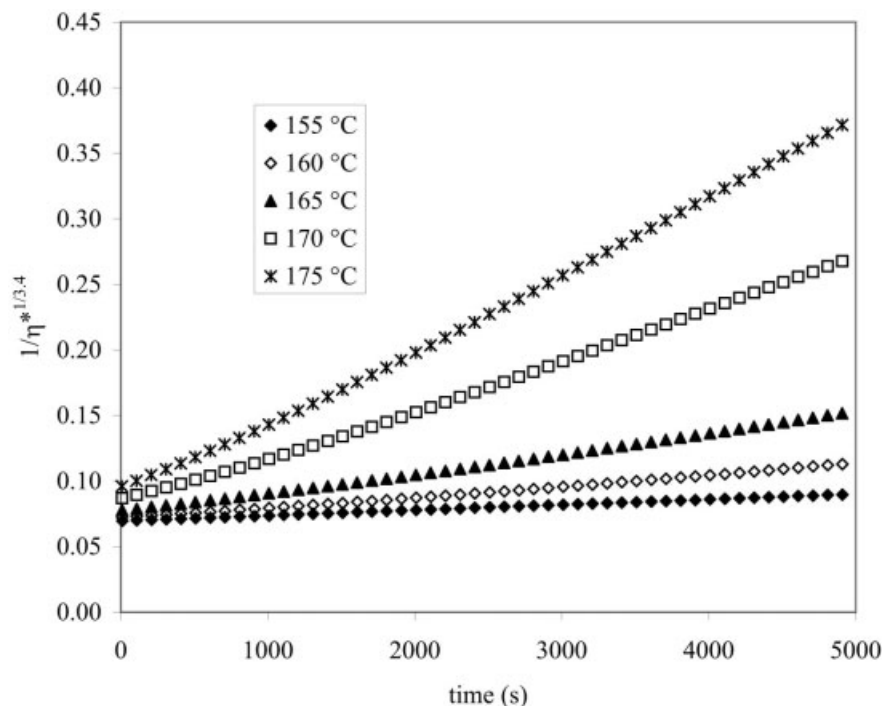


Figure 8 Linearization of the rheological data used to determine the degradation kinetics of Nodax. A frequency of 10 rad/s was used in all experiments.

Degradation kinetics

The kinetics of thermal degradation of Nodax induced during rheological testing were investigated. Similar studies have been performed on other PHAs and the thermal degradation was found to exhibit first-order kinetics.⁸ The degradation kinetics were determined using data presented in the previous section for two types of transient rheological tests: dynamic time sweep tests and transient constant shear rate tests.

The thermal degradation was assumed to be the result of random chain scission, where the rate of bond cleavage is proportional to the concentration of polymer links as shown in eq. (1):

$$\frac{d\phi}{dt} = -k_T\phi \quad (1)$$

where ϕ is the number of polymer links per unit volume and k_T is the thermal degradation rate constant. The degree of polymerization (DP) and M_w are related to ϕ by the following relationships:

$$\ln \phi = \ln \left[N \left(1 - \frac{1}{DP} \right) \right] \cong \ln(N) - \frac{1}{DP} = \ln(N) - \frac{M_o}{M_w} \quad (2)$$

where N is the total number of monomer units, M_o is the molecular weight of a monomer unit, and DP is

assumed to be much greater than 1. Combining eq. (2) with the integrated form of eq. (1) yields the following:

$$\frac{M_o}{M_{w,0}} - \frac{M_o}{M_w} = -k_T t \quad (3)$$

where $M_{w,0}$ is the initial M_w of the polymer.

For many polymers the following can be used to relate the M_w to the viscosity¹¹:

$$\eta = KM_w^{3.4} \quad (4)$$

where K is a coefficient that depends on the temperature and polymer type. Finally, eqs. (3) and (4) yield the form of the rate equation that was used to determine the observed degradation rate constant:

$$\frac{1}{\eta^\alpha} = \frac{1}{\eta_0^\alpha} + k_2 t \quad (5)$$

In eq. (5), η is the viscosity at t , η_0 is the viscosity at $t = 0$, α is 1/3.4, and k_2 is the observed degradation rate constant.⁹ It should be noted that k_2 is not equivalent to k_T . The relationship between k_2 and k_T is defined as follows:

$$k_2 = \frac{k_T K^{-1/3.4}}{M_o} \quad (6)$$

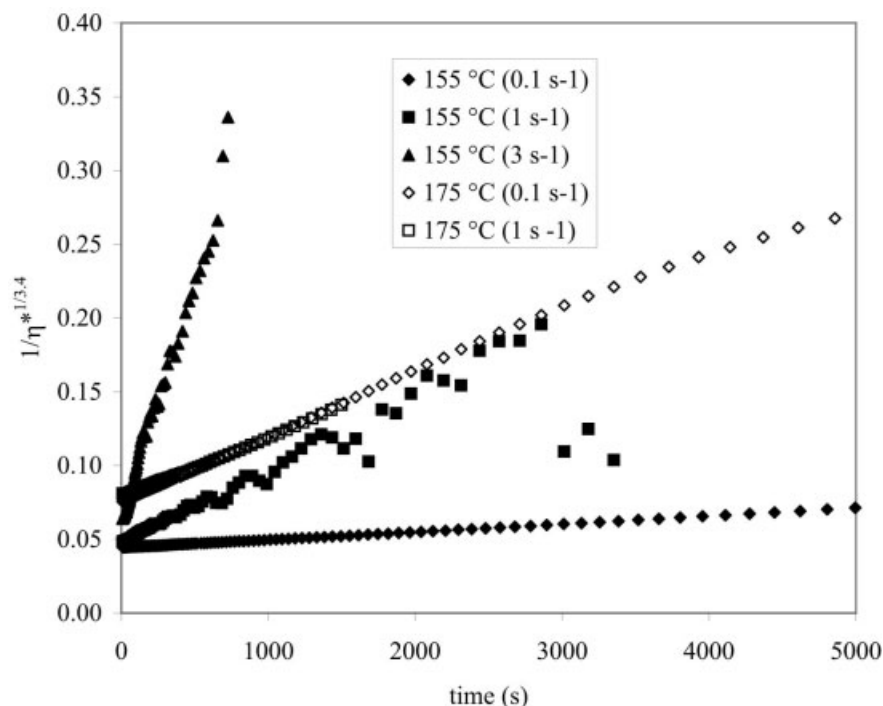


Figure 9 The effect of the deformation rate on the value of the degradation rate constant (k_2) for samples tested at 155°C at 0.1, 1, and 3 s^{-1} and at 175°C at 0.1 and 1 s^{-1} .

Plots of $1/\eta^\alpha$ versus t (shown in Fig. 8 for the 10 rad/s experiments at all test temperatures) show a linear relationship for all of the test conditions. Thus, it was assumed that the first-order chain scission, power-law model was sufficient to describe the degradation kinetics of Nodax. Subsequently, a degradation rate constant was calculated for each test condition. As expected for polymer degradation, k_2 increased with increasing test temperatures. Indeed, k_2 increased by more than an order of magnitude (a factor of 12) over the 20°C variation in temperature (155–175°C) probed in these experiments. The effect of the shear rate on k_2 as well as the dependence of the mechanical degradation effects on the temperature can be seen in Figure 9. There was a dramatic increase in the value of k_2 (i.e., the slope of the line) at 155°C when the shear rate was increased, whereas there is no variation in k_2 with the shear rate at 175°C. This indicates that the effects of mechanical degradation on the rate of degradation are much more pronounced at lower temperatures.

It was assumed that k_2 followed the Arrhenius relationship with temperature as shown by eq. (7):

$$k_2 = Ae^{(E_a/RT)} \quad (7)$$

where A is the preexponential factor, R is the gas constant, T is the absolute temperature, and E_a is the apparent activation energy for thermally induced chain scission.

An Arrhenius plot of the rate constants for this system is shown in Figure 10. The rate constants are for the transient constant shear rate test at 0.1 s^{-1} and the dynamic time sweep tests at 10 rad/s. The apparent activation energy determined from the linear least-squares fit of the data was 189 ± 5 kJ/mol. This compares favorably with the E_a values found in the literature. For example, an apparent E_a of 160 ± 26 kJ/mol was found for poly(3-hydroxybutyrate-co-3-hydroxyvalerate) in the torque measurement experiment mentioned previously.⁸ We believe that the use of a rotational rheometer, with a well-defined flow field and a constant shear rate, along with control of the temperature to within $\pm 0.1^\circ\text{C}$ throughout the sample leads to a better measurement of the activation energy.

CONCLUSIONS

Transient rheological tests were used to determine the degradation kinetics of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), a member of the Nodax family of polymers. The apparent activation energy of thermal degradation was calculated to be 189 ± 5 kJ/mol. It was shown that the shear and complex viscosities decreased with increasing time for all temperatures, reflecting the thermal degradation of the polymer. The rate at which the viscosity decreased was increased with increasing temperature, and it was dramatically

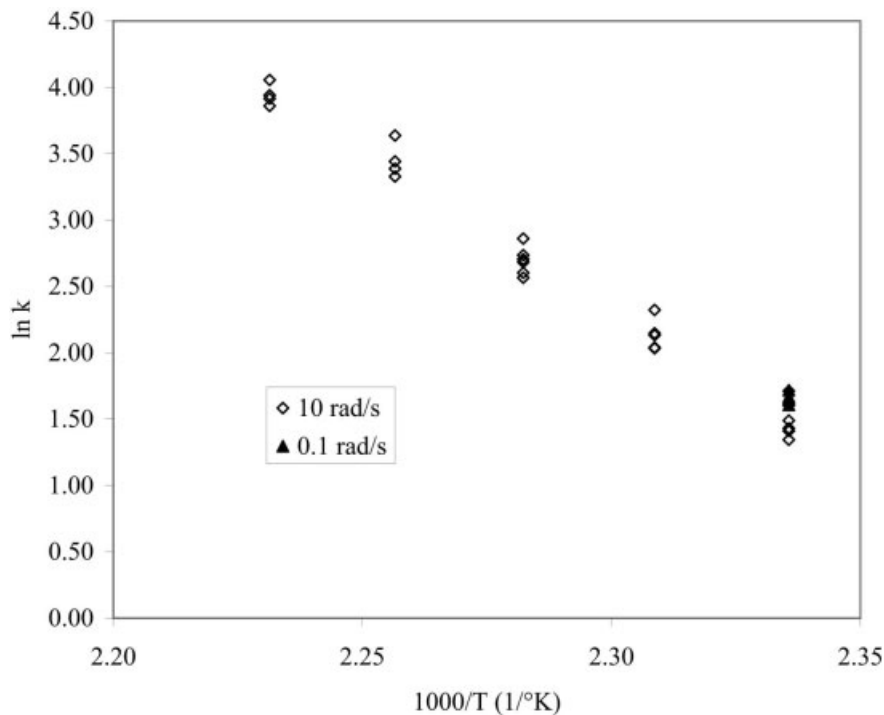


Figure 10 The Arrhenius plot for tests performed at 0.1 s^{-1} and 10 rad/s for all test temperatures.

higher for temperatures greater than 165°C . The degradation of Nodax was more pronounced at higher shear rates (1 and 3 s^{-1}) compared to tests performed at a shear rate of 0.1 s^{-1} or a dynamic frequency of 10 rad/s . The increase in the rate of degradation seen at higher shear rates decreased with increases in the temperature and was negligible at 175°C . The measured M_w decreased with increasing test time and higher temperatures as a consequence of increasing degradation.

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