Thermal Stability of Bio-Derived Polymer Feedstock

Keywords: Rheology, thermal stability, degradation, sustainable polymers, environmental conditions, oscillatory shear

ABSTRACT

Bio-derived and biodegradable polymer feedstocks are a popular form of polymers which can be derived from sustainable resources and/or are able to undergo biodegradation. While the degradation/decomposition is favorable from a sustainability point of view, it presents new characterization challenges for processing, where conditions must be optimized to preserve the properties of the initial feedstock. Rheology is an indispensable tool to characterize structural molecular changes induced due to processing conditions and processing time.

INTRODUCTION

Poly-lactic acid (PLA) is a semicrystalline polyester thermoplastic that can be synthesized chemically or through fermentation.[1] It has useful properties including mechanical properties comparable to olefin based thermoplastics, moderate thermal resistance, and biocompatibility.[1,2] Depending on the stereo isomer composition, the crystallinity can be tuned to tailor the mechanical and optical properties.[3] As such, PLA has a wide variety of uses including consumer goods, medical products, and some forms of packaging. What makes PLA particularly popular is that it can be produced from renewable resources and is biodegradable.[2] This positions PLA as a very useful polymer for single use or disposable products as the world increasingly takes into account sustainability into the economics of production. As a biodegradable product, PLA can be mechanically/chemically recycled, composted, or incinerated.[4,5]

Figure 1. PLA feedstock with leaf representing the bioderived nature of the polymer.

Although PLA is biodegradable, this results in a potential lack of thermal stability when processing it in polymer melt form. High temperatures and exposure to moisture saturated gases (and/or oxygen containing gases) such as air can pose a problem, as the PLA can degrade during processing. This results in properties that vary from the raw feedstock after processing. PLA is known to degrade through four mechanisms. In the presence of moisture PLA degrades through hydrolytic degradation.[6] At high temperatures, PLA undergoes thermal degradation which includes the breakdown of chains into chains of smaller molecular weight, cyclic oligomers, and side reactions.[7] In the presence of oxygen, PLA undergoes oxidative degradation resulting in chain scission.[8] Lastly, PLA undergoes photodegradation when exposed to UV light.[9] Understanding and quantifying the degradation is key for producers to produce the strongest and most consistent parts, with similar properties to the input feedstock.

Figure 2. TA Instruments ARES-G2 Rheometer with forced convection oven (FCO) equipped.

Rheology allows for the characterization of degradation in the melt phase, as it is very sensitive to changes in molecular structure and can measure the changes of a fluids material properties with time. The TA instruments ARES-G2 equipped with a forced convection oven (FCO) is particularly useful in this case, as it provides exceptional torque and strain resolution. The FCO oven is very thermally responsive and has the ability to change the testing atmosphere between dry air and nitrogen in the same experiment. With the melt ring preparation kit, samples can be loaded directly from raw feedstock in pellet form (minimizing melt press degradation), with excellent reproducibility. In this applications note, the time dependent degradation of PLA during processing is characterized at various temperatures, and under the presence of air and nitrogen.

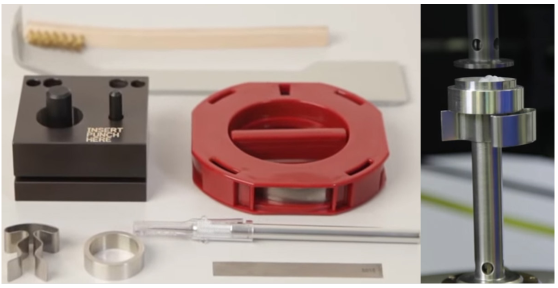

Figure 3. TA Instruments ARES-G2 melt ring kit, allowing for sample loading from pellet feedstock.

EXPERIMENTAL DESIGN

Oscillation time sweep experiments were setup with an angular frequency of 1 rad/s, a strain of 1% (which was within the linear viscoelastic region), a gap of 1 mm, for 1 hour, at temperatures of either 170, 180, or 190 °C, and with a chamber environment of either a nitrogen or air.

DATA AND RESULTS

Using rheology, the viscosity and viscoelastic properties of a material can be measured over time without the deformation physically changing the sample. This can be done by performing an oscillatory time sweep, in which the sample is deformed in a sinusoidal manner at small amplitudes within the linear viscoelastic region (LVR). One of the ways degradation may be quantified is by the percentage change of the complex viscosity over time, this is an alternative method to test for degradation rather than using thermogravimetric analysis (TGA). Figure 4 features oscillatory time sweep data, where the complex viscosity is plotted as a function of time for oven temperatures of 170 °C, 180 °C, and 190°C in a nitrogen environment. At elevated temperatures enhanced speed of degradation is increased. Just about a minute into processing at 190 °C, the PLA viscosity drops by about 10%. After an hour at 190 °C, the PLA viscosity drops by approximately 35%. This contrasts with the lower temperatures of 170 °C and 180 °C, where after an hour the viscosity drops by around 5% and 14% respectively. This presents 170 °C as an ideal candidate temperature for melt processing. Note that the melting point of this grade of PLA is 155 °C, so a lower temperature can also be used, but the melt viscosity increases significantly as the temperature is decreased which can cause additional processing issues.

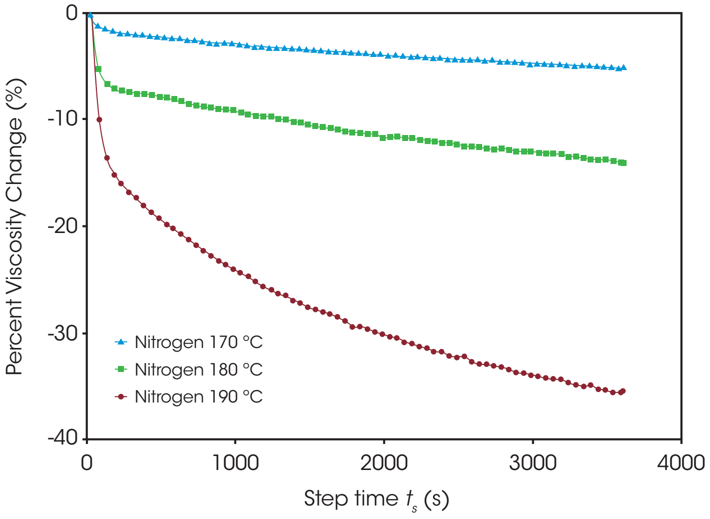

Figure 4. (Time Sweep Data) Percent viscosity change is plotted as a function of time for three PLA samples subjected to a nitrogen atmosphere at various temperatures of 170 °C, 180 °C, and 190 °C.

In the presence of dry air PLA is known to undergo oxidative degradation resulting in chain scission, which is the breakdown of molecular chains. The ARES-G2 FCO allows for careful and accurate comparison of degradation in the presence of different environments. Just before the start of the test, the chamber atmospheric gas was switched to air. Figure 5 features complex viscosity plotted as a function of time for all temperatures considered, and for each atmospheric gas. The blue curves highlight the difference in degradation between samples subjected to 170 °C in air and nitrogen environments. Under air, the degradation is more severe, resulting in a 22% drop in viscosity after an hour, relative to the 5% drop in the presence of nitrogen. At the highest temperature of 190 °C, initially the viscosity as a function of time follows a very similar path for samples subjected to either atmosphere. However, by the end of the hour test, the sample shows a higher degradation in air compared to nitrogen. This illustrates that polymer melt rheology is a powerful technique to understand a material's stability at high temperatures it would experience during processing which is critical for ensuring consistent finished product quality with lower rates of reject

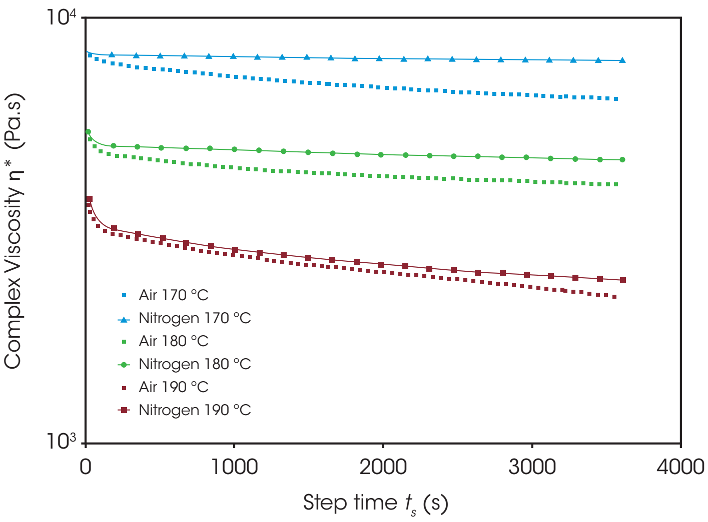

Figure 5. (Time Sweep Data) Complex Viscosity is plotted as a function of time for PLA samples subjected to either an inert nitrogen (solid curves) or reactive air atmosphere (dashed curves), at various temperatures of 170 °C, 180 °C, and 190 °C.

CONCLUSIONS

In this applications note, the thermal stability of PLA, a sustainable polymer has been characterized at different temperatures under air and nitrogen environments. These experiments assist in quantifying the extent of both thermal and oxidative decomposition at high temperatures which is crucial metrics for understanding ideal melt processing. The tests were performed on a TA Instruments ARES-G2 rheometer equipped with a forced convection oven, providing excellent ease of use, reproducibility, thermal responsiveness, and the ability to test under different atmospheres. The use of the polymer melt ring kit for the ARES-G2 allowed for the loading of samples directly from feedstock, rather than using a melt press which changes the thermal and processing history of the feedstock and may cause premature degradation. This methodology is critical to understanding and optimizing the processing conditions for polymers, and specifically sustainable polymers which are often utilized due to the ability to degrade and/or decompose at shorter time scales.

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