

# Understanding Biopolymer Behavior

A guide to optimizing material selection for product performance and processing conditions





# Table of Contents

---

<b>Introduction</b>	2
<b>Composition Analysis of a Filled Biopolymer: Polyhydroxyalkanoate (PHA) with Wood Flour</b> Master the understanding of evolved gas analysis to understand polymer compositions, ensuring consistent incoming raw materials	3
<b>Thermal Stability of Bio-Derived Polymer Feedstock</b> Identify the influence of environmental conditions on complex biopolymers during processing	12
<b>Tensile and Fatigue Properties of Additively Manufactured Polyamides</b> Understand how mechanical testing can reveal differences in product performance when using biopolymer substitutes	15
<b>Characterization of Bio-Derived Polymer Under Controlled Humidity</b> Ensure product performance during product life by understanding the effect of humidity and temperature on biopolymers	19

---



# INTRODUCTION

The drive for consumers, brand owners, and corporations to become more eco-conscious in their purchases has led to an increased demand in sustainably sourced materials. Several industries have started initiatives to incorporate the use of recycled materials as well as bio-derived materials. In the case of bio-derived materials, industries using polymers have interest in biopolymers; however, these materials come with unique challenges.

Even though biopolymers use has increased in recent years, there is limited standardization of processes to characterize incoming materials and ensure consistency and efficacy in product designs. While biopolymers aim to be a one for one substitute for their petroleum-based polymeric counterparts, it is rarely a simple case. These materials must be carefully characterized to ensure the proper material is selected for an end use application. Additionally, processing of these materials can be more complex than petroleum-based polymers.

Analytical techniques such as thermal analysis, rheology, and mechanical analysis are commonly used to characterize the composition, behavior, and physical properties of these materials. These techniques will help answer:

- Is the biopolymer received the same as the last batch?
- How will this biopolymer behave during processing?
- Do atmospheric conditions impact processing performance?
- Will this biopolymer perform safely in my application?
- Is the life of the component impacted by my biopolymer selection?
- Will the biopolymer selected be able to sustain a variety of temperature and humidity conditions?

Evolved gas analysis is a comprehensive material characterization technique that couples thermogravimetric analysis with a range of gas analysis technology like gas chromatography-mass spectrometry (GCMS) or Fourier transform infrared (FTIR). With this combination researchers can monitor weight loss and the gas evolved simultaneously, gaining a full understanding of polymer decomposition mechanisms and composition.

Rheology is the study of the flow and deformation of materials under stress and plays a crucial role in understanding how to optimize polymer processing. With a wide range of techniques within the study of rheology, it can be used to get a robust picture of how materials behave when different conditions are presented such as atmosphere and temperature.

Mechanical analysis encompasses three primary techniques: monotonic testing, fatigue testing, and dynamic mechanical analysis (DMA). Monotonic testing, often referred to as pull-to-failure testing, is used to measure material elongation and tensile strength, which are used to interpret a materials' ability to stretch without losing strength as well as point of catastrophic failure. Fatigue testing uses cyclical imposition of force to assess material life under specific conditions. As processing techniques change and advance, it is important to understand their impact on the resulting lifetime performance of a part. This cannot be seen using simple monotonic techniques and thus fatigue testing is becoming a requirement. Lastly, DMA is a method used to study the viscoelastic behavior of polymers. DMA analysis can be performed on a variety of TA Instrument products, however a specific use case for biopolymers is understanding the impact of humidity on the material's properties. Combining TA Instruments DMA 850 with a relative humidity unit can provide insights on how materials soften in different conditions.

Using these techniques enables research scientists to better select and understand their biopolymer, process engineers to enhance the manufacturability, and design engineers to ensure their product design will last using a new biopolymer. See how today's leading instruments help improve the material selection process.

## Our commitment

TA Instruments understands the demands of qualifying new biopolymers to enable a more sustainable world. We know your research requires accurate, practical techniques to maximize the development period, reduce cost, and expedite time to market. TA Instruments offers superior reliability coupled with industry-leading support so you can efficiently evaluate biopolymers for successful processing and product design.

# Composition Analysis of a Filled Biopolymer: Polyhydroxyalkanoate (PHA) with Wood Flour

## Abstract

Renewable and biodegradable polymer resins are increasingly used to reduce the environmental impact of plastic waste. Thermal characterization of these resins is necessary to determine processability, stability, and fundamental properties. In this work, thermogravimetric analysis (TGA) was performed on a sample of poly-3-hydroxybutyrate (PHB). Onset of decomposition and three mass loss events were detected. Modulated TGA (MTGA) was used to determine the activation energy at the temperature where the highest rate of mass loss occurred for the two main mass loss events. Evolved gas analysis (EGA) combining TGA/FTIR/GCMS was used to determine decomposition products which include 2-butenoic acid, 3,6-Dimethyl-1,4-dioxane-2,5-dione, and various polymer chain fragments. Identification of the unknown sample by comparison to constructed composite FTIR spectra utilizing the vendor software shows good agreement with GC/MS data.

## Introduction

The need to reduce the environmental impact of plastic waste has led to a great interest in renewable, biodegradable resins with properties similar to more common plastics like polypropylene and polyethylene. Thermal, physical, and rheological characterizations of these polymers are important for assessing stability, processability, and fundamental properties.

Polyhydroxyalkanoates (PHA) are biopolymers produced from microorganisms forming as water insoluble granules within the cytoplasm of the cell [1]. Poly-3-hydroxybutyrate (PHB) is the most studied PHA and a commercial sample with wood flour was obtained for this application note, which demonstrates the use of TGA, EGA, and MTGA as first steps in analyzing this polymer. The combination of these techniques allows characterization of decomposition, including decomposition products and activation energy. Tests were conducted using a TA Instruments™ Discovery™ 5500 TGA.

## Experimental

Samples of PHA/wood flour composites with 3 mm nominal granule size were obtained from Sigma Aldrich (catalogue number GF28484343-1EA) for this work. The chemical structure of the material is shown in Figure 1. Neat samples were cut from the PHB pellets and used for the analyses.

The onset of decomposition, mass loss events, and temperature at 2% and 5% mass loss were detected using TGA. MTGA was then used to determine the activation energy at the highest rate of mass loss. Experimental conditions for the TGA and MTGA experiments are summarized in Tables 1 and 2, respectively.

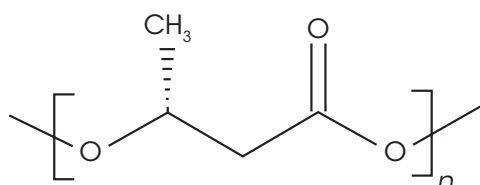


Figure 1. Structure of Poly-3-hydroxybutyrate sample

Table 1. TGA experimental conditions

Instrument	TA Instruments Discovery 5500 TGA
Crucible	100 $\mu$ L platinum
Purge	N <sub>2</sub> at 25 mL / min
Temperature Range	Ambient to 1000 °C
Heating Rate	10 °C / min
Sample mass	7 mg nominal

Table 2. MTGA experimental conditions

Instrument	TA Instruments Discovery 5500 TGA
Crucible	100 $\mu$ L platinum
Purge	N <sub>2</sub> at 25 mL / min
Temperature Range	Ambient to 1000 °C
Sample Mass	4 mg nominal
Heating Rate	2 °C / min
Modulation Period	200 second
Modulate Temperature Amplitude	+/- 5.00 °C



## Experimental

### Evolved Gas Analysis

To determine decomposition biproducts, EGA was done using the Discovery 5500 TGA using the TL9000 TGA/FTIR/GCMS interface system by RedShift srl with a Nicolet™ iS50 FTIR by Thermo Fisher Scientific Inc (Thermo), and a 7890 GC by Agilent Technologies, Inc., (Agilent) with a 5977B mass spectrometry detector (MSD). A schematic of the interface is shown in Figure 2 and a photograph of the system is shown in Figure 3.

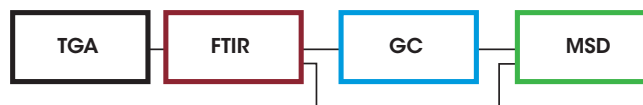


Figure 2. Schematic of EGA interface system

Figure 3. EGA System



A summary of the conditions used for the EGA work can be found in Table 3. The samples were not subjected to any thermal history before conducting the analyses. Mass losses were identified where the derivative of mass loss with respect to temperature reached the maximum. TGA data reduction was done using TA Instruments TRIOS™ software; FTIR and GC/MS data reduction was done using the vendor instrument software.

Table 3. EGA instruments and conditions

Technique	Details
TGA	Discovery 5500 TGA, same conditions summarized in Table 1
FTIR	Nicolet iS50 FTIR by Thermo; four scans, 4 cm <sup>-1</sup> resolution
GC	7890N GC by Agilent, HP 5MS 5% Phenyl methyl siloxane; 30m x 250 μm x 0.25 μm column
Mass Spec Detector	5977B MSD by Agilent, mass range m/z 50-500
Sample mass	7 mg nominal

## Results and Discussion

### Thermogravimetric Analysis (TGA)

The onset of decomposition was determined to be 270.8 °C. Prior to this onset enough mass loss can occur to adversely affect material properties. At 248.6 °C, 2% mass loss occurs and 5% mass loss at 268.8 °C (Figure 4). This shows good agreement with a study by Arcos-Hernandez, et al [2].

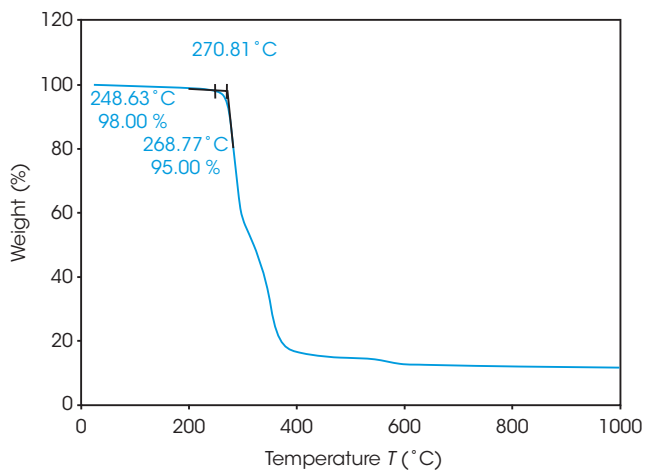


Figure 4. TGA onset of decomposition for PHA sample

As seen in Figure 5, two large mass losses were observed: 46.78% with rate maximum at 289 °C and 39.36% with a rate maximum at 354 °C. A smaller mass loss with rate maximum at 572 °C was also observed. Residue of 11.77% remained. These results are summarized in Table 4.

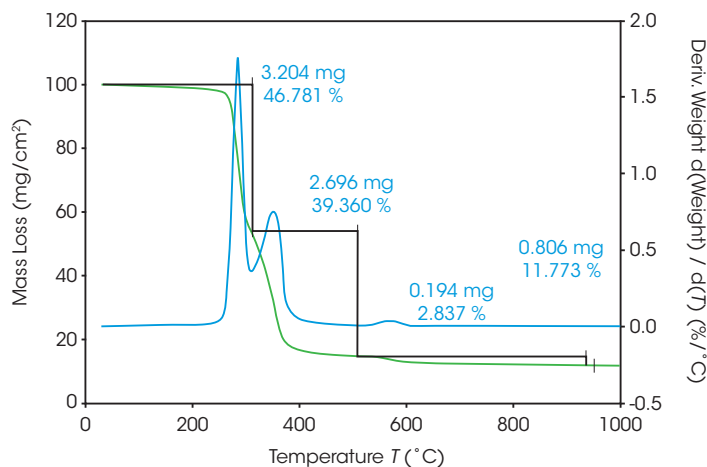


Figure 5. TGA mass loss and rate of mass loss for PHA sample

Table 4. Summary of TGA mass losses

Transition	Mass Loss (%)
1st Mass Loss	46.78
2nd Mass Loss	39.36
3rd Mass Loss	2.837
Residue (%)	11.77
Sample mass	7 mg nominal

## Modulated TGA (MTGA)

The activation energy of the two main mass losses were calculated using MTGA, in which the activation energy can be plotted as a discreet signal as a function of temperature or conversion with user-defined variables [3]. For the first mass loss, the activation energy is 116.9 kJ/mol; for the second, 141.4 kJ/mol. MTGA data is presented in Figure 6.

The activation energy can also be plotted as a function of mass fraction converted as shown in Figure 7. MTGA allows for activation energy to be plotted as a signal from one run, versus using several runs needed to calculate activation energy using the common Flynn and Wall method [4].

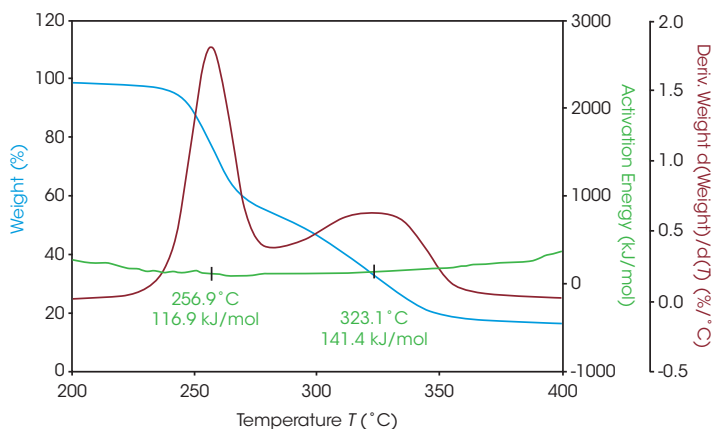


Figure 6. MTGA data showing activation energy at the two major mass losses

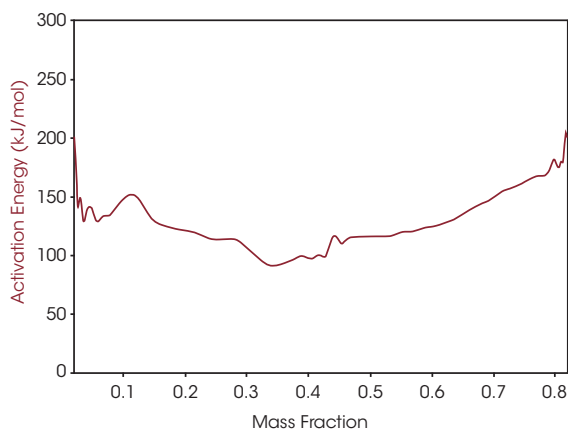


Figure 7. Activation energy as function of mass fraction converted.

## Evolved Gas Analysis (EGA)

Figures 8 through 26 and Tables 5 & 6 are located in an appendix starting on page 7.

Figure 8 Shows an overlay of the TGA mass loss with the derivative and the Gram-Schmidt reconstruction, which contains the FTIR spectral data. The data shows the similarity between the derivative and the Gram-Schmidt data. There are many methods to analyze and present the data. For this paper, mass loss events are identified at the temperature where the derivative of mass loss is at its local maximum. Coincidentally, this is typically where the Gram-Schmidt reconstruction has its local maximum. Careful inspection of the spectra throughout the entirety of the Gram-Schmidt reconstruction is necessary, and this is easily done with the instrument software.

The FTIR spectrum for the mass loss at 289 °C is shown in Figure 9. Key features of the spectrum include constrained carbonyls, free hydroxyl, strong C-O single bonds, and unsaturation. One obvious species is an unsaturated organic acid with carbonyl split at 1771 and 1755  $\text{cm}^{-1}$ . Closer examination of the fingerprint region shows at least three carbonyls and carbon-oxygen single bonds, indicating the organic acid would not account for all the oxygen-containing species (Figure 10). Zooming in on the carbonyl region (Figure 11) shows possibly four different carbonyls. The higher energy absorbance ( $> 1790 \text{ cm}^{-1}$ ) is likely due to carbonyl species with significant ring strain commonly observed as decomposition products in many plastics, while the lower energy carbonyls may be an ester. Secondary features that would indicate an aldehyde are not apparent.

One of the powerful features of TGA/FTIR is the search capabilities of the OMNIC™ Mercury TGA software [5]. The software allows searching of the spectral data contained in the Gram-Schmidt reconstruction and builds a composite spectrum from available commercial reference libraries. For the sample spectrum, a composite was constructed containing 1-Methylpentyl 2-butenate, 3,6-dimethyl-1,4-dioxane-2,5-dione, and 2-butenic acid. An overlay of the composite spectrum and sample at 289 °C is shown in Figure 12. An overlay of the three components used to build the composite spectrum is shown in Figure 13. An overlay of the calculated evolved gases as a function of time is shown in Figure 14. The results of the search and composite should be scrutinized but provide a time-saving device that can make complex interpretation of FTIR spectra obtained in an EGA analysis more accessible to the analyst.

The total ion chromatogram (TIC) is shown in Figure 15. A summary of the mass spectral data with retention times (RT) is shown in Table 5. Main components appear to be 2-butenic acid, and fragments of the polymer which account for the ester functionalities observed in the FTIR spectrum. Some 3,6-dimethyl-1,4-dioxane-2,5-dione was also detected.

The FTIR spectrum for the mass loss at 354 °C is shown in Figure 21 and the TIC in Figure 22. The mass loss is mainly 3,6-dimethyl-1,4-dioxane-2,5-dione with some contribution from 2-butenic acid, CO<sub>2</sub>, and CO. The two retention times associated with the 3,6-dimethyl-1,4-dioxane-2,5-dione may be due to trans and cis isomers. Table 6 summarizes the species detected and corresponding figures.

FTIR spectrum at 572 °C (Figure 27) shows CO<sub>2</sub>, constrained carbonyls likely the dioxane compound, and some organic acid. Mass spectral data was not obtained for this mass loss.

## Conclusions

The emergence of renewable and naturally sourced polymers necessitates the need for extensive analytical characterization, especially thermal analysis. TGA is typically the first step in this process. TGA provides stability, onset of decomposition, and mass loss events. The decomposition activation energy of each mass loss event can be determined in a single experiment using MTGA. Finally, evolved gas analysis which combines TGA with FTIR and GC/MS yields compositional information about decomposition products. Modern search capabilities of spectroscopy software facilitate identification of the evolved species.

TA Instruments Discovery 5500 TGA anchors this powerful tandem, providing excellent sensitivity, baseline, controlled furnace chamber environment, and intuitive TRIOS software for data management.

## Appendix

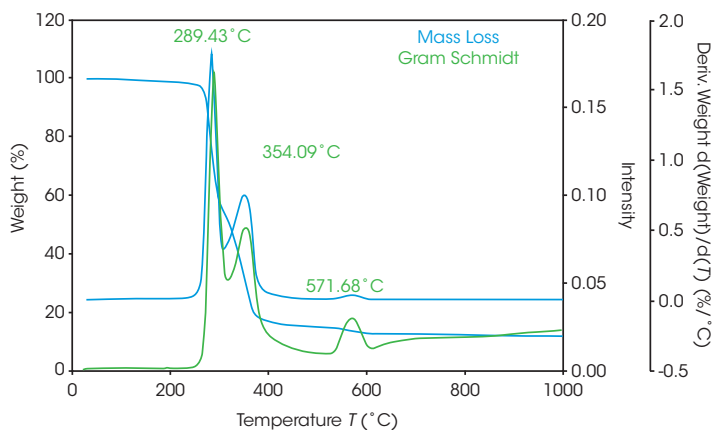


Figure 8. Mass loss, derivative of mass loss, and Gram-Schmidt reconstruction

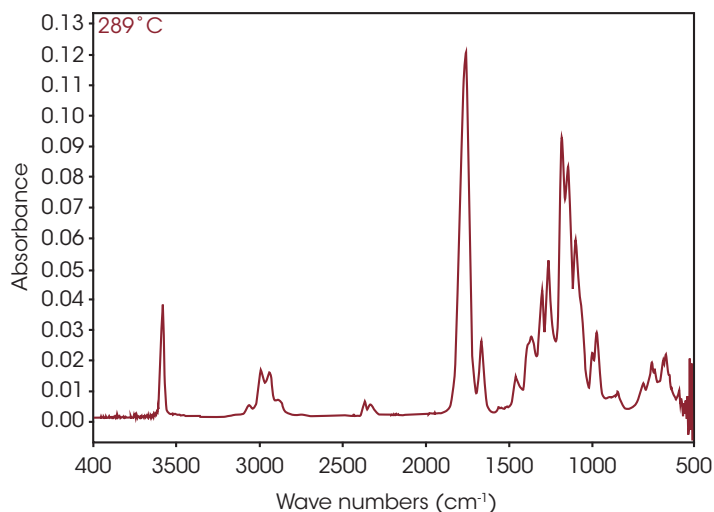


Figure 9. FTIR spectrum at 289 °C

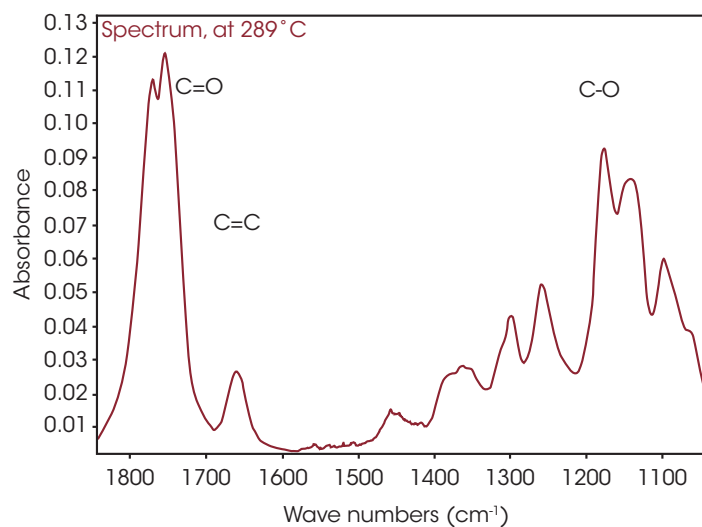


Figure 10. Fingerprint of spectrum at 289 °C

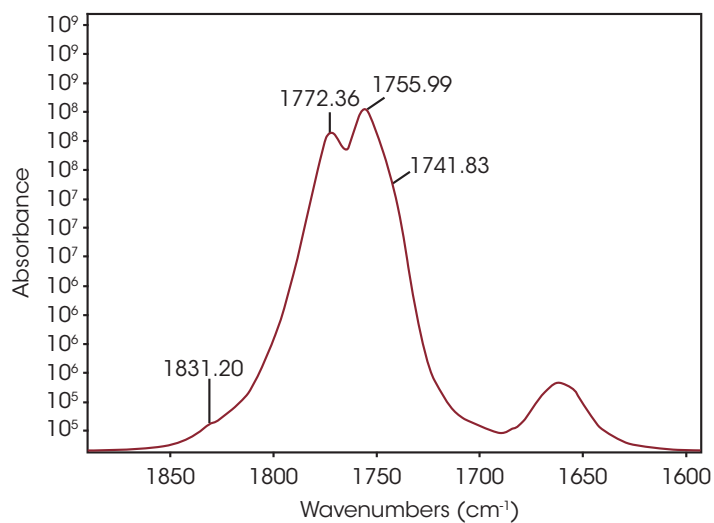


Figure 11. Carbonyl region of spectrum at 289 °C



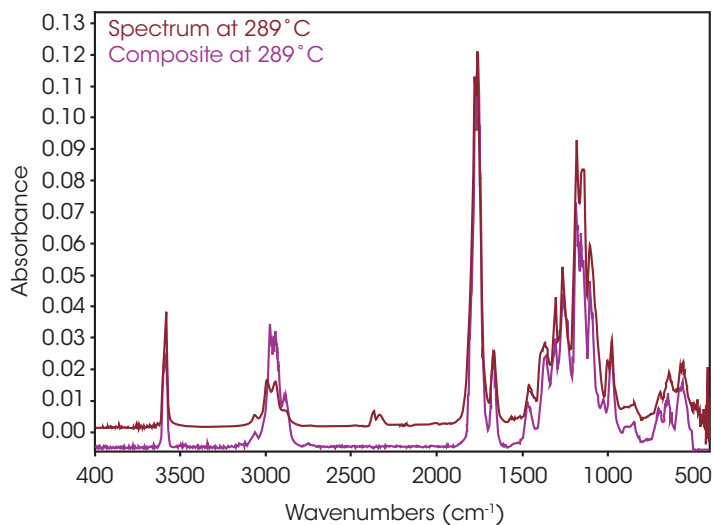


Figure 12. Spectrum and composite built from search results for 289 °C

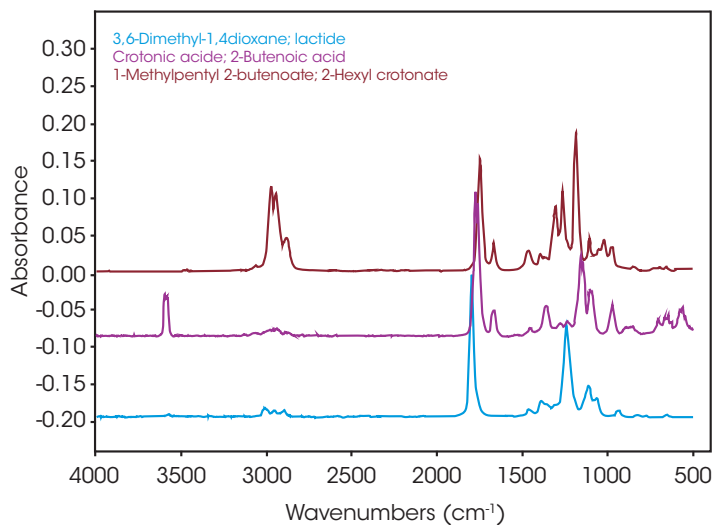


Figure 13. Search results used to build composite spectrum at 289 °C (residuals omitted)

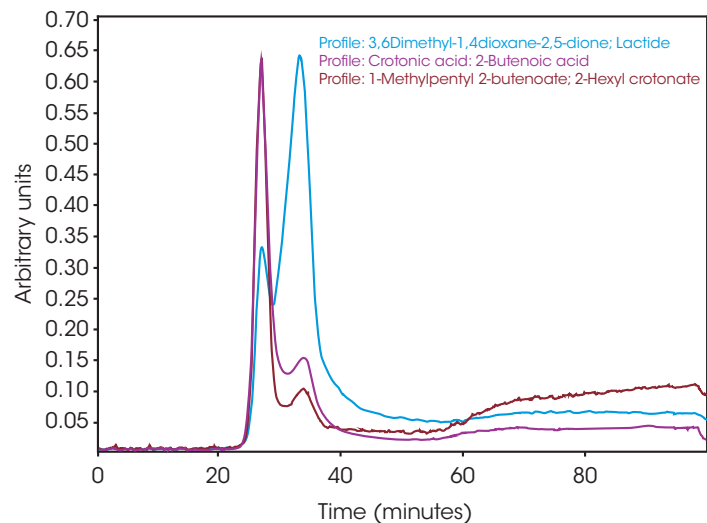


Figure 14. Calculated time profiles of evolved gases (residuals omitted)

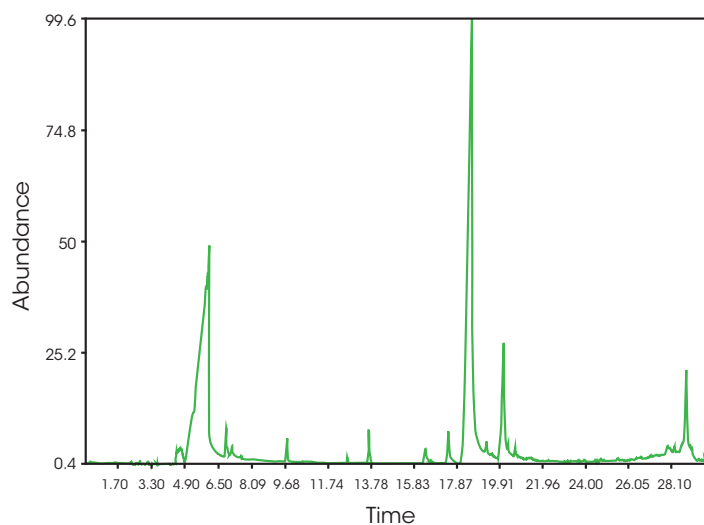


Figure 15. Total ion chromatogram (TIC) at 289 °C

Table 5. Summary of mass spectral data at 289 °C

RT (min)	Species
6.025	2-butenic acid (Figure 16)
13.692	3,6-dimethyl-1,4-dioxane-2,5-dione (Figure 17)
18.443	Polymer fragment (Figure 18)
19.939	Polymer fragment (Figure 19)
28.801	Polymer fragment (Figure 20)

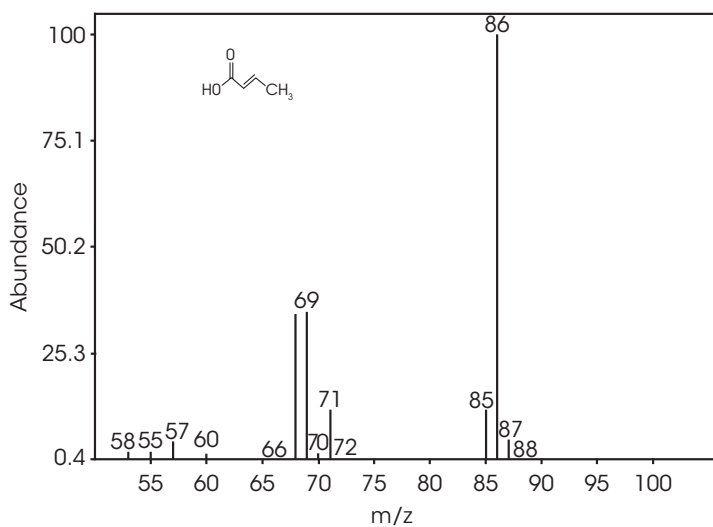


Figure 16. Mass spectrum at RT 6.025 min

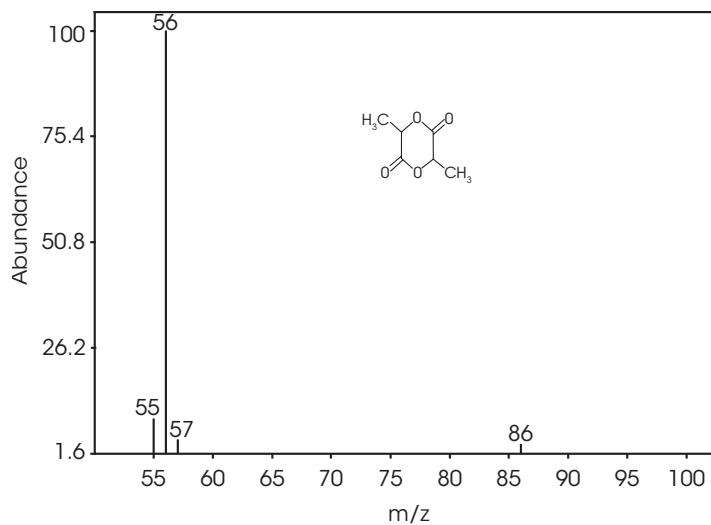


Figure 17. Mass Spectrum at RT 13.692 min

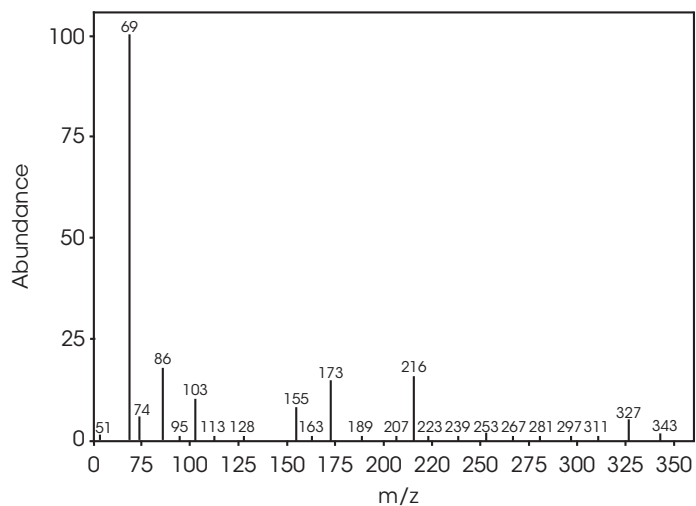


Figure 20. Mass spectrum at RT 28.801 min

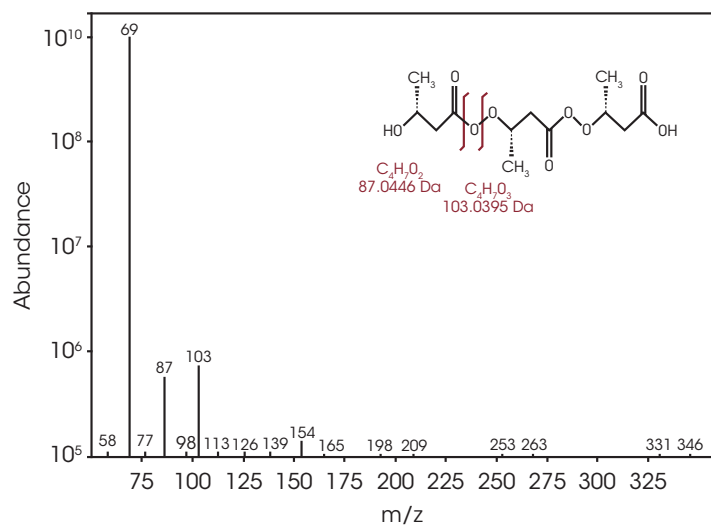


Figure 18. Mass spectrum at RT 18.443 min

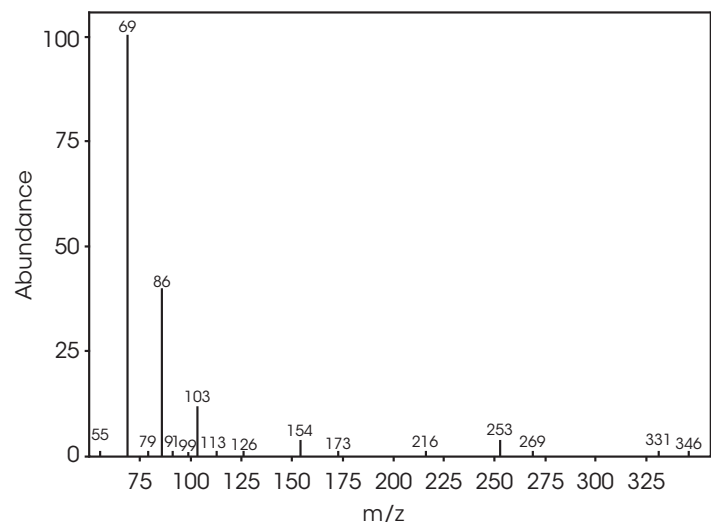


Figure 19. Mass spectrum at RT 19.939 min

Table 6. Mass spectral data at 354 °C

RT (min)	Species
5.028	2-butenoic acid (Figure 23)
12.685	3,6-dimethyl-1,4-dioxane-2,5-dione (Figure 24)
13.379	3,6-dimethyl-1,4-dioxane-2,5-dione (Figure 25)
18.132	Polymer fragment (Figure 26)

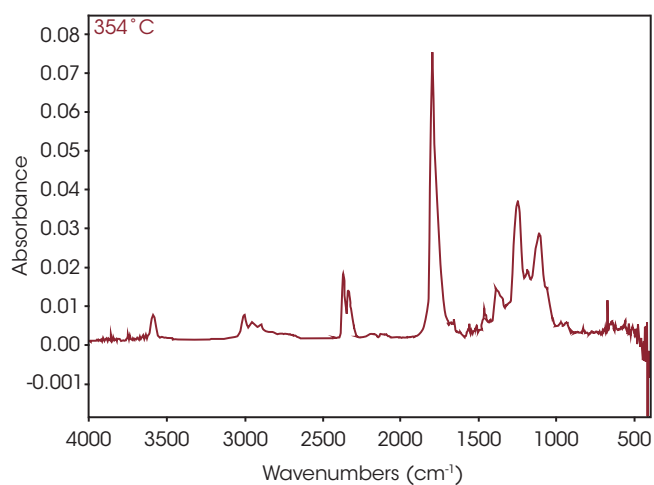


Figure 21. FTIR spectrum at 354 °C

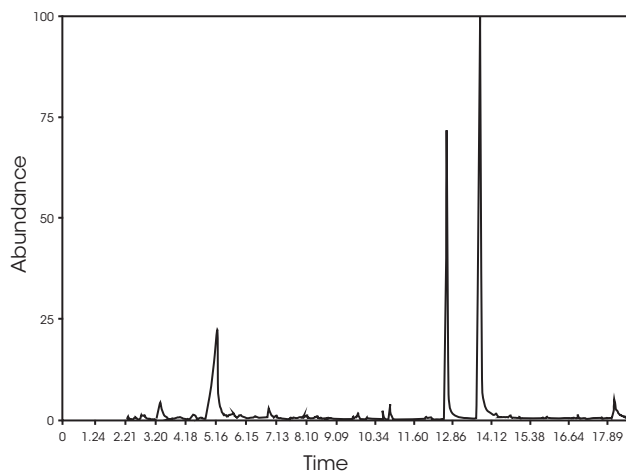


Figure 22. TIC for mass loss at 354 °C

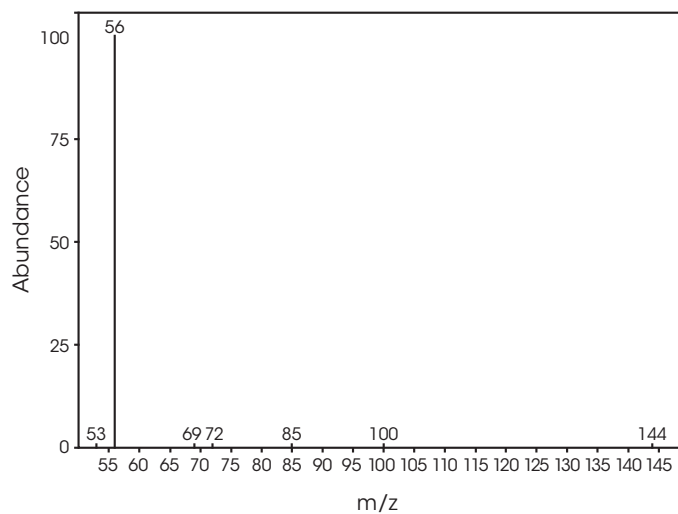


Figure 25. Mass spectrum at RT 13.739 min

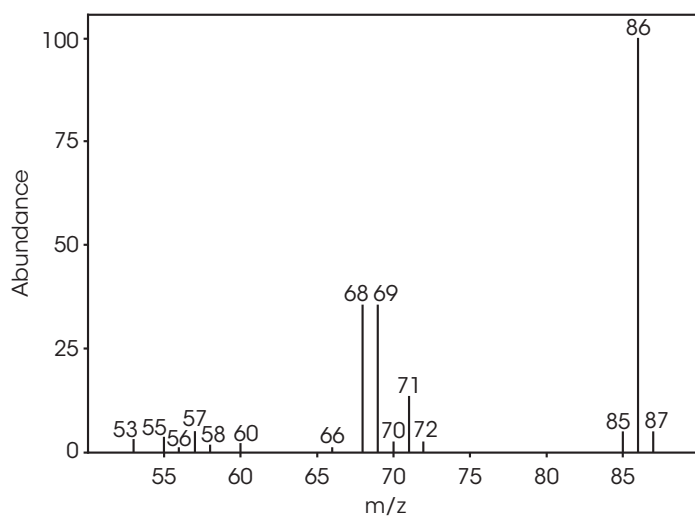


Figure 23. Mass spectrum at RT 5.028 min

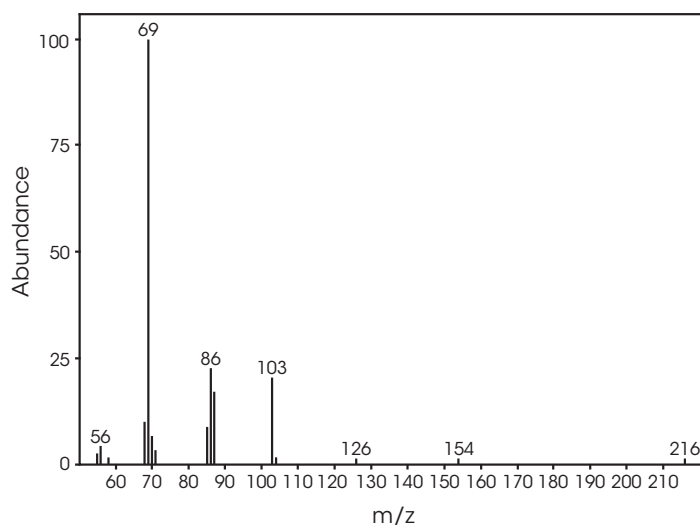


Figure 26. Mass spectrum at RT 18.132 min

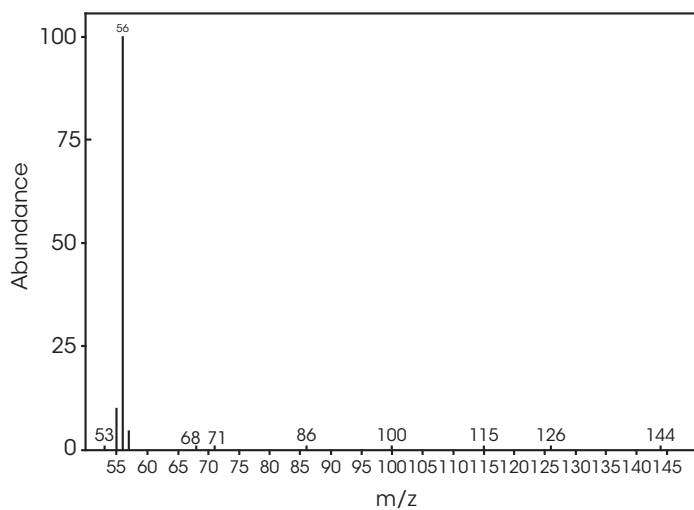


Figure 24. Mass spectrum at RT 12.685 min

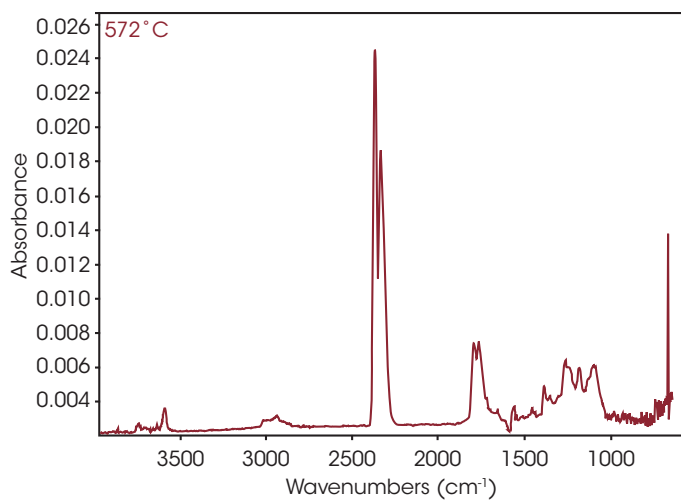


Figure 27. FTIR spectrum at 572 °C



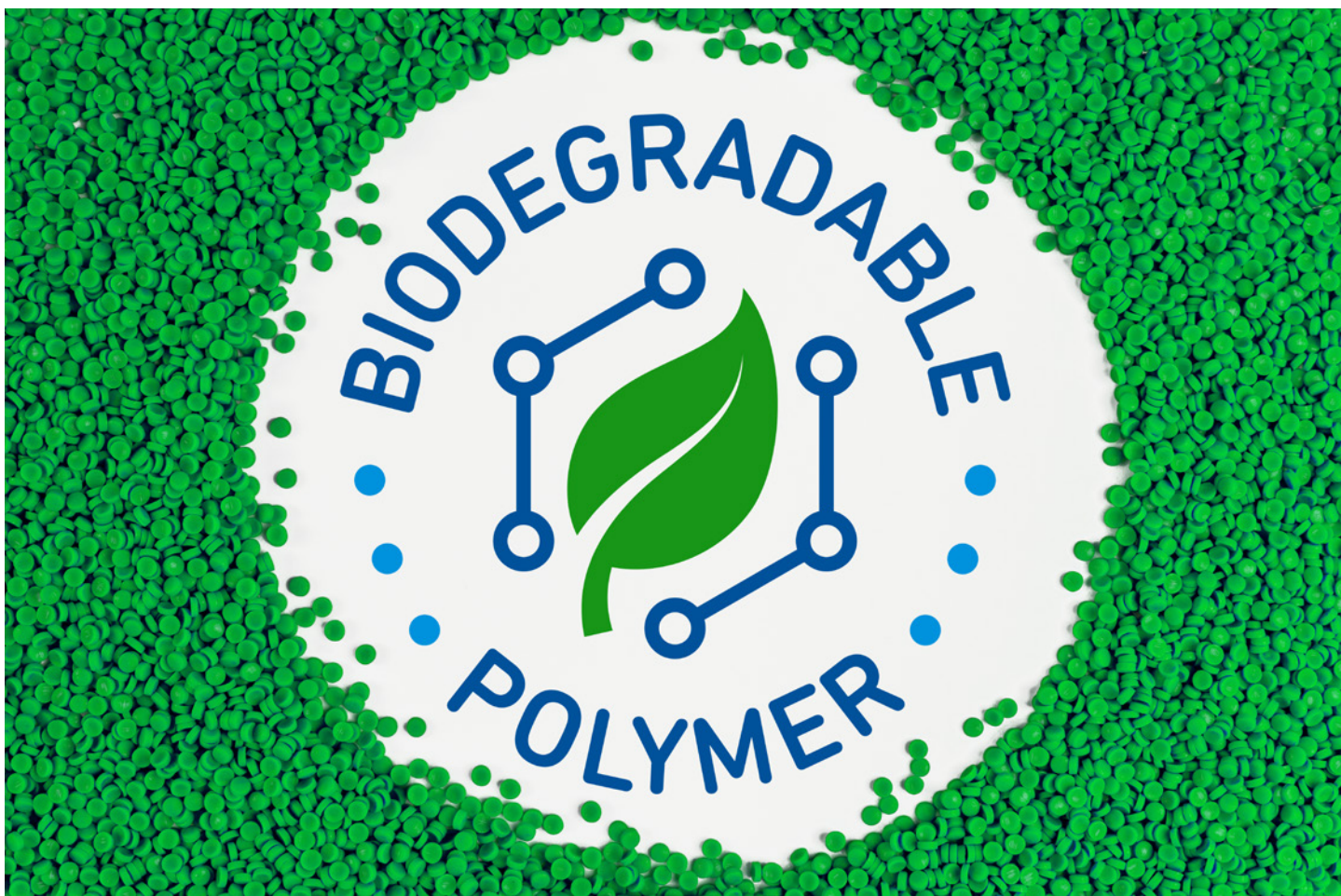
## References

1. R. Sehgal and R. Gupta, "Polyhydroxyalkanoate and its efficient production: an eco-friendly approach toward development," Biotech, pp. 1-14, November 2020.
2. M. Arcos-Hernandez and e. al, "Physicochemical and mechanical properties of mixed culture polyhydroxyalkanoate (PHBV)," European Polymer Journal, vol. 49, pp. 904-913, 2013.
3. R. Blaine and B. Hahn, "Obtaining Kinetic Parameters by Modulated Thermogravimetry," Journal of Thermal Analysis, vol. 54, pp. 695-704, 1998.
4. "E 1641 Standard Method for Decomposition Kinetics by Thermogravimetry," ASTM, Conshohocken, 2007.
5. Bradley, Michael, "TGA-IR Analysis Using the OMNIC Mercury TGA Software," [Online]. Available: [https://assets.thermofisher.com/TFS-Assets/CAD/Application-Notes/Whitepaper\\_TGA-IR\\_L.pdf](https://assets.thermofisher.com/TFS-Assets/CAD/Application-Notes/Whitepaper_TGA-IR_L.pdf).

## Acknowledgement

This paper was written by James Browne, Senior Applications Scientist at TA Instruments.

TA Instruments, Discovery, and TRIOS are trademarks of Waters Technologies Corporation. Nicolet and OMNIC are trademarks of Thermo Fisher Scientific Inc.



# Thermal Stability of Bio-Derived Polymer Feedstock

## 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]

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.

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



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



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.

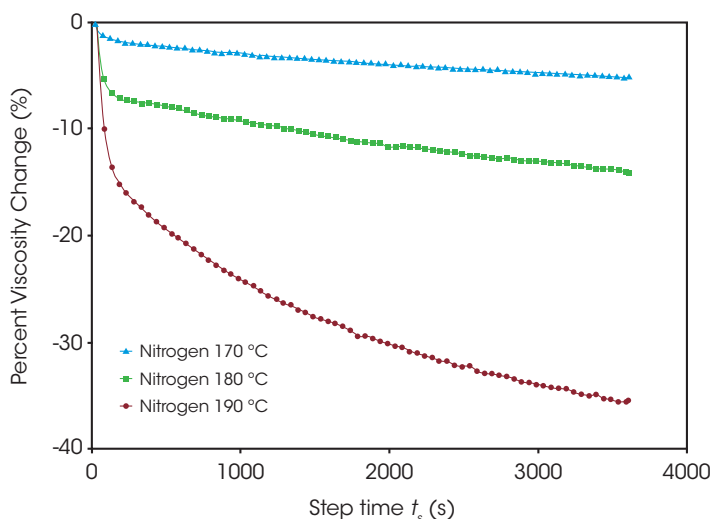


Figure 4. (Time Sweep Data) Percent viscosity change is plotted as a function of time for three PLA samples subjected to a nitrogen atmosphere at various temperatures of 170 °C, 180 °C, and 190 °C.

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

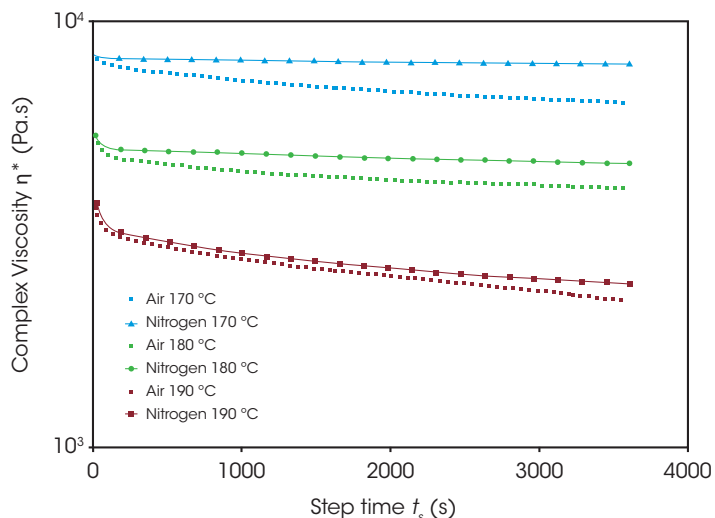


Figure 5. (Time Sweep Data) Complex Viscosity is plotted as a function of time for PLA samples subjected to either an inert nitrogen (solid curves) or reactive air atmosphere (dashed curves), at various temperatures of 170 °C, 180 °C, and 190 °C.



## 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.

## References

1. Masutani, K., and Kimura, Y. "Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications" The Royal Society of Chemistry, 2015, pp. 1-36
2. Tokiwa, Y., Calabia, B.P. Biodegradability and biodegradation of poly(lactide). *Appl Microbiol Biotechnol*, 2006, Vol. 72
3. Sodergard, A., and Stolt, M. "Properties of lactic acid based polymers and their correlation with composition" *Progress in Polymer Science*, 2002, Vol. 27
4. McKeown P. Jones MD. "The Chemical Recycling of PLA: A Review" *Sustainable Chemistry*, 2020, Vol. 1
5. Cosate de Andrade, M.F., Souza, P.M.S., Cavalett, O. et al. "Life Cycle Assessment of Poly(Lactic Acid) (PLA): Comparison Between Chemical Recycling, Mechanical Recycling and Composting". *Journal of Polymers and the Environment*, 2016, Vol. 24
6. Elsayy, M. A., Kim, K., Park, J., and Deep, A. "Hydrolytic degradation of polylactic acid (PLA) and its composites" *Renewable and Sustainable Energy Reviews*, 2017, Vol. 79
7. Signori, F., Coltelli, M., and Bronco, S. "Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) and their blends upon melt processing" *Polymer Degradation and Stability*, 2009, Vol. 94
8. Rasselet, D., Ruellan, A., Guinault, A., Miquelard-Garnier, G., Sollogoub, C., and Fayolle, B. "Oxidative degradation of polylactide (PLA) and its effects on physical and mechanical properties" *European Polymer Journal*, 2014, Vol. 50
9. Copinet, A., Bertrand, C., Govindin, S., Coma, V., and Couturier, Y. "Effects of ultraviolet light (315 nm), temperature and relative humidity on the degradation of polylactic acid plastic films" *Chemosphere*, 2004, Vol. 55

## Acknowledgement

This paper was written by Keith Coasey, Ph.D., Rheology Applications Engineer at TA Instruments.

# Tensile and Fatigue Properties of Additively Manufactured Polyamides

## Abstract

Through technological advancements, additive manufacturing has surpassed its niche application space of prototyping and is increasingly used to fabricate end-use parts. It is important to understand the mechanical properties of additively manufactured parts, including time dependent behavior such as fatigue life, to ensure performance and reliability. This work evaluates the mechanical properties and time dependent response to loading of laser sintered dog bone samples of two polyamides, bio-based polyamide-11 (PA11) and petroleum-based polyamide-12 (PA12), through monotonic pull-to-failure tensile tests and cyclic fatigue testing. The TA Instruments™ ElectroForce 3300 load frame was utilized for its versatility to execute both monotonic and fatigue testing due to its electromagnetic motor and non-contact precision sensor technologies. The results identify mechanical and fatigue life superiority of PA11 compared to PA12. The approach presented can be utilized to compare materials when it is important to evaluate both ultimate strength and durability under repeated loading.

## Introduction

Additive manufacturing (AM) has quickly emerged as an innovative technology that allows production of materials with complex three-dimensional (3D) geometries [1]. It was initially used as a prototyping technique but is being increasingly adopted to produce end-use parts. Laser sintering is a common AM technique that involves using powdered material to print the desired geometry. To understand performance of the final product, as well as investigate any potential variability caused by AM, it is necessary to mechanically characterize a laser sintered sample of the material. Time and load dependent properties, such as fatigue life, are of interest to determine the material reliability for these AM parts. These properties are of particular importance in industries such as aerospace and biomedical, where a thorough understanding of the material lifetime is critical in avoiding catastrophic failures [2].

Two polymers commonly used in the AM process of laser sintering are polyamide-11 (PA11) and polyamide-12 (PA12), which belong to the Nylon family of polymers. PA11 is bio-based, derived from castor oil, whereas PA12 is petroleum-based and contains an extra methylene group between the amide groups in the polymer backbone. While the smaller carbon footprint of PA11 is desirable, the extra methylene group of PA12 results in different mechanical properties of the two materials [3] [4]. PA11 is generally stronger and more ductile compared to PA12, but the latter has better chemical resistance [5]. With this consideration, the performance properties of PA11 and PA12 must be thoroughly understood to weigh the environmental impact against the ultimate material performance.

The mechanical property differences of these two polymers have been explored, but little has been studied on the fatigue life [4] [6]. Often, mechanical and fatigue testing are performed using separate instruments, requiring greater investment and a larger space. In this application note the quasi-static and cyclic response of laser sintered PA11 and PA12 dog bone samples are examined utilizing the ElectroForce 3300 load frame. Potential variability induced by the laser sintering process is also explored.

## Experimental

Commercially obtained PA11 and PA12 samples were fabricated into type V dog bone samples [7] using a laser sintering AM process. Figure 1a shows the PA12 (left) and PA11 (right) dog bone samples before and after testing to failure.

Monotonic and fatigue tests were performed on the ElectroForce 3300 from TA Instruments. The 3300 was selected for this work due to its versatility and ability to execute the slow testing needed to measure elongation and tensile strength, as well as fast, cyclic testing to study fatigue. Figure 1b shows the instrument with a tensile testing configuration. Sample geometry and testing conditions followed the requirements of ASTM D638-22 [7]. Monotonic tensile testing was

performed at a rate of 1.2 mm/min (strain rate of  $0.0018 \text{ s}^{-1}$ ) until failure for all samples. Three samples were tested for both PA11 and PA12 to examine the mechanical property variability.

Fatigue testing was performed at maximum stress levels of 25, 30, 32.5, 35, and 40 MPa with a 25 Hz frequency. The 40 MPa stress level was approximately 80% of the ultimate strength of the stronger PA11 sample as determined from the pull-to-failure monotonic testing. An R-ratio of 0.1 was used to maintain tension in the sample. The lower maximum stress levels were chosen to systematically study how the material lifetime increases with decreasing stress. Three samples were run for each stress level to examine the variability between the PA11 and PA12 parts. The strain was monitored using an Epsilon ONE optical extensometer, model One250CE/280. A representative dog bone sample within the grips is shown in Figure 1c.

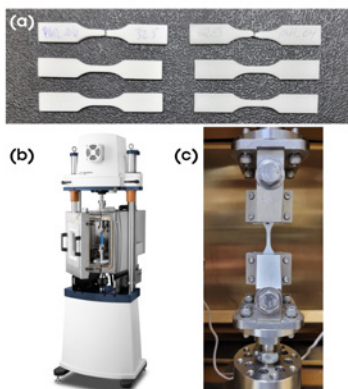


Figure 1. (a) PA12 (left) and PA11 (right) Type V dog bone samples intact and after failure, (b) ElectroForce 3300 instrument with a tensile configuration and temperature control system attached, and (c) representative Type V dog bone clamped in tension for monotonic and fatigue testing.

## Results and Discussion

### Monotonic Testing

The mechanical properties of PA11 and PA12 were assessed using monotonic tensile tests. Figure 2 shows the resulting stress versus strain curves when the samples were strained at a rate of  $0.0018 \text{ s}^{-1}$ . The PA11 sample has a greater ultimate tensile strength (UTS) and a longer percent elongation at failure for all samples.

The values for UTS and elongation percent to failure are shown in Tables 1 and 2, along with the average values from the three curves and the standard deviation.

Table 1. Ultimate tensile strength (UTS) and % elongation at failure for PA11 with the triplicate run average and standard deviation ( $\sigma$ ).

PA11	UTS (MPa)	Elongation (%)
1	49.24	44.76
2	49.40	54.24
3	49.87	41.87
Average	49.50	46.96
$\sigma$	0.33	6.47

Table 2. Ultimate tensile strength (UTS) and % elongation at failure for PA12 with the triplicate run average and standard deviation ( $\sigma$ ).

PA12	UTS (MPa)	Elongation (%)
1	39.91	23.35
2	40.35	23.40
3	40.51	26.56
Average	40.25	24.44
$\sigma$	0.31	1.84

The higher strength and longer elongation for PA11 has been observed before when a powder bed fusion process is used to produce PA11 and PA12 parts [3]. The monotonic testing results show that PA11 has a greater ability to stretch without losing strength compared to PA12. This makes PA11 a better choice for end-use parts and for applications where a stronger and more ductile material is required.

Testing the samples in triplicate provides the opportunity to look at the potential variability in the laser sintering process itself. Laser sintering is a powder bed fusion AM process and has received criticism from a reproducibility standpoint [8]. In laser sintering, variability tends to come from powder bed properties, laser characteristics, and process parameters. Table 1 shows that percent elongation to failure has the most variability, while the UTS remains consistent for both materials. The PA11 and PA12 samples each have one curve in Figure 2 that elongates noticeably further compared to the other two replicates and this imparts a higher standard deviation as seen in Table 1. Inconsistencies from the AM process can manifest as mechanical property variations, which is not desirable for an end-use product.

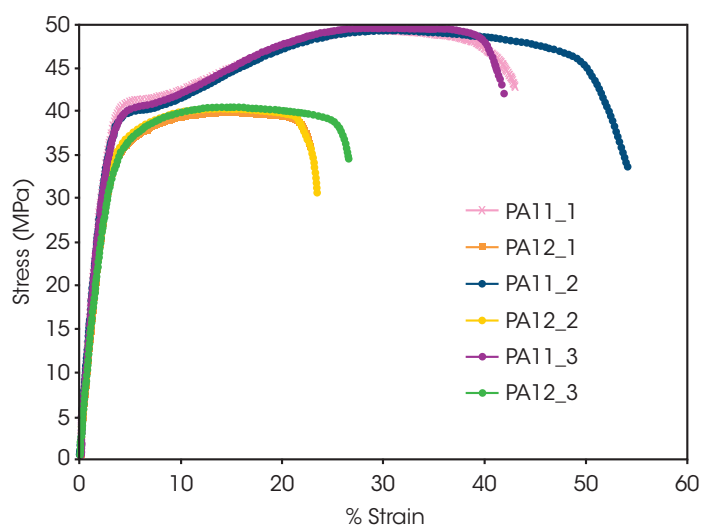


Figure 2. Tensile test curves run in triplicate for PA11 and PA12 at a strain rate of  $0.0018 \text{ s}^{-1}$ .

### Fatigue Testing

Monotonic testing has been extensively utilized to characterize the mechanical properties of AM parts. As AM techniques are increasingly used, it's important to understand the resulting part's reliability and expected lifetime performance. This requires characterization beyond simple and quick monotonic tensile testing and requires the product to be evaluated over time under the loads and deformations it will encounter in the intended application.

Fatigue testing was performed on the PA11 and PA12 samples to evaluate the robustness of the materials under constant cyclic loading. To illustrate this testing, Figure 3, shows the total displacement versus time for one of the PA11 samples during cyclic loading until failure at a stress



level of 30 MPa. Over the entire experimental time, 0 to ~2800 s ( $7 \times 10^4$  cycles), the sample length increases gradually throughout the test, as seen by an increasing displacement from its original position. Towards the end of the test, just before 2400 s ( $6 \times 10^4$  cycles), the displacement begins to increase at a faster rate. This continues until the material fails, indicated by a sudden and sharp increase in displacement due to the material breaking.

The inset of Figure 3 shows a 1 s interval during testing to view what is happening to the material on a shorter time scale. All testing was performed at 25 Hz. In this one second interval, the material is exposed to 25 sinusoidal cycles with a well-defined amplitude that is cyclically stressing the material to the 30 MPa level. Viewing this test from these two different timescales shows how the continuous short time scale deformations lead to a bulk increase in sample length and this leads to the ultimate material failure.

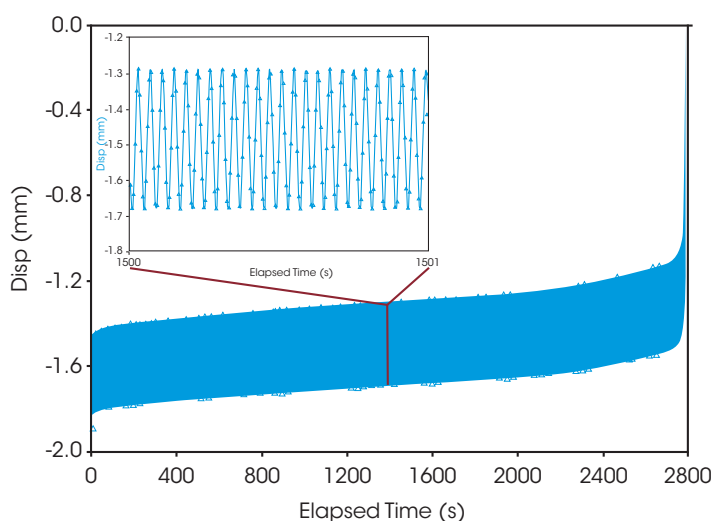


Figure 3. Sample displacement versus time of fatigue test on PA11 with a 25 Hz frequency at a stress level of 30 MPa. Inset shows a zoomed image of a 1 s time interval during the test.

Figure 4 shows the resulting S/N curves, also called Woehler curves, with stress levels ranging from 40-25 MPa. The S/N curve plots the cyclic stress (S) amplitude versus the number of cycles to failure (N), making it useful for visualizing fatigue. At 25 MPa all samples reached 107 cycles, which was established as the run-out cycle limit for this study. When a stress level results in run-out samples, that stress level is considered to be below the endurance limit.

For both samples, the number of cycles to failure decreases as the stress level is increased. At stress levels between 30-40 MPa, PA12 reaches failure at a lower cycle number compared to PA11. Best fit trendlines were created for the curves with the data from 40-30 MPa; the 25 MPa level samples were omitted due to the absence of failure. At high stress levels, the number of cycles to failure are on the same order of magnitude at a few hundred cycles. From the trendlines, it is observed

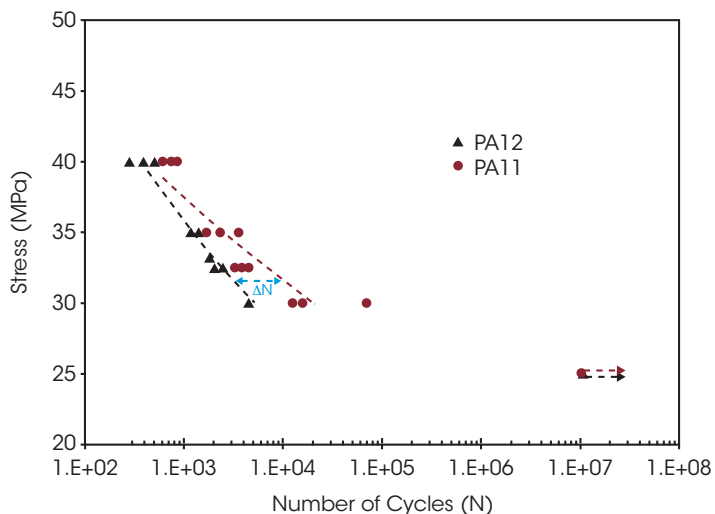


Figure 4. Maximum fatigue stress (S) versus fatigue life (N) (S/N) curves for PA12 (black) and PA11 (red) at stress levels of 40, 35, 32.5, 30, and 25 MPa. Dashed lines are best fit trendlines. The arrows indicate sample run-out at the 25 MPa stress level.

the difference in cycles to failure ( $\Delta N = N_{PA11} - N_{PA12}$ , blue line in Figure 4) increases as the stress level decreases. This result is consistent with the monotonic data, as the stronger and more ductile PA11 is expected to be more robust under cyclic loading.

Performing triplicate tests at each stress level allows the reproducibility of the AM process to be analyzed in a similar manner to the monotonic testing. The PA12 S/N curve has little spread in the data at each stress level. However, PA11 has a noticeable spread in the data for stress levels of 35 and 30 MPa. From the monotonic data it was also observed the standard deviations on the UTS and % elongation at failure were greater for PA11 compared to PA12. This identifies that PA11 may be hindered by reproducibility issues in the laser sintering AM process and this manifests as variability in the mechanical and fatigue properties of the material.

The variability observed in this work shows that comprehensive evaluation of laser sintered PA11 parts should be carried out prior to application use. This will involve testing a larger number of samples at the given application stress levels and therefore more rigorously establishing the confidence levels of the subsequent fatigue limits. Systematic fatigue testing should also be performed between 25 and 30 MPa to establish a precise endurance limit based upon the results where the 25 MPa stress level caused run out for all samples. In addition, further characterization of the material by direct and indirect methods such as electron microscopy, X-ray diffraction, and thermal analysis should accompany this testing to identify the microstructural origins of this variation.

## Conclusions

As AM parts become more widely utilized in end-use applications, it is necessary to understand the mechanical performance and reliability of the parts, as well as the potential variability caused by the manufacturing process. In this note PA11 and PA12 were examined in relation to their mechanical and fatigue life properties using the ElectroForce 3300. The ElectroForce 3300 proved well suited for these measurements, utilizing a single piece of equipment for both mechanical and fatigue tests under a wide range of test methods:

- The monotonic tensile testing identified that PA11 has superior mechanical strength and ductility properties with a greater UTS and % elongation at failure compared to PA12.
- Fatigue life testing identified that PA11 had a longer fatigue life cycle compared to PA12 at every given stress level tested. The difference between the life cycle increase of PA11 over PA12 grew as the stress level decreased.
- Performing multiple iterations for each sample allowed repeatability of part design in the AM process to be assessed.

The variation in mechanical properties, especially in PA11, identified that work still needs to be done to overcome part-to-part variability that has plagued AM processes. Based upon the mechanical and fatigue analysis, PA11 is the polymer of choice for an end-use product as it will be expected to remain robust and have a longer lifetime compared to PA12. Along with these mechanical property considerations, the low carbon footprint of producing PA11 from bio-derived sources compared to the petroleum-based PA12 makes it a clear materials choice from a sustainability standpoint as well.

## References

1. G. N. Mhetre, V. S. Jadhav, S. P. Deshmukh and C. M. Thakar, "A Review on Additive Manufacturing Technology," *ECS Trans.*, vol. 107, p. 15355, 2022.
2. S. S. Alghamdi, S. John, N. R. Choudhury and N. K. Dutta, "Additive Manufacturing of Polymer Materials: Progress, Promise, and Challenges," *Polymers*, vol. 13, p. doi.org/10.3390/polym13050753, 2021.
3. A. Salazar, A. Rico, J. Rodriguez, J. S. Escudero and F. M. de la Escalera Cutilas, "Monotonic loading and fatigue response of a bio-based polyamide PA11 and a petrol-based polyamide PA-12 manufactured by selective laser sintering," *European Polymer Journal*, vol. 59, pp. 36-45, 2014.
4. N. Lammens, M. Kersemans, I. De Baere and W. Van Paepegem, "On the visco-elasto-plastic response of additively manufactured polyamide-12 (PA-12) through selective laser sintering," *Polymer Testing*, vol. 57, pp. 149-155, 2017.
5. S. C. Lao, W. Yong, K. Nguyen, T. J. Moon, J. H. Koo, L. Pilato and G. Wissler, "Flame-retardant Polyamide 11 and 12 Nanocomposites: Processing, Morphology, and Mechanical Properties," *Journal of Composite Materials*, vol. 44, pp. 2933-2951, 2010.
6. B. Van Hooreweder, D. Moens, R. Boonen, J. P. Kruth and P. Sas, "On the difference in materials structure and fatigue properties of nylon specimens produced by injection molding and selective laser sintering," *Polymer Testing*, vol. 32, pp. 972-981, 2013.
7. A. D638-22, "Standard Test Method for Tensile Properties of Plastics," *ASTM International*, 2022.
8. L. Dowling, J. Kennedy, S. O'Shaughnessy and D. Trimble, "A review of critical repeatability and reproducibility issues in powder bed fusion," *Materials and Design*, vol. 186, p. 108346, 2020.
9. V. Malmgren, "PA11 vs PA12-one atom different," *wematter*, 01 2022. [Online]. Available: <https://wematter3d.com/pa11-vs-pa12-one-atom-different>. [Accessed 5 05 2023].

## Acknowledgement

This paper was written by Mark Staub, PhD at TA Instruments.

# Characterization of Bio-Derived Polymer Under Controlled Humidity

## Abstract

Bio-derived and biodegradable polymers are increasingly important materials that serve to improve the sustainability of a product from initial synthesis and manufacturing to end of life. However, in the presence of humidity the properties of these materials can change greatly, from the softening point to the mechanical characteristics. With humidity chambers, DMA and rheology can give insights into the changes that occur with moisture, thus greatly expanding the characterization and understanding of these materials. The TA Instruments DMA 850 equipped with a relative humidity unit provides the ability to comprehensively study the various effects of moisture on bio-derived polymers while they are in the solid state. In this apps note, the properties of PLA are studied under various controlled humidity and temperature conditions.

## Introduction

Bio-derived and biodegradable polymers play an increasingly important role in mitigating industrial pollution associated with petroleum-based and/or non-recyclable polymers. Poly-lactic acid (PLA), which is a semicrystalline polyester that can be both bioderived and biodegradable depending on the synthesis mechanism, has grown in popularity in recent years.[1,2] It is one of few bioderived polymers that feature tensile properties comparable to traditional thermoplastics. Additionally, PLA is suitable for applications requiring biocompatibility such as implants, meshes, tissue scaffolds in addition to applications such as packaging, and consumer products. [1]

An important consideration of bio-derived and biodegradable polymers such as PLA is analyzing the overall affinity for water and the effects this may have on performance, such as mechanical properties and changes in sample dimensions.[3] Atmospheric moisture (relative humidity) can have the effect of plasticizing the polymeric material, effectively decreasing the elasticity, altering the mechanical performance of the polymer as a function of deformation frequency, and causing swelling (dimensional changes).[3] Unfortunately, these effects cannot be captured in a typical DMA or rheology experiment lacking humidity control, where typically only the temperature or atmospheric gas can be modulated. However, with the relative humidity fixture for the DMA 850, the complex mechanical properties of solid and/or rubbery materials can be characterized at a variety of environmental conditions, with the ability to modulate both temperature and humidity.

In this applications note, dynamic mechanical analysis (DMA) and rheology are used to characterize PLA's response to humid environments, including the dependence of the glass transition temperature on humidity, mechanical properties as a function of frequency at various temperatures and humidity setpoints, and the expansion or contraction of a sample in response to moisture.

## Experimental

The grade of PLA used in this work was LX175 purchased from Filabot (Vermont, USA). DMA samples were rectangular compression molded films, 7.5 mm long, 5 mm in width, and 0.35 mm in thickness. The DMA film tension clamp was used in all experiments in conjunction with the RH chamber add on. The operating range of the RH chamber can be found in Figure 1. To measure the effect of moisture on glass transition temperature, the samples were equilibrated at 25 °C, then conditioned at a humidity of 5, 30, 55, or 80% RH for 300 minutes, and finally subjected to an oscillation temperature ramp of 1 Hz at 0.05% strain from 25-85 °C at a rate of 1 °C/min. The viscoelastic response of the PLA at 5, 30, 55, and 80% RH was measured by again doing thermal and humidity conditioning steps, following by an oscillation frequency sweep of 0.1-10 Hz at 0.05% strain. Finally, hygroscopic expansion was investigated by performing an oscillation time sweep after thermal conditioning to a temperature of 25, 37.5, or 50 °C. Samples underwent 1 Hz at 0.05% strain for 300 minutes at a set humidity of either 5, 30, 55, or 80% RH. After the sweep completed, the humidity was conditioned to the next setpoint at a rate of 2% RH/min and another oscillation time sweep was performed.



DMA-RH Operating Range

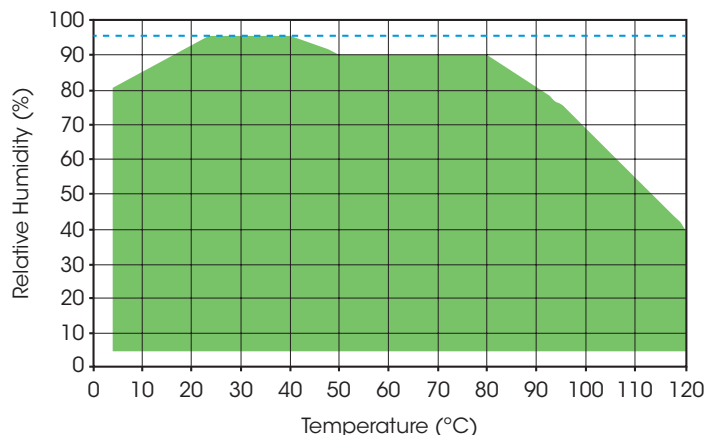


Figure 1. (Top) TA Instruments DMA 850 with relative humidity (RH) unit equipped. (Bottom) The DMA-RH operating range is shown where relative humidity is plotted as a function of temperature. The green represents the usable region.

## Results and Discussion

### Glass Transition Dependence on Humidity

Figure 2 shows oscillation temperature ramp data, where tan delta is plotted as a function of temperature for various humidity setpoints. Moisture acts as a plasticizer to PLA, effectively lowering the strength of the molecular interactions of the polymer matrix, thus lowering the glass transition. [4,5] The peak points of the tan delta represent one method of determining the glass transition temperature. As humidity increases, the effective glass transition temperature decreases. Between a relative humidity of 5-80%, the glass transition temperature varies over 10 °C (62-73 °C). This is a major consideration for not only processing various grades of PLA, but also the softening point (upper thermal limit, heat deflection temperature) which has implications for the final product. This effect is well known for Nylon, among other polymers, but is also of critical importance for bio-derived and/or biodegradable polymers. [4] Polymer processors can use this information to observe how humidity may be introducing variability to their process, or to condition a polymer to a humidity level to take advantage of the plasticizing effect of the moisture.

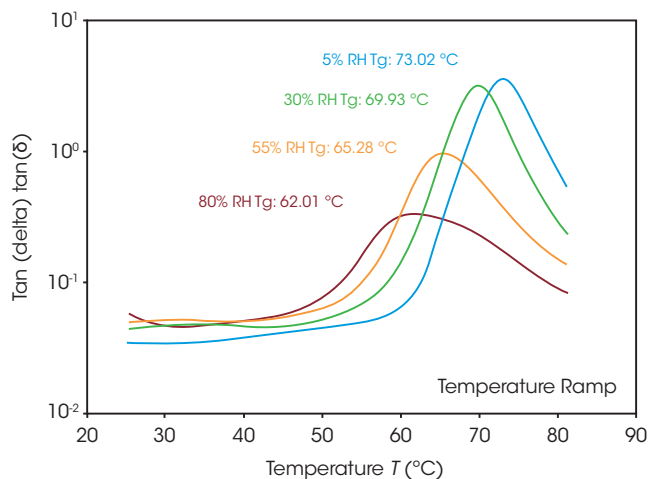


Figure 2. (Temperature ramp data) Tan delta is plotted as a function of temperature for samples subjected to various humidity setpoints of 5, 30, 55, and 80% RH.

### Viscoelastic Response to Moisture at Different Temperatures

Frequency sweeps provide complex viscoelastic data such as storage modulus, loss modulus, tan delta as a function of the deformation frequency, effectively measuring the mechanical properties, or the extent to which a material responds in a liquid or elastic modality and related molecular relaxation processes as a function of timescale or frequency. The viscoelastic data as a function of frequency for the PLA films has been characterized at a variety of humidity settings (5, 30, 55, 80% RH), and for three overall temperatures all below the glass transition of the PLA (25, 37.5, and 50 °C relative to a glass transition temperature range of 62-73 °C).

Figure 3 features an overlay of frequency sweep data at each humidity setpoint, at a testing temperature of 25 °C. Storage modulus and tan delta are both plotted as a function of frequency. As a result of increased humidity, storage modulus decreases slightly and tan delta increases, which both demonstrate the softening of the PLA. It is worth noting, however, that the changes are very small in magnitude at this temperature.

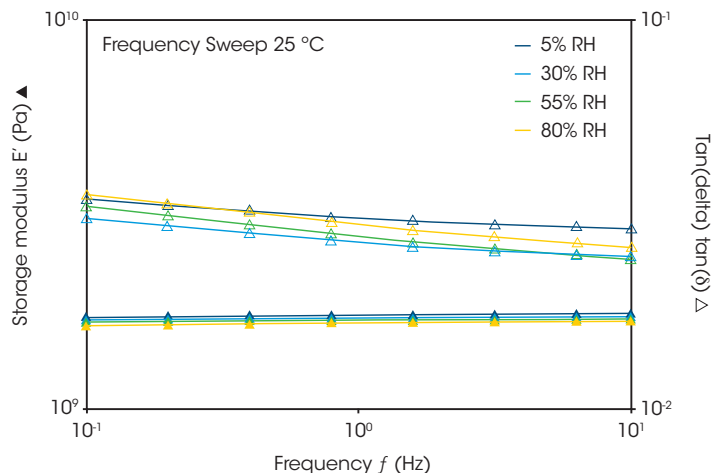


Figure 3. (Frequency sweep data) Storage modulus and tan delta are plotted as a function of frequency for samples held at 25 °C.

This contrasts with the results at 37.5 °C, shown in Figure 4, where again storage modulus and tan delta are plotted as a function of frequency for the various humidity setpoints. While changes to the storage modulus are still marginal with increased humidity, the changes to tan delta are much more substantial at this temperature. The increase in the tan delta with humidity indicates that the PLA is becoming less elastic and more viscous in terms of mechanical response.

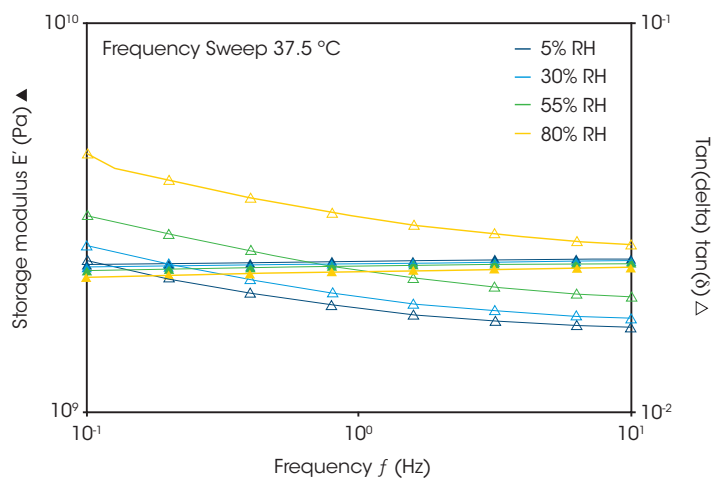


Figure 4. (Frequency sweep data) Storage modulus and tan delta are plotted as a function of frequency for samples held at 37.5 °C.



Finally, in Figure 5 storage modulus and tan delta are plotted as a function of frequency for the various humidity setpoints, when the PLA sample is held at a temperature of 50 °C. At this temperature, the effect of humidity on the mechanical response is considerably larger than at the previous temperatures. At a frequency of 0.1 Hz, the change in storage modulus and tan delta are over a decade in magnitude, when considering humidity setpoints of 5% and 80%. Additionally, the complex mechanical response also has a much stronger frequency dependence, which wasn't observed at the other temperatures.

This data illustrates that even below the glass transition temperature, the viscoelastic properties of semicrystalline PLA polymer still show sensitive response to the environmental temperature and humidity, where the polymer exhibits different mechanical properties than expected. These measurements allow a producer or manufacturer to define limits for the use of the material, which are dependent on the environment.

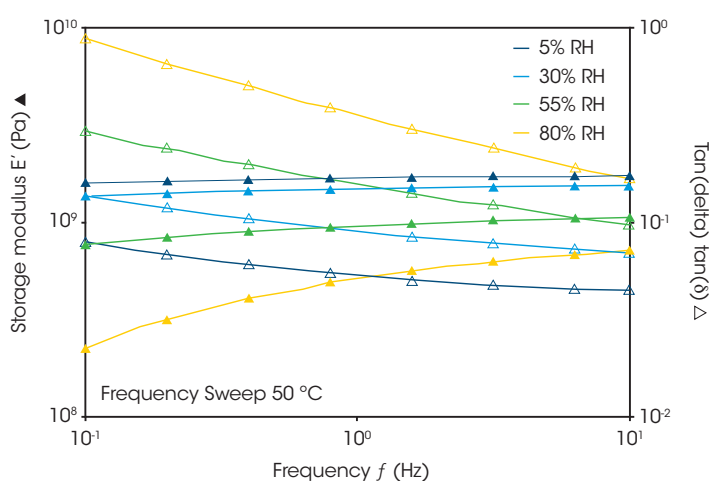


Figure 5. (Frequency sweep data) Storage modulus and tan delta are plotted as a function of frequency for samples held at 50 °C.

## Hygroscopic Expansion

Analogous to the changes in mechanical response due to a combination of temperature and moisture as seen in the last section, the expansion or contraction of a material can also be characterized in response to these factors. From an oscillation time sweep step in procedure, the length change of the sample can be observed as a function of time.

Figure 6 features oscillation time sweep data, where sample length is plotted as a function of time for temperatures of 25, 37.5, and 50 °C respectively. The curves in each plot are representative of sample length after held at the setpoint environmental temperature and the various humidity setpoints. From the starting point of each curve, the humidity is ramped in increments every 300 minutes (see inset), the ramping period can be observed through small gaps in the curves.

At 25 °C, it can be observed that regardless of the humidity setpoint, the magnitude of sample expansion over the course of the observation window is negligible. When the temperature is increased to 37.5 °C, the sample undergoes a bit more elongation but the overall percent change is still quite small, expanding approximately 1% in length. This demonstrates that at these temperatures and humidity setpoints, the changes in the sample dimensions are still very small.

When held at 50 °C, the sample undergoes significant expansion at elevated humidity setpoints. At a humidity setpoint of 55%, around 800 minutes into the experiment, the sample elongates over 20% from the start to the end of the oscillation time step. This effect is accelerated at higher humidity setpoints, until the sample is saturated with moisture and the length starts to reach a plateau. Between 37.5 °C and 50 °C and above 30% relative humidity, the sample has major dimensional expansion compared to the lower setpoints. This sets an upper limit on the environmental conditions that this grade of PLA can be used in before the product geometry expands.

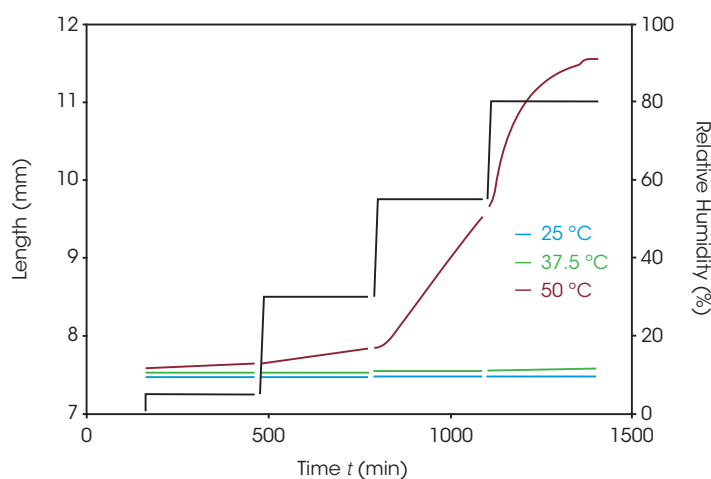


Figure 6. (Time sweep data) Sample length is plotted as a function of time for samples held at 25, 37.5, and 50 °C at various humidity setpoints. From the first point of each curve, humidity is ramped in intervals of 300 minutes.

## Conclusions

The TA Instruments DMA 850 equipped with the relative humidity chamber is a powerful tool and workstation to comprehensively characterize bio-derived sustainable polymers, as well as a host of other materials. In this applications note, the effect of moisture on the properties of a bio-derived polymer (PLA) were characterized using three methods:

- One method characterized the glass transition temperature at different relative humidity setpoints. This can be of critical importance for polymer processing or in applications where the heat deflection temperature or upper thermal limit are critical.
- The next method characterized the frequency dependent mechanical properties at several temperatures and humidity setpoints. Depending on the timescale (frequency) of mechanical deformations applied to the polymer, the humidity, and the temperature, the polymer may have mechanical properties that differ from the material data sheet.
- The last method characterized changes in the dimensions of the PLA sample (percent length change) when subjected to a several temperatures and humidity setpoints. This is critical for final products, which are generally molded or machined to specific dimensions and tolerances

The data obtained from these methods offers powerful insight into the effect of moisture and humidity on the processing and performance of bio-derived polymers, a key understanding needed to produce and utilize these sustainable polymers.

## References

- 1 Masutani, K., and Kimura, Y. "Poly(lactic acid) Science and Technology: Processing, Properties, Additives and Applications" The Royal Society of Chemistry, 2015, pp. 1-36
- 2 Tokiwa, Y., Calabia, B.P. Biodegradability and biodegradation of poly(lactide). Appl Microbiol Biotechnol, 2006, Vol. 72
- 3 Holm, V.K., Ndoni, S. and Risbo, J. (2006), The Stability of Poly(lactic acid) Packaging Films as Influenced by Humidity and Temperature. Journal of Food Science, 71: E40-E44. <https://doi.org/10.1111/j.1365-2621.2006.tb08895.x>
- 4 Rocca-Smith, J. R. and Whyte, O. and Brachais, C-H and Champion, D. and Piasente, F. and Marcuzzo, E. and Sensidoni, A. and Debeaufort, F. and Karbowski, T. "Beyond Biodegradability of Poly(lactic acid): Physical and Chemical Stability in Humid Environments". ACS Sustainable Chemistry & Engineering, 2017, Vol. 5
- 5 Grunina, N. A. and Belopolskaya, T.V. and Tsereteli, G. I. "The glass transition process in humid biopolymers. {DSC} study". Journal of Physics: Conference Series, 2006, Vol. 40

## Acknowledgement

This paper was written by Keith Coasey, Ph.D., Rheology Applications Engineer at TA Instruments.



©2024 TA Instruments/Waters Corporation.

**TA Instruments**  
159 Lukens Drive  
New Castle, DE 19720 U.S.A.  
T: 1 302 427 4000  
F: 1 302 427 4041  
[www.tainstruments.com](http://www.tainstruments.com)

**Waters Corporation**  
34 Maple Street  
Milford, MA 01757 U.S.A.  
T: 1 508 478 2000  
F: 1 508 872 1990  
[www.waters.com](http://www.waters.com)