Investigation of Biodegradable Plastics using EGA and Pyrolysis-GC/MS

Author:

Karen Sam

Application Note
Polymer, Packaging

Abstract
This application note follows the pyrolysis application decision making tree with EGA and pyrolysis to study biodegradable plastics.

Introduction
With the rapidly increasing production of disposable plastic products, plastic pollution has become a pressing environmental issue. Biodegradable plastics, which can be decomposed by the action of living organisms, are part of the solution to this problem[1]. In this application note, EGA plus analytical pyrolysis was used investigate biodegradable polymers.

Experiment Setup
For analysis, 100µg of polylactide standard was first added into a DISC (Drop-In-Sample Chamber) tube and then analyzed using Evolved Gas Analysis (EGA) on a Pyroprobe 6150 and a vent free adapter as an initial screening step. Using the information from this step, single step pyrolysis GC-MS was performed on different types of biodegradable consumer products.

EGA

Pyroprobe		GC-MS	
DISC:		Column:	fused silica (1m x 0.10mm)
Initial:	100°C	Carrier:	Helium 1.25mL/min,
Final:	800°C		80:1 split
Ramp Rate:	100°C per min	Oven:	isothermal 300°C
Interface:	300°C	Ion Source:	230°C
Transfer Line:	300°C	Mass Range:	35-600amu
Valve Oven:	300°C		

Pyrolysis

Pyroprobe		GC-MS	
Pyrolysis:	500°C 30s	Column:	5% phenyl (30m x 0.25mm)
Interface:	300°C	Carrier:	Helium 1.00mL/min
Transfer Line:	300°C		50:1 split
Valve Oven:	300°C	Injector:	360°C
		Oven:	40°C for 2 min
			8°C/min to 300°C (15min)
		Ion Source:	230°C
		Mass Range:	25-600amu

Results and Discussion
From the Evolved Gas Analysis of polylactide, it is observed that degradation begins at 300°C, peaks at 400°C, and is fully degraded by 500°C (Figure 1), therefore a temperature of 500°C was chosen for pyrolysis GC/MS, which is shown in Figure 2. At 500°C, acetaldehyde and cyclic lactide dimer isomers are the most prominent peaks, followed by a repeating pattern of oligomers.

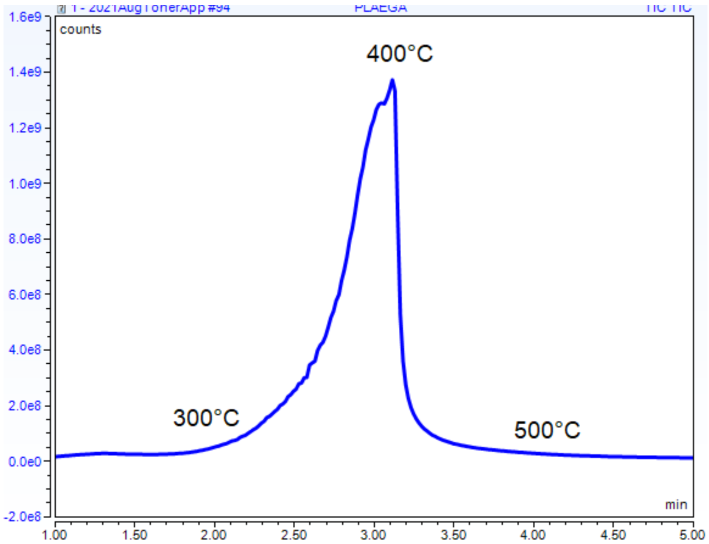

Figure 1. Evolved Gas Analysis of polylactide at 100°C per minute from 100°C to 1000°C.

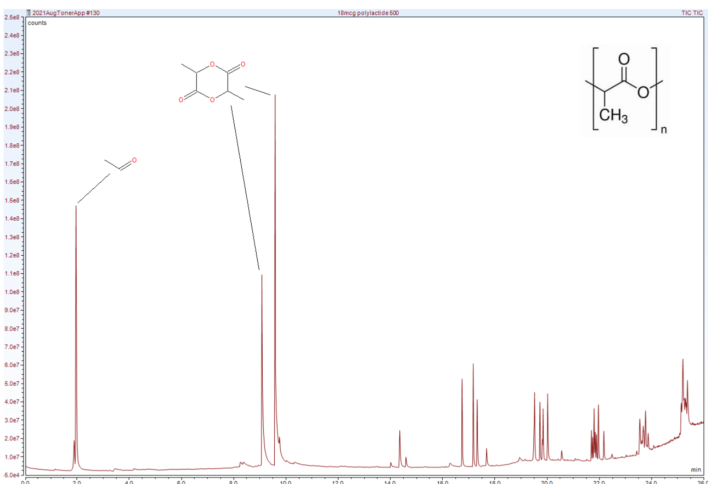

Figure 2. Pyrolysis of polylactide at 500°C.

To verify the quantitative performance on biodegradable samples, a polylactide standard was dissolved in 2-Butanone at a concentration of 9μg/μL. Aliquots, 2μL, of the standard, were added to a quartz fiber filters placed in the well of DISC tubes, resulting in 18μg of polylactide in each tube. These were pyrolyzed at 500°C. Peak Area ratios of m/z 56 of the lactide dimer was found to have an RSD of 1.9% (Table 1).

Table 1. Peak Area Ratios of m/z 56, lactide isomers in a polylactide standard at 500°C.

Replicates	Lactide Peak Area Ratio
Rep 1	1.60
Rep 2	1.56
Rep 3	1.63
Rep 4	1.64
Rep 5	1.63
Rep 6	1.65
Rep 7	1.61
Average	1.62
RSD (%)	1.94

After the EGA and RSD study, a selection of consumer products, which were labeled as biodegradable, were examined. Figure 3 contains pyrograms of a juice bottle, and the label on the juice bottle. Both of them have a large peak for lactide, indicating polylactide is present, but the pyrograms are not identical. The label has an additional peak, 2-oxepanone. This was confirmed to be from another biodegradable polyester, polycaprolactone, by comparing it against a standard (Figure 4).

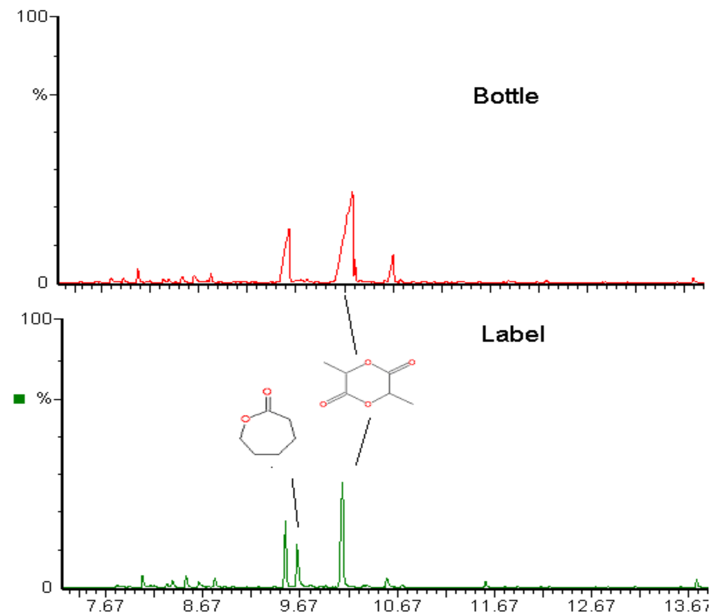

Figure 3. Pyrolysis of a Juice Bottle and Label.

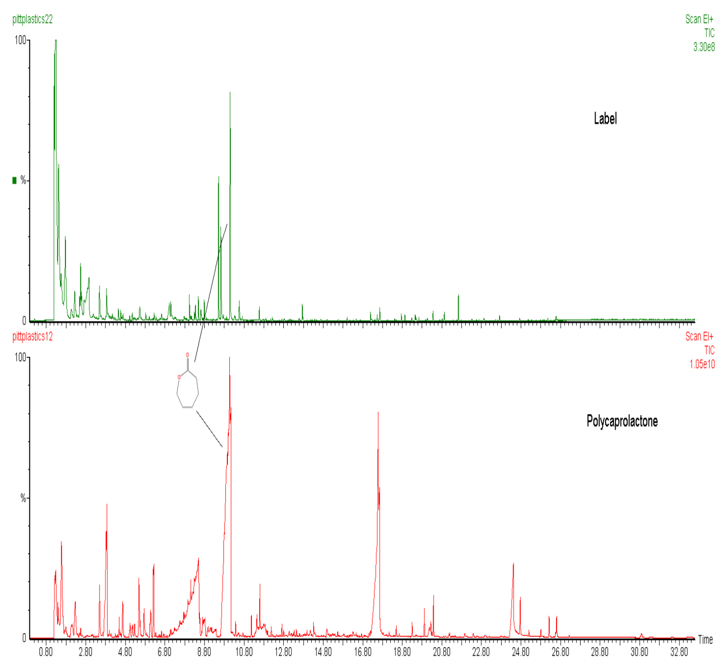

Figure 4. Label (top) and Polycaprolactone (bottom).

A popular brand of snack chips with biodegradable packaging, is composed of 3 layers. Figure 5 shows pyrolysis of the innermost layer, which has the lactide dimer isomers seen in the polylactide standard, and it is also a match for polylactide against the polymer library (Figure 6).

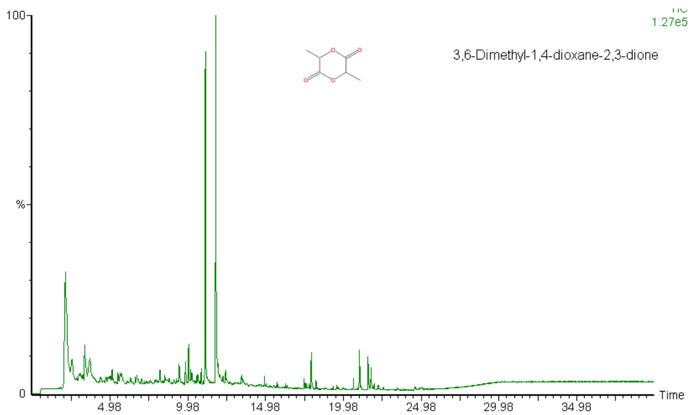

Figure 5. Inner layer of snack packaging.

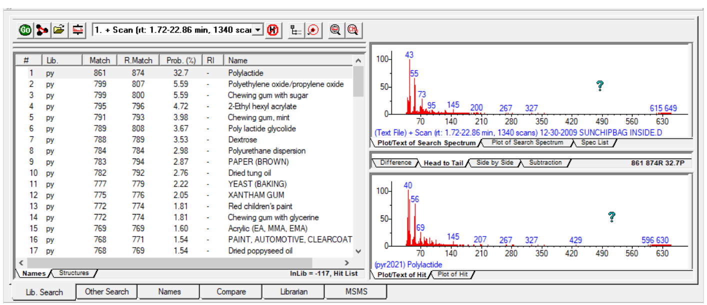

Figure 6. Polymer Library Search Results

Conclusion

CDS Pyroprobe provides distinct and highly repeatable pyrograms, allowing it to be useful for determining the structure of unknown plastics, including biodegradable plastics.

References

1. M. Agarwal, K. Koelling, J. Chalmers, Characterization of the Degradation of Polylactic Acid Polymer in a Solid Substrate Environment, Biotechnology Progress, 05 September 2008.