#200

Investigation of Biodegradable Plastics using Pyrolysis-GC/MS

Author:

Karen Sam

Application Note

Polymer, Packaging, Pharmaceutical

Abstract

This application note uses pyrolysis and multi-step pyrolysis to study biodegradable plastics.

Introduction

The recent growing concern for our ecosystem quality as well as limits of natural resources, such as petroleum, lead to development of biodegradable plastics. These are plastics that can be decomposed by the action of living organisms. These degradable plastics may be made from plant starch; still others are blends of starch and synthetic polymers. Analytical pyrolysis extends the applications of a gas chromatograph to nonvolatile materials such as polymers. Here, analytical pyrolysis was used investigate manmade biodegradable polymers.

Experiment Setup

A CDS Pyroprobe was interfaced to a GC/MS Each sample of 100 micrograms was heated inside a quartz sample tube using the platinum coil of the Pyroprobe. The resulting volatiles were transferred via a transfer line to the gas chromatograph for analysis. The gas chromatograph was equipped with a 30M HP5MS column, which was held at an initial temperature of 40°C for 2 minutes, then ramped at 8°C per minute to a final temperature of 300°C, which was held for 5 minutes. The detector was set to scan from 25 to 550 amu.

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

Results and Discussion

Consumer Packaging

Most beverage bottles are made from the polyester, polyethylene terephthalate, which is not degradable. More recent, degradable packaging uses polylactic acid, or polylactide, which is a polyester derived from cornstarch, or sugar cane. Some beverage manufacturers use packaging made of polylactic acid. Figure 1 contains pyrograms of a juice bottle, and the label on the juice bottle.Both of them have a large peak for lactide, but the pyrograms are not identical. The label has an additional peak, 2-oxepanone. This is also found in the degradable polyester, polycaprolactone, (Figure 2).

A popular brand of snack chips with biodegradable packaging, is composed of 3 layers. Figure 3 shows pyrolysis of the innermost layer, which is a polymer library match for polylactide.

An Italian company, Novamont makes a degradable plastic they call Mater-Bi. Their literature says it is made of plant starch and polyesters, and vegetable oils. A multi-step pyrolysis sequence on a piece of a trash bag made of Mater-Bi. First the plastic was heated to 150°C, then 300°C, and then finally at 750°C (Figure 4). No desorption products are released at 150°C. However, at 300°C, the bag starts to degrade, revealing a small amount of lactide, a pyrolysis product of polylactice polymer. Finally, the pyrolysis run at 750°C provides a large peak of benzoic acid and biphenyl. These are typical of polyesters that have terepthtalate. Also, butadiene is present. The combination of these pyrolysis products may from the compostable polyester, polybutylene adipate/terephthalate. The plant starch material, listed as an ingredient, may have been structurally altered into polylactic acid, which produces lactide upon pyrolysis.

Polyvinyl alcohol and polyvinyl acetate have similar structures. Polyvinyl alcohol is often used in packaging applications that dissolve in water to release a product, like laundry detergent. Polyvinyl acetate is used as glue. One has a hydroxyl group while polyvinyl acetate has an acetate group. Although structure is similar, pyrograms differ largely (Figure 5). The acetate bond in polyvinyl acetate is weaker than the hydroxyl bond in polyvinyl alcohol, so the acetic acid strips off, leaving an unsaturated backbone that stabilizes by forming conjugated rings.

Medical Plastics

Polylactide, polyglycolide and polycaprolactone are not new plastics to the medical community. They are used in biomedical applications such as sutures and drug delivery systems. Polylactide and Polyglycolide have similar structures. Pyrograms of Polylactide, Polyglycolide, and Poly(colactide glycolide) are found in Figure 6. It can be noted that the copolymer Poly(colactide glycolide) has pyrolysis products from each homopolymer. Polycaprolactone is a repeating unit with 5 carbons. When Pyrolyzed, it regenerates caprolactone monomer (Figure 8).

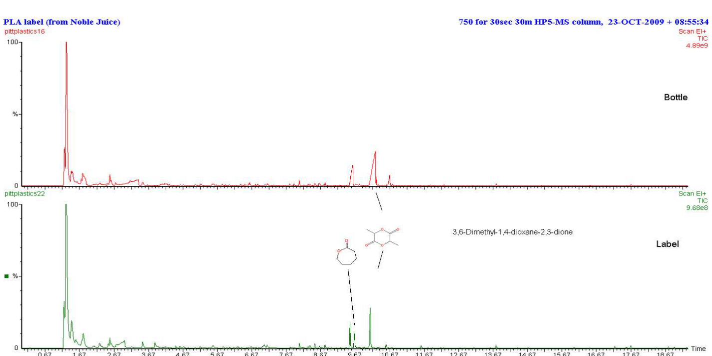

Figure 1: Pyrolysis of a Juice Bottle and Label, (700°C)

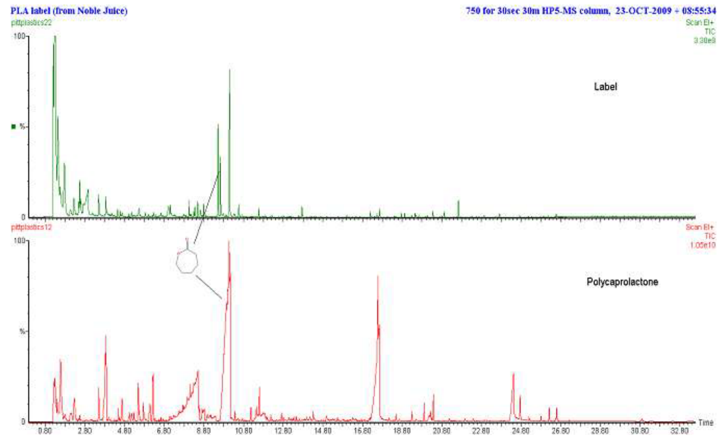

Figure 2. Label (top) and Polycaprolactone (bottom), 700 °C.

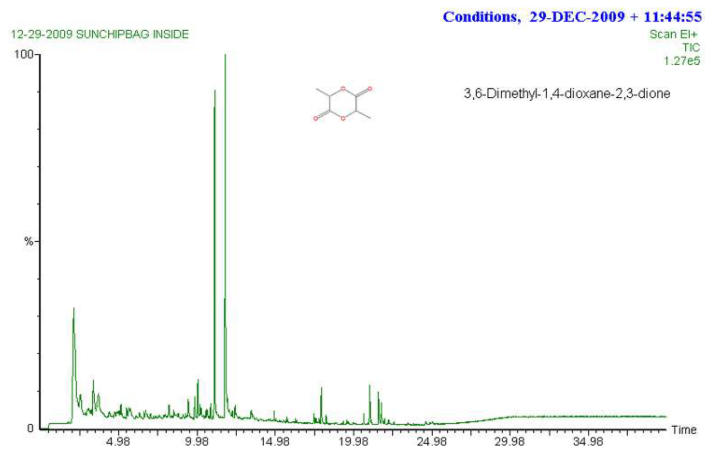

Figure 3. Inner layer of snack packaging, 700°C.

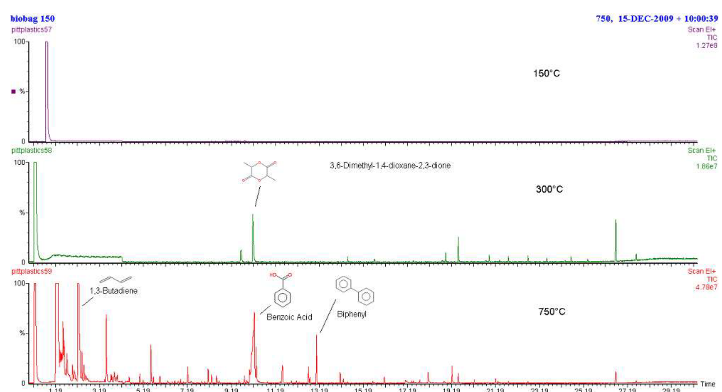

Figure 4. Multistep pyrolysis (150°C, top, 300°C center, 700°C bottom) of degradable trash bag.

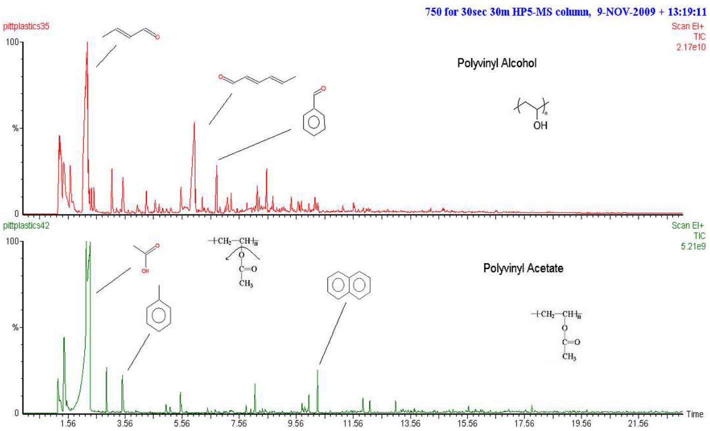

Figure 5: Pyrograms of Polyvinyl alcohol(top), and Polyvinyl acetate (bottom).

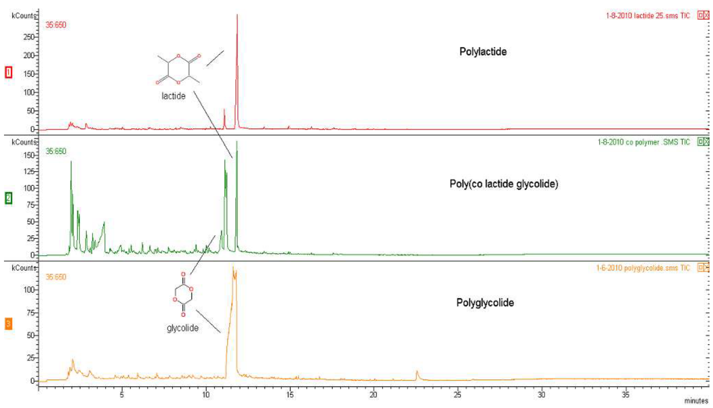

Figure 6. Pyrograms of Polylactide (top), Poly (co lactide glycolide (center), and polyglycolide (bottom).

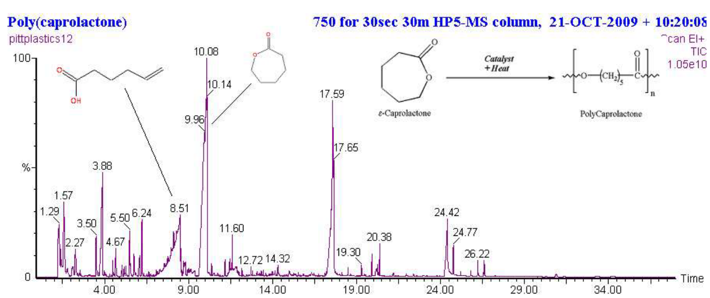

Figure 7. Pyrogram of Polycaprolactone.

Conclusion

Analytical pyrolysis and multi-step pyrolysis GC/MS with the CDS Pyroprobe provides distinct repeatable chromatograms based on polymer structure. This allows it to be useful for determining the structure of unknown plastics, including biodegradable plastics.