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Evaluation of Bioplastics by Pyrolysis-GC/MS

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ABSTRACT

As concern about the impact of conventional, petroleum-based plastics grows, bioplastics (BPs) have emerged as potential, sustainable alternatives. But the fate of BPs in the environment remains unclear and some may breakdown into nano- and micro-plastics forms in a similar manner to petroleum-based plastics. Potential adverse ecological effects of nano- and micro-BPs are generally unknown. Methods and approaches will be needed to measure and identify these classes of plastics. To evaluate methods for identifying and quantifying these new plastics in the environment, polylactic acid (PLA), poly-L-lactic acid (PLLA), polyhydroxybutrate (PHB), polyhtdroxyalkanoate (PHA) and a PHB/PHV (polyhydroxyvalerate) copolymer were analyzed by single shot and double shot pyrolysis-GC/MS methods as solids and after dissolution. Results indicate that the method of analysis can affect the pyrolyzates formed and may ultimately affect the identification of the biopolymer.

INTRODUCTION

Micro- and Nano-Plastics (MP and NP):

Microplastics (5mm - 1 nm) are generally the result of the breakdown of larger plastics. This definition includes the smaller fraction, nanoplastics (1000 - 1 nm).

Biopolymers (BPs):

- Bio-based, not petroleum-based, polymers.
  - ✓ Used in compostable food service items and packaging as well as medical devices.
- Generally considered more biodegradable and sustainable than conventional plastics.
  - ✓ **The enhanced degradability of BP may impact traditional methods of analysis.**

Pyrolysis-GC/MS (PYR-GC/MS):

- Tool used for the analysis of polymers.
- Materials heated in inert atmosphere (N_2) and degraded into smaller units called pyrolyzates.
- Pyrolyzates separated by gas chromatography and detected by mass spectrometry.
  - ✓ Pyrogram: chromatogram of pyrolyzates
- Evaluation of pyrogram, mass spectra of individual and/or combined pyrolyzates allows for polymer or additive identification.
  - ✓ Additives can include antioxidants, stabilizers, and plasticizers.
- Mass spectral and pyrogram libraries have been developed expressly for PYR-GC/MS.
- Single Shot (SS) (flash pyrolysis) or Double Shot (DS) (thermal desorption (TD) followed by flash pyrolysis) analyses can provide complementary information about polymers and mixtures.
  - ✓ TD can be used to remove interfering natural organic matter (NOM) from samples containing traditional polymers.
  - ✓ Traditional polymers generally not affected (i.e., degraded) by temperatures below 450°C while most NOM degrades below 450°C.
  - ✓ **TD may impact biopolymers and affect analysis, identification and quantitation.**

OBJECTIVES

- Generate SS pyrograms of BP as solids and after dissolution.
- Generate SS and DS pyrograms of biopolymer solids.
- Evaluate effect of the selection of solvent and pyrolysis method on pyrograms and library matching.

MATERIALS & METHODS

- Biopolymers from Goodfellow Corp. Huntingdon, UK. Structures not available from the manufacturer.
  - ✓ PLA (Polylactic Acid) - #ME346310
  - ✓ PHB (Polyhydroxybutyrate) - #BU396311
  - ✓ PHA (Polyhydroxyalkanoate) - #PH326301
  - ✓ PLLA (Poly-L-Lactic Acid) - #ME331050
  - ✓ PHB92%/PHV8% - (copolymer-PHB/Polyhydroxyvalerate) - #BV301010
- Optima grade Methylene Chloride and Chloroform
- GC/MS: ThermoFisher 1300 Gas Chromatograph with TSQ9000 Tandem Mass Spectrometer
  - ✓ Column: Frontier UltraAlloy-5 - 30m.
- Pyrolysis system: Multi-Shot Pyrolyzer 3030D Frontier Laboratories, Fukushima, Japan
- Spectral matching program: F-Search Frontier Laboratories, Fukushima, Japan

Pyrolysis programs:

- Single shot (SS) - 600°C for 12 seconds
- Double-shot (DS) - TD: 80 to 450°C at 30°C/min followed by flash pyrolysis at 600°C for 12 seconds

GC/MS program:

- Matched temperature gradient of pyrograms in F-Search Library
- Initial Temp: 40°C, hold 2 minutes
- Final Temp: 320°C at 20°C/min, hold 14 minutes
- Helium flow: 1ml/min
- Split ratio: 100/1
- Mass Range: 29-600amu

RESULTS & DISCUSSION

Figure 1: Pyrograms of PHA as a solid and dissolved in chloroform.

- Best match for solid: Poly(3-hydroxy butyrate-co-3-hydroxy valerate) (C1-C20) (56%)
- Best match for dissolved: Polyhydroxybutyrate (90%).
- Additional pyrolyzates in solid sample may indicate that dissolution in CCl_3 causes changes in PHA structure.

Figure 2: Pyrogram of solid PHB and best F-Search library match.

- Largest PHB peak at 13.9min is plasticizer additive tributyl acetylcitrate. Not present in PHB library pyrogram.

Figure 3: Method of thermal degradation (SS vs DS) can impact pyrolyzate formation of BPs.

- Flash pyrolysis provides a searchable pyrogram, but TD does not provide a match for PHB.

Figure 4: Double shot pyrolysis could mask the presence of BP microplastics as PHB is completely degraded during TD.

Figure 5: Library matches must be evaluated closely as many BPs have similar pyrograms or a limited number of pyrolyzates.

Figure 1

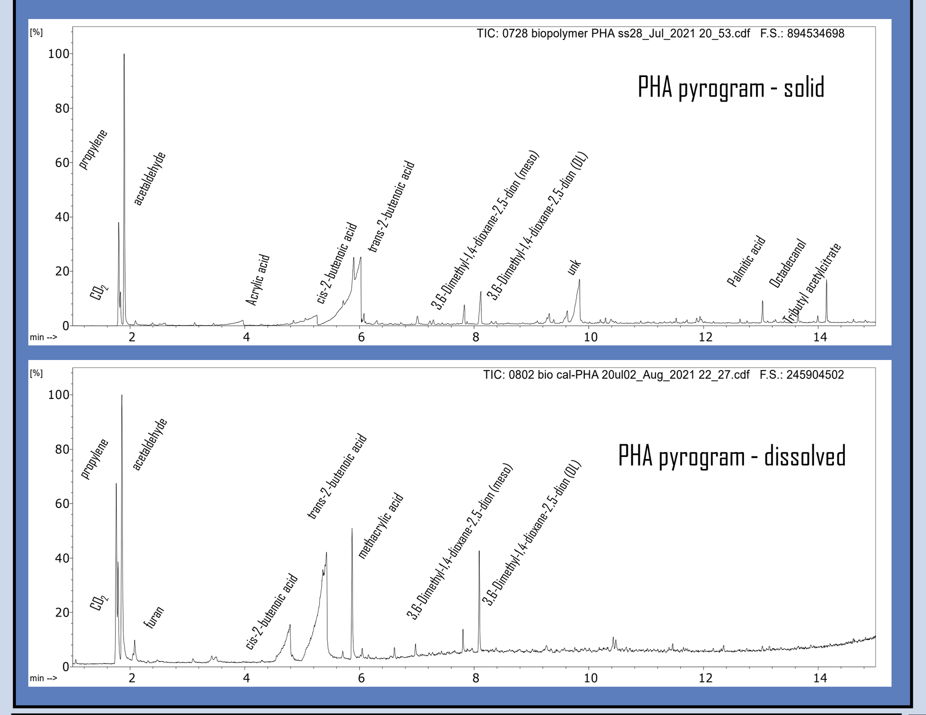


Figure 2

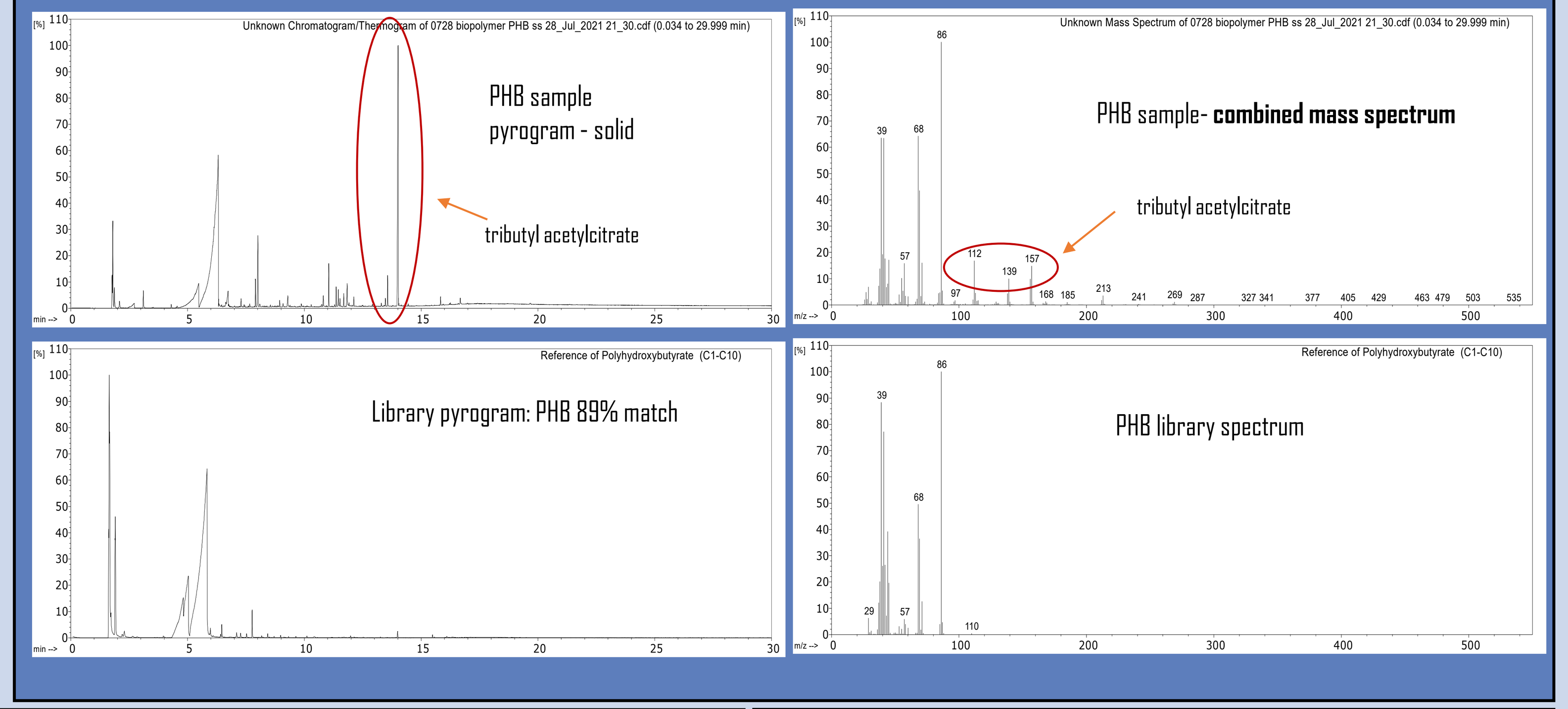


Figure 3

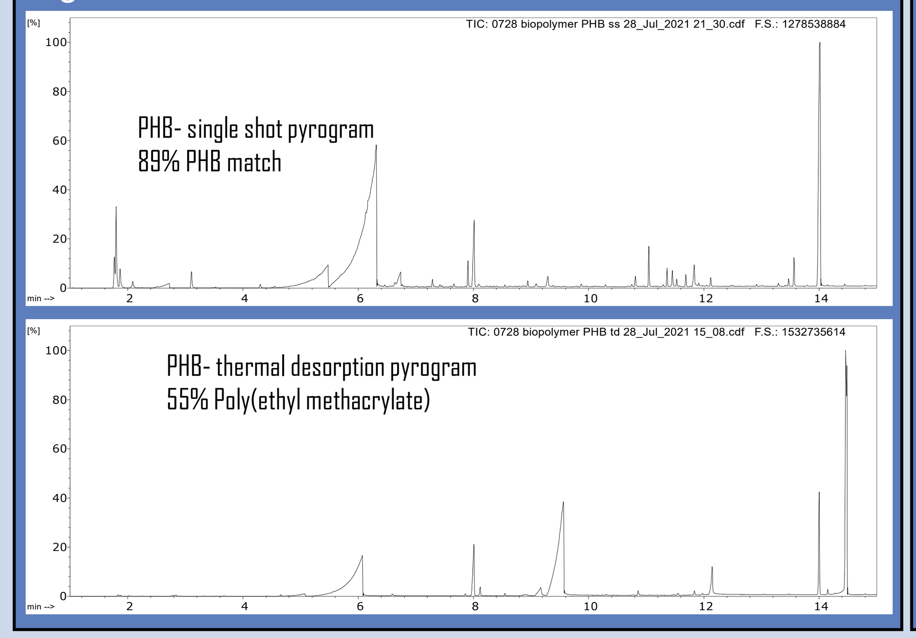


Figure 4

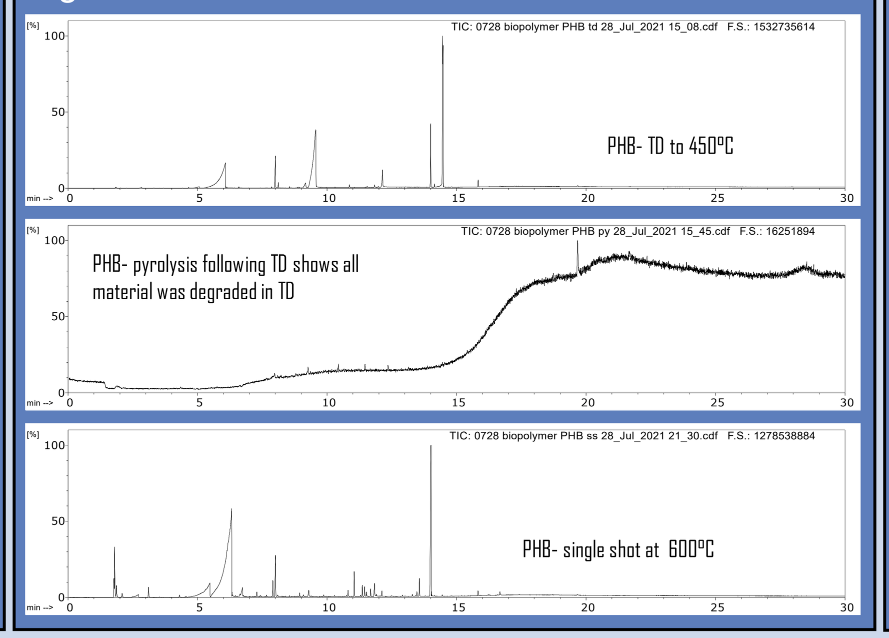
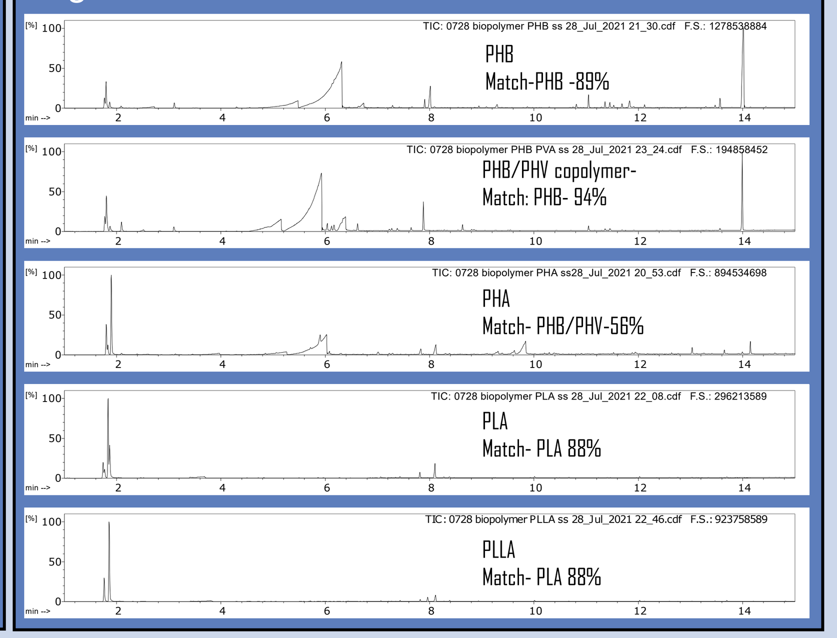


Figure 5



Special considerations when both BPs and traditional plastics are present in a sample

- Polymer additives can negatively impact the ability of spectral libraries to make adequate matches
- User-developed libraries should include both dissolved and solid forms
- Extraction solvents may impact ability to characterize MP and NP in environmental samples
- Methods to remove naturally-occurring organic molecules (e.g., humic acids) may limit or inhibit detection of BPs
- Commercial pyrogram libraries may not include BPs

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