Thermochemical Approaches for the Characterization of Materials

Rodrigo Devivar, Ph.D.
Jacobs Technology / NASA-Johnson Space Center
ES4 Materials Analysis Laboratory
Houston, Texas

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Analytical Chemistry Laboratory Equipment

Key Laboratory Equipment

– Optical Instrumentation
  • UV-Vis, Fluorimeter, Solar Reflectance, Infrared Emittance, Raman
– Thermal Analysis Instrumentation
  • DSC, DMA, TGA, TMA, LFA, Rheometer
– Chemical Analysis Instrumentation
  • FT-IR, Ion trap GC-MS, Py-GC-MS, TGA-MS, TGA-IR
The Analytical Chemistry Cycle

Sample Preparation
- Can the Sample Be Destroyed?

Sample Collection
- How Much Sample is Available?

Sample Measurement
- What Test is Needed?

Destructive Vs. Non-Destructive Analysis
- Are the Results Valid?

Data Analysis
- Is it Urgent?

Information To Customer
- What Test is Needed?

To Customer
- Are the Results Valid?
- Is it Urgent?
Optical Vs. Thermal Techniques

**Light**
- Reflectance
- Emittance
- Absorbance/Transmission
- Fluorescence
- UV-Vis Absorbance
- FT-IR Analysis
- Raman Analysis

**Heat**
- Material Curing
- Thermal Transition-Tg
- Melting Point/ Boiling Point
- Residual Solvent
- Identification of additives
- Material Decomposition
- Elimination of labile functional groups
- Identification of Material Components
- Identification of Inorganic Components
Thermogravimetric Analysis (TGA)

- A TGA instrument consists of an analytical balance and a furnace.
- A small sample of material is heated and its change in mass is measured as a function of temperature.
- Experiments can be conducted under inert or oxidizing atmospheres.
- Information gained from TGA includes:
  - Thermal stability for conducting additional thermal analysis
  - Identification of the number of components in the sample if the decomposition temperatures are different
  - Residual mass for assessing the extent of inorganic additives
Traditional thermal analysis of materials is performed by DSC (Differential Scanning Calorimetry) and by TGA (Thermogravimetric Analysis) instrumentation. Most Thermal Analysis is performed at temperatures below the onset of decomposition. Thermochemical Techniques for Material Characterization will utilize elevated temperatures until the material is fully degraded.
Many industrial laboratories have only one technique available for characterization of the manufactured product. In many situations, one type of analytical technique is not adequate for assessing the product.
Pyrolysis for GC-MS of Solids

- Sample size is relatively small:
  50 to 200 μg is sufficient for solids
  50 to 200 nL is sufficient for liquids

- Sample preparation is easy:
  Place sample inside 1.5 inch quartz tube containing filler tube and plug with glass wool.

- Samples can be solids, gels, viscous liquids, greases, crystalline, emulsions, foams, fabrics

- Pyrolysis temperatures are almost instantaneous

- Sample components can be quantified with the use of software

Pyrolysis is the thermal degradation of any substance through the fast application of heat.
Thermal Analysis of HDPE and LDPE

Polyethylene: \(-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\)
FT-IR Analysis of Silicone Materials

FT-IR is a non-destructive technique that is very diagnostic. However, if infrared light cannot penetrate the sample, any signal obtained through reflectance is only valid for the external surface of a sample.
The Silicone samples that were nearly identical by FT-IR displayed very different properties by thermal analysis.
TGA Analysis of Fluorinated Materials

- **Krytox 143 AZ**
  - Krytox 143AZ oil in N2 to 1000°C
  - Krytox 143AZ oil in air to 1000°C
- **Brayco 815Z**
  - Brayco 815Z oil in N2 to 1000°C
  - Brayco 815Z oil in air to 1000°C

**Notes**:
- Universal V3.9A TA Instruments
- Weight (%) vs Temperature (°C) graphs for each material under different conditions.
FEP Vs. PTFE Teflon

**FEP Teflon**

- 497.48°C 89.29%
- 562.04°C 42.90%
- 521.69°C 81.55%

**PTFE**

- 563.05°C 46.16%
- 550.2°C 46.18%

**Graphs**

- Chromatogram Plots
- Overlaid Chromatogram Plots
- Deriv. Weight (%/°C)
- Temperature (°C) Universal V4.7A TA Instruments

**Formulas**

- \[ \begin{align*}
&\text{FEP:} \quad \left[ \begin{array}{c}
F \quad F \\
C \quad C
\end{array} \right]_m \\
&\text{PTFE:} \quad \left( \begin{array}{c}
F \quad F \\
C \quad C
\end{array} \right)_n
\end{align*} \]
During pyrolysis, materials undergo thermal degradation via chemical pathways dictated by the thermal stability of the components. When pyrolysis is slowed to simulate TGA conditions, a thermal response pattern similar to what was observed with TGA first derivative plot.
The large difference in thermal stability between cotton and silicones can be used to easily characterize the silicone sample collected on a cotton swab.

The cotton may be completely decomposed by application of heat without adversely affecting the silicone.
Under conditions of increasing temperature, the only difference between the two Viton Gaskets was found below 400°C, where the old sample lost a larger percentage of its mass compared to the new sample.
Thermal extraction of the two samples was performed to account for the difference observed in the TGA experiments at temperatures below 400°C. Such an experiment indicated the Old sample contained various fragments that are attributed to polyethylene oxide. Other substances found included Glycerin and Butylated hydroxy toluene (BHT).
Relay sensor boxes along the shuttle’s wing leading edge were composed of Ultem 1000. One lot used to make these relay sensor boxes had failed. Various manufacture lots of sensor boxes were analyzed by Py-GC-MS and an extra peak was noted in one of those lots. The extra peak was due to dichlorobenzene, a solvent used during manufacture of Ultem 1000.
Thermal Response of Travertine in Different Atmospheres

- 599.46°C 97.25%
- 732.56°C 65.50%
- 745.03°C 66.43%
- 800.75°C 56.79%

Weight (%) vs. Temperature (°C)

Travertine N2

Travertine air

Universal V4.5A TA Instruments
CaCO₃ $\rightarrow$ CaC₂ or Calcium Bentonite

Travertine

Travertine TGA ashes (Helium or Nitrogen)

Travertine TGA ashes (Air)
The Role of Gaseous Atmosphere During Thermal Decomposition of Travertine

TGA of Travertine in Air

TGA of Travertine in Nitrogen

Calcium Carbonate

Calcium Bentonite

Calcium Carbide
TGA-MS Analysis of Travertine

Substances being measured during mass loss near 700°C include CO$_2$, CO, and O.
TGA Analysis of Geothite in Helium
Detected Mass Losses of Goethite

At 120°C, Mass losses include:
- m/z 14 (CH₂), 16 (O), 32 (O₂)

At 308°C, Mass losses include:
- m/z 17 (OH), 18 (H₂O), 32 (O₂)

At 1290°C, Mass losses include:
- m/z 16 (O), 18 (H₂O), 32 (O₂)

Goethite α-FeO(OH)
TGA Analysis of Kieserite

[Graph showing TGA analysis data with time and temperature on the x-axis and weight percentage on the y-axis. Key points include:
- Value: 24 min, 100.09 %
- Value: 54 min, 97.64 %
- Value: 112 min, 94.19 %
- Value: 302 min, 91.50 %
- Value: 362 min, 86.97 %
- Value: 447 min, 81.45 %
- Value: 81.6 min, 80.30 %
- Value: 81.6 min, 83.62 %
- Value: 117.7 min, 1197.2 °C
- Value: 111.6 min, 1135.8 °C
- Value: 137.3 min, 1392.8 °C
- Value: 129.5 min, 1314.8 °C
- Value: 129.5 min, 30.57 %
- Value: 137.3 min, 28.17 %
- Value: 111.6 min, 47.58 %
- Value: 117.7 min, 34.55 %
- Value: 81.6 min, 80.30 %
- Value: 24 min, 32.4 °C
- Value: 6.4 min, 78.1 °C
- Value: 21.2 min, 233.3 °C
- Value: 30.2 min, 323.1 °C
- Value: 11.2 min, 131.7 °C

Note: Kieserite is analyzed with a heating rate of 10°C/min, starting at 30°C to 1400°C in helium for TGA-MS 2010, with air to zero.]

[Graph details: Green line indicates TGA data, red dashed line represents temperature, with annotations for key values and temperature ranges.]
Detected Mass Losses of Kieserite

At 78°C, Mass losses include: m/z 17 (OH), 18 (H₂O), 28 (CO)

At 382°C, Mass losses include: m/z 16 (O), 17 (OH), 18 (H₂O), 28 (CO)

At 1136°C, Mass losses include: m/z 16 (O), 28 (CO), 32 (O₂), 48 (SO), and 64 (SO₂)

At 1315°C, Mass losses include: m/z 17 (OH), 48 (SO), and 64 (SO₂)
Applying Thermal Energy to Extract Chemical Information

Using Thermal Energy:
- How much Thermal Energy do we add
- How fast do we add the Thermal Energy
- What atmosphere do we use
- How much sample do we use

Chemical Information
- Trapped solvent
- Organic additives
- Labile Functional Groups
- Monomer identification
- Off-gassing information
- Inorganic additives

TGA          Pyrolysis-GC-MS          TGA-MS-IR