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High Temperature Decomposition of Organic Materials

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Introduction: Material Stability at Elevated Temperature

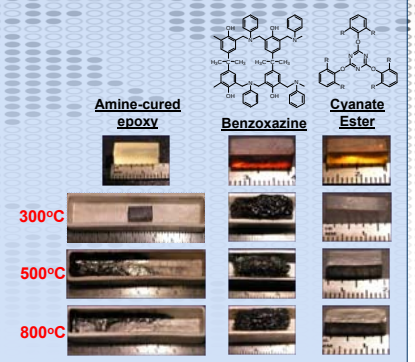
The ability to predict material behavior in abnormal temperature conditions requires a better understanding of thermal degradation processes

Thermal decomposition is one of many degradation processes that ultimately lead to material failure. Understanding the nature of polymer decomposition products is critical for predicting how material failure will affect other system components. Concerns include:

- Production of conductive materials in the form of pyrolyzed, graphitic carbon char resulting in non-predictable electrical behavior.
- Condensable low Mw contaminants.
- Generation of gaseous products leading to pressurization and damage to other components.

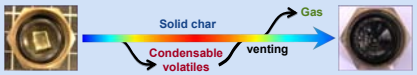
Two experimental approaches were explored:

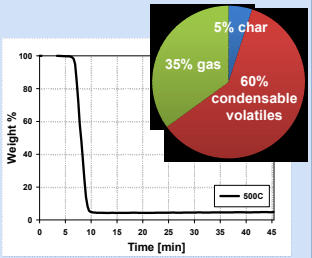
- Extensive studies of weight and volume retention as well as basic conductivity and Raman spectroscopic measurements after high temperature furnace exposure of various thermoset materials
- Pressurization and gas yield measurements in small volumes



Discussion: Solid, Liquid, and Gaseous Decomposition Fractions

Pyrolytic decomposition products are material-dependent





Mass of gas fraction was measured by placing the sample in a separate chamber and taking initial and final masses after exposure to 500°C for 45 minutes and venting. Total volatile and solid residue fractions were determined by isothermal TGA at 500°C.

Conclusions:

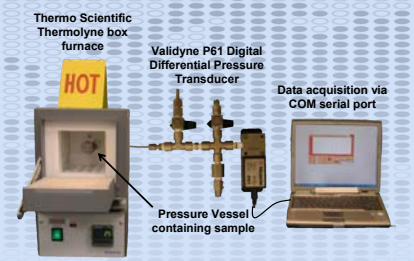
- Residual char levels depend greatly on the type of polymer
- Conductivity becomes an issue for thermoset residues when heated above 550-600°C
- Pressurization is not a major concern for amine-cured epoxy thermoset
  - Gas fraction of ~35%
  - Condensable volatiles of ~60% at high temperature, forming an uneven distribution of viscous liquid residues
  - Solid char reside of ~5%

Future Work:

- Characterization of volatile liquid and solid residues
- Determination of dielectric strength of degraded material
- Continuation of Raman spectroscopy studies to probe heterogeneous nature of decomposition

Aim: Better Understanding of Thermal Decomposition Processes

Setup to determine gas yields



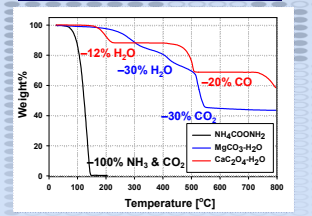
Prediction of presssure increase

Pressurization resulting from thermal expansion of ideal gas in furnace was calculated with the following equation:

$$\frac{P_{amb}}{P} = 1 + \frac{V_{hot}}{V_{total}}\left(\frac{T_{amb}}{T_{hot}} - 1\right)$$

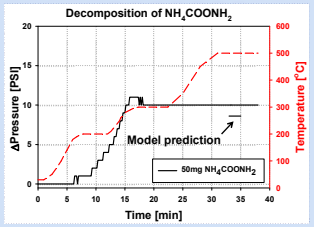
The equation divides the apparatus into two volumes V_{amb} (tubing and transducer manifold) and V_{hot} (sample vessel) at temperatures T_{amb} and T_{hot} respectively. Experimental measurements for the pressurization of air and nitrogen gas at 500°C agree well with analytical predictions. To establish predictability and validity of experimental approach, we explored several inorganic salts which yield gaseous products upon thermal decomposition.

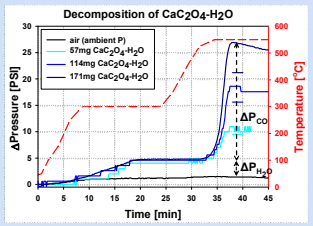
TGA of model compounds



Gas yield per mass of inorganic reference materials was determined by TGA, converted to moles, and used with the ideal gas equation to calculate anticipated pressure increases in confined volumes.

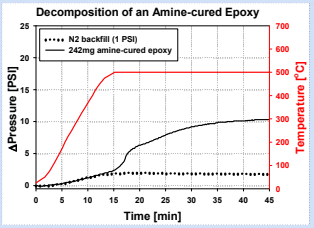
System calibration using known thermal decomposition yield





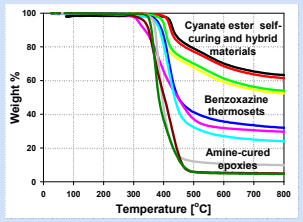
Comparison of model predictions and experimental measurements of gas yield pressurization for decomposition of ammonium carbamate (left figure) and calcium oxalate (right figure). Some deviations occur at higher carbon monoxide yields for calcium oxalate system.

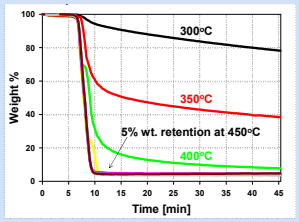
Pyrolytic decomposition of a polymer



An amine-cured epoxy material was selected for pyrolytic decomposition under nitrogen at 500°C.

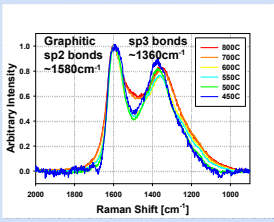
TGA of different polymers shows great variability in char formation





Weight retention depends greatly on the type of polymer (left figure). Isothermal TGA of an amine-cured epoxy material (right figure). Basic conductivity data (not shown) demonstrates that conductivity becomes an issue for residues when heated above 550-600°C.

Raman spectroscopy



Characterization of carbon transition from sp3 to conductive graphitic sp2 as a function of temperature proved challenging due to heterogeneity of char formation.

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