Modeling Vapor/Liquid Equilibrium of Polymer/Solvent Solutions During Thermal Decomposition of Removable Epoxy Foam

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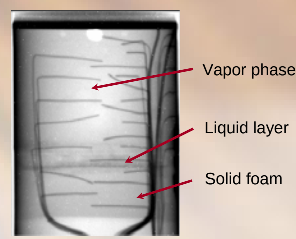
Research Objectives

- Develop a model for the non-ideal vapor/liquid equilibrium behavior of polymer solutions formed during the decomposition of Removable Epoxy Foam (REF)
- Collect experimental vapor/liquid equilibrium data for representative polymer solutions at high temperatures to compare with model predictions

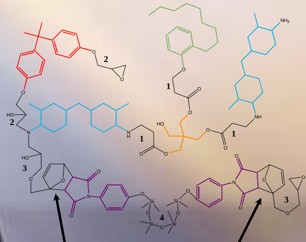
Background

- Removable Epoxy Foam (REF) is used in missiles to protect electronic components
- Above 100 ºC REF begins to decompose to solvent-like and polymer-like products
- Production of vapor raises pressure in missile casing until explosion is possible
- Liquid phase can cause important safety elements to fail
- Previous decomposition models included only solid and vapor phases, or only limited treatment of vapor/liquid equilibrium



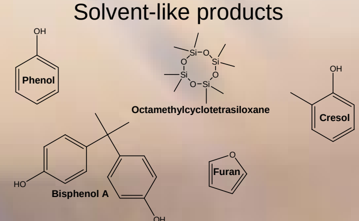
X-ray image of a confined sample of REF being heated from the top

REF Repeating Unit

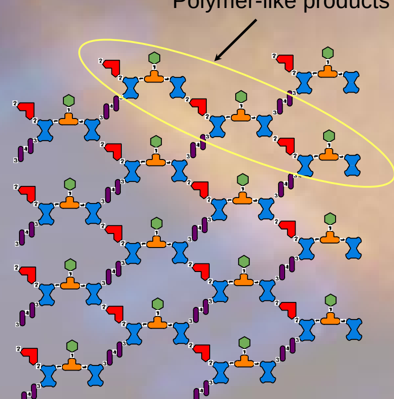


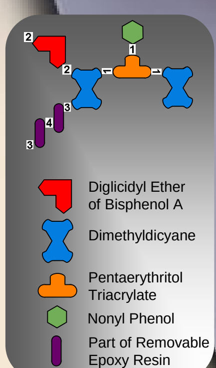
Above 100 ºC, reverse Diels-Alder reactions break epoxy network

Solvent-like products



Polymer-like products





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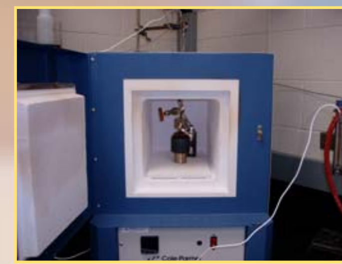
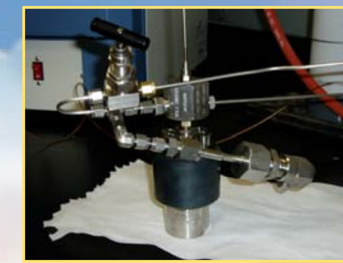
Experimental

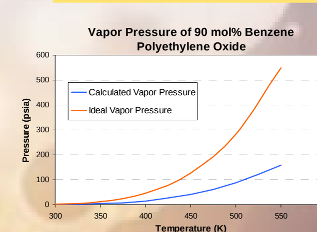


High Temperature Vapor/Liquid Equilibrium Facility



Modeling

- Polymer solutions exhibit non-ideal vapor/liquid equilibrium behavior
- Modeling is done using an equation of state combined via mixing rules with an activity coefficient model suitable for polymer solutions



Equation of State (EOS)

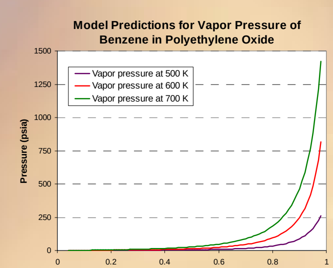
- Relates pressure to temperature and molar volume
  - Good for vapor mixtures and at high temperatures and pressures
- Peng-Robinson equation of state chosen

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$$

- Two parameters, *a* and *b*, for each component

Activity Coefficient Model (ACM)

- Models the deviation of liquid mixtures from ideal solutions
  - Better than EOS for describing behavior of liquid mixtures
  - Not good at high temperatures and pressures
- ACM's designed specifically for polymer solutions include Flory-Huggins, UNIFAC-FV



Mixing Rules

- Mixing rules combine EOS parameters for pure substances into parameters for mixture
- Wong-Sandler mixing rules chosen
  - Combine the activity coefficient model and the EOS
  - Extend benefits of activity coefficient model to high pressures and temperatures

Numerical Solution

- Solve equilibrium equation for each species, *i*:

$$y_i \hat{\phi}_i^V \left(y_{j=1\,to\,n}, T, P\right) = x_i \hat{\phi}_i^L \left(x_{j=1\,to\,n}, T, P\right)$$

- Temperature and liquid mole fractions, x_j, are known; pressure and vapor mole fractions, y_j, are unknown

Fortran Program Algorithm

- Guess pressure, P
- Guess vapor mole fractions, y_i's, from Raoult's law
- Calculate partial fugacity coefficients in liquid, $\hat{\phi}_i^L$'s
  - Calculate partial fugacity coefficients in vapor, $\hat{\phi}_i^V$'s
  - New guess for y_i's : $y_i = \dfrac{x_i \hat{\phi}_i^L \left(x_{j=1\,to\,n}, T, P\right)}{\hat{\phi}_i^V \left(y_{j=1\,to\,n}, T, P\right)}$
  - Normalize y_i's : $y_i = \dfrac{y_i}{\sum y_i}$
- New guess for P : $P = P \sum y_i = P \sum \dfrac{x_i \hat{\phi}_i^L (x_{j=1\,to\,n}, T, P)}{\hat{\phi}_i^V (y_{j=1\,to\,n}, T, P)}$