Vapor/Liquid Equilibrium of Polymer Solutions During Thermal Decomposition of Rigid Foams

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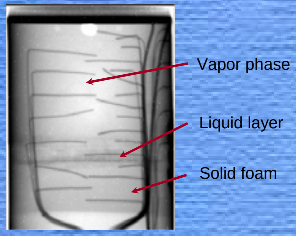
Research Objective

- Determine experimentally the vapor/liquid equilibrium (VLE) behavior of high-temperature polymer solutions similar to degradation products of rigid foams, including Removable Epoxy Foam (REF), and model this behavior. This research will serve as a basis for similar studies with other cross-linked polymeric materials.

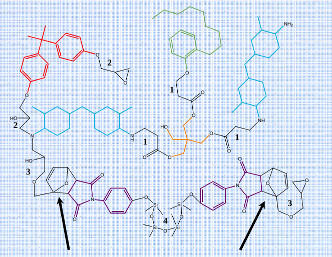
Background

- Rigid polyurethane and epoxy foams are used in many engineered systems as insulation or for protection of sensitive components
- During thermal degradation (fire), large polymer-like network fragments as well as small solvent-like molecules are formed
- Liquid and vapor phases may be formed
- Equilibrium between phases affects composition and amounts of phases, which affect system physical properties
- Previous decomposition models treat only solid and vapor phases, or treat VLE very simply, but polymer solutions exhibit highly non-ideal VLE behavior
- Removable Epoxy Foam (REF) was developed at Sandia to replace polyurethane foam as an encapsulant
- Above 100 ºC REF undergoes reverse Diels-Alder reaction



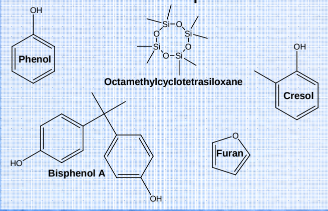
X-ray image of a confined sample of REF being heated from the top

REF Repeating Unit

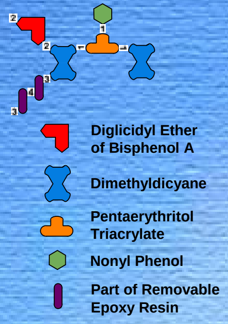


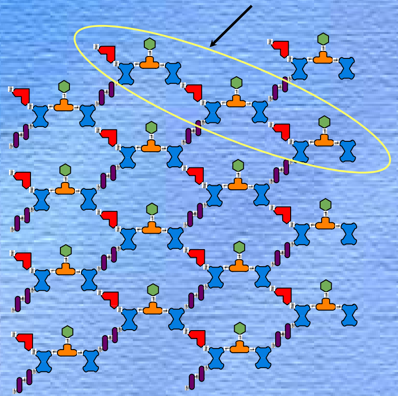
Above 100 ºC, reverse Diels-Alder reactions break epoxy network

Solvent-like products



Polymer-like products



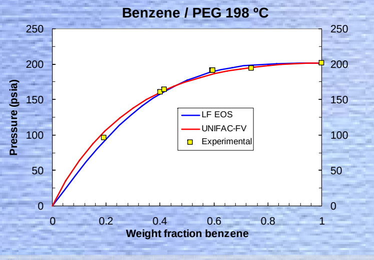


Experimental

High Temperature Vapor/Liquid Equilibrium Facility

Modeling

- Modeling is done using an either a polymer-suitable equation of state (Lattice Fluid) or a cubic equation of state combined via mixing rules with an activity coefficient model suitable for polymer solutions



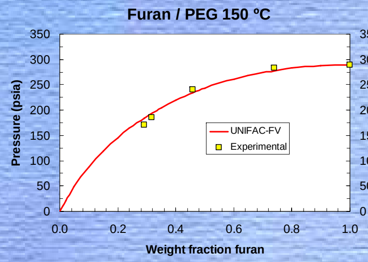
Equation of State (EOS)

- Relates pressure to temperature and molar volume
  - Good for vapor mixtures and at high T and P
- Lattice Fluid EOS good for comparing to data, but requires polymer-specific parameters that aren't available for network fragments from foam degradation
- Cubic EOS simpler, but not accurate for polymer solutions by itself – may be combined with activity coefficient model through mixing rules
  - Peng-Robinson EOS used (two parameters, *a* and *b*)

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

Activity Coefficient Model (ACM)

- Models 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, Entropic-FV, 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 T & P

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

- Calculate bubble- and dew-point pressure, and total volume at those pressures
- Use secant method to get pressure guess
- Guess K_i's using Raoult's law
  - Find liquid fraction, *L*, by solving: $\sum_i \frac{(1-K_i)z_i}{L + K_i(1-L)} = 0$
  - Calculate new x_i's and y_i's: $x_i = \frac{z_i}{L + K_i(1-L)}$ $\quad y_i = K_i x_i$
  - Calculate new K_i's: $K_i = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V}$
- Calculate total volume

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