Phenolic Polymer Interactions with Water and Ethylene Glycol Solvents

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Ablative Heat Shields

Mars Science Lander

Ablative Composites for Re-entry
(carbon fiber/phenolic matrix)

Next Generation Resins for Heat Shields

Phenolic (SOA)

Cyanate Esters

Polyimides

New resin chemistries for heat shields require different solvents for processing
Phenolic Polymers

Polymers

ortho-ortho novolac

ortho-para novolac

ortho-ortho resole

Solvents

ethylene glycol

water

H₂O

Design rules for SOA polymer and solvents
Outline

Quantum Chemical Calibration: understand basic polymer-solvent interactions and benchmark MD models
- combination of DFT, MP2, CCSD(T)
- water and ethylene glycol dimers
- solvent-monomer dimers

Molecular Dynamics Simulation: characterize polymer solubility in solvents
- OPLS-AA-SEI force field
- single polymers in large solvent boxes
- 500-100,000 solvent molecules
- polymers with 3-27 units

Ethylene glycol-phenolic dimer

Phenolic in Water
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Water and Ethylene Glycol Interactions

**Conformers of Ethylene Glycol**

**Water and Ethylene Glycol Dimers**

OPLS energetics within 2 kcal/mol of CCSD (T)

H = black; O = red; C = gray
Phenolic-Water Interactions

OPLS interactions within 2 kcal/mol of MP2/CBS

H = black; O = red; C = gray
Phenolic-Ethylene Glycol Interactions

OPLS interactions within 3 kcal/mol of MP2/CBS

H = black; O = red; C = gray
Ethylene glycol-phenolic dimer

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Phenolic in Water

Molecular Dynamics Simulation: characterize polymer solubility in solvents
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Diffusion and viscosity of solvent strongly affect polymer dynamics.
RES type phenolic chains are observed, as demonstrated in as well as the intermolecular interactions present within each result from the di... that the solvation di... evidences the collapsed oligomer structure that is illustrated qualitatively di... molecular weight phenolic chains considered here do not... From a conformational perspective, the three types of low... 4. DISCUSSION... Figure 1... The Journal of Physical Chemistry B... Figure 7... Mean Square Displacement (nm²) Mean Square Displacement (nm²) Simulation Time (ns) Simulation Time (ns) Larger diffusion coefficients in water...
## Solvation Free Energy

### Solvation Free Energy (kcal/mol)

<table>
<thead>
<tr>
<th></th>
<th>Ethylene Glycol</th>
<th>Water</th>
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<tr>
<td></td>
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<td>-8.5</td>
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Polymers more soluble in ethylene glycol
Resole most soluble polymer
Solvation Shell of Polymer

**Figure 3.** First solvation shell of the OPN chain in a) EGL and b) H\textsubscript{2}O solvents. Hydrogen bonds are denoted in red.

Solvation structure governs properties

- polymer = gray; O = yellow; C = green; H = white
Solvated Polymer Structure

ortho-ortho novolac  ortho-para novolac  ortho-ortho resole

Self hydrogen bonding in ortho-ortho systems
Ortho-para novolac and ortho-ortho resole have free –OH groups
Specific Types of Polymer-Solvent Bonding

Three primary interactions found in polymer-ethylene glycol solvation; one type in polymer-water solvation

O = red; C = green; H = white
Specific Types of Polymer-Solvent Bonding

Figure 4. Illustrations of different interaction types between solvent molecules and solute element groups using a binary descriptor (1 = present, 0 = not present); specifically a) phenolic hydroxyl and solvent, denoted [100], b) center of phenolic ring and solvent, denoted [010], and c) phenolic methylene linker and solvent, denoted [001].

Figure 5. Average number of solvent/phenolic interactions during simulations of phenolic solvated in EGL. Binary code employs naming scheme illustrated in Fig. 4. Inset shows phenolic solvated in H₂O.

Hydrogen bonding and carbon linker interactions dominate
Hydrogen bonding common to both solvents and most prevalent bonding

O = red; C = green; H = white
Hydrogen bonding more persistent in ethylene glycol
Conclusions

• OPLS-AA-SEI energetics agree with high accuracy CCSD(T) solvent computations

• OPLS-AA-SEI polymer-solvent interactions within a few kcal/mol of MP2/CBS computations

• Ethylene glycol more readily solvates the polymers because of more, longer-lived hydrogen bonding than water

• Resole is more soluble than the novolac polymers: more hydrogen bonding and hydrophobic-hydrophobic interactions

Questions?