Phenolic Polymer Interactions with Water and Ethylene Glycol Solvents

Justin B. Haskins,¹ Eric W. Bucholz,² Charles W. Bauschlicher,³ Joshua D. Monk,¹ John W. Lawson³

¹AMA, Inc., Thermal Protection Materials Branch, NASA Ames Research Center
²EAP, Thermal Protection Materials Branch, NASA Ames Research Center
³Thermal Protection Materials Branch, NASA Ames Research Center
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
Figure 1. Structures of phenolic chains considered in this study illustrating (a) ortho-ortho repeating novolac-type (OON) phenolic chain indicating ortho and para linking sites on a phenol ring, (b) ortho-para repeating novolac-type (OPN) phenolic chain, and (c) ortho-ortho repeating resole-type (RES) phenolic chain. Images on the right are the corresponding 9-phenol ring chains, and the chains are colored as: carbon backbone (red), non-backbone carbon (cyan), oxygen (yellow), and hydroxyl hydrogen (white). Translucent bonds indicate intramolecular bonding. Aromatic and methylene hydrogens are removed for clarity.

Phenolic Polymers

**Polymers**

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

**Solvents**

- ethylene glycol
- water

Design rules for SOA polymer and solvents
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
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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

2 Unit Novolac  2 Unit Resole  3 Unit Novolac

OPLS interactions within 2 kcal/mol of MP2/CBS

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

H = black; O = red; C = gray

OPLS interactions within 3 kcal/mol of MP2/CBS

2 Unit Novolac

2 Unit Resole

3 Unit Novolac
Quantum Chemical Calibration: understand basic polymer-solvent interactions and benchmark MD models
- combination of DFT, MP2, CCSD(T)
- water and ethylene glycol dimers
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Molecular Dynamics Simulation: characterize polymer solubility in solvents
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Dynamics of Solvated Phenolic

Diffusion and viscosity of solvent strongly affect polymer dynamics.
Polymer Diffusion

**ortho-ortho novolac**

**ortho-ortho novolac**

Mean Square Displacement (nm$^2$)

Simulation Time (ns)

Simulation Time (ns)

| Larger diffusion coefficients in water | 12 |
## Solvation Free Energy

**Solvation Free Energy (kcal/mol)**

<table>
<thead>
<tr>
<th></th>
<th>Ethylene Glycol</th>
<th>Water</th>
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<td>-53.1</td>
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<tr>
<td></td>
<td>-8.5</td>
<td>-23.8</td>
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</tbody>
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**Polymers more soluble in ethylene glycol**

- Resole most soluble polymer

**Structures of phenolic chains considered in this study illustrating**

- (a) ortho-ortho repeating novolac-type (OON) phenolic chain indicating ortho and para linking sites on a phenol ring,
- (b) ortho-para repeating novolac-type (OPN) phenolic chain,
- (c) ortho-ortho repeating resole-type (RES) phenolic chain.

Images on the right are the corresponding 9-phenol ring chains, and the chains are colored as: carbon backbone (red), non-backbone carbon (cyan), oxygen (yellow), and hydroxyl hydrogen (white). Translucent bonds indicate intramolecular bonding. Aromatic and methylene hydrogens are removed for clarity.
Figure 3. First solvation shell of the OPN chain in a) EGL and b) H$_2$O solvents. Hydrogen bonds are denoted in red.

Solvation structure governs properties

polymer = gray; O = yellow; C = green; H = white
Self hydrogen bonding in ortho-ortho systems
Ortho-para novolac and ortho-ortho resole have free –OH groups
Three primary interactions found in polymer-ethylene glycol solvation; one type in polymer-water solvation

O = red; C = green; H = white
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 H$_2$O.

Specific Types of Polymer-Solvent Bonding

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

O = red; C = green; H = white
Polymer-Solvent Hydrogen Bonds

Within OON and RES are mostly constant and long lived, respectively. As can be seen, intramolecular H-6 of the three types of H-bonds at 298 K within the solvated systems are illustrated for OON in O (b, d, f). Solutes are OON (a, b), OPN (c, d), and RES (e, f). Legend notes: P and S refer to phenolic and solvent OHs, respectively.

Hydrogen bond autocorrelations using intermittent definition for nine-ring solvated phenolic simulations at 298 K. Solvents are EGL (a, c, e) is ortho-para repeating novolac (yellow), and hydroxyl hydrogen (white). Translucent bonds indicate intramolecular hydrogen bonding.

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?