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HANSEN SOLUBILITY PARAMETERS FOR FLUOROALKYL SILICATES

October 17, 2012

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Outline

• Background / Motivation
  – Fluoro-POSS Applications as Polymer Modifiers
  – Relationships Between Surface and Bulk Energy
    • Hansen Solubility Parameters for Bulk Energy
    • Girifalco-Good Parameters for Surface Energy
• Previous Work on Fluoro-POSS Surface Energy
• Current Work on Fluoro-POSS Bulk Energy
  – HSP of Fluoro-POSS and Related Silicate Compounds
  – Group Contribution Estimates
• Comparisons of Surface and Bulk Energy Values

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Effect of Fluorodecyl-POSS on Poly-(chlorotritluoroethylene) Surfaces

Water Contact Angles ...

88° No POSS

128° 10 wt% POSS

Hexadecane Contact Angles

Significant improvements in repellence of both water and oil are seen when fluoro-POSS is added to PCTFE
Another example of a fluoropolymer with liquid repellence improved by addition of fluoro-POSS, presumably due to the lower surface energy of Fluoro-POSS.
EDX/AFM of POSS/PFCB Surfaces

EDX shows that the surface becomes enriched in fluoro-POSS; AFM shows that surface migration alters the surface topography in addition to lowering surface energy.

The performance of fluoropolymers with added fluoro-POSS depends on both bulk (phase separation) and surface (migration) energies.
Pure PMMA is hydrophilic, yet phase separation and surface migration drastically alter water repellence. Understanding both bulk and surface interactions between fluoro-POSS and polymers is the key to controlling performance. At present, a quantitative understanding of these phenomena is lacking.
Helicopter vortex tubes are used to exclude dust and contaminants from engine intakes. Requirements include light weight, ease of manufacturing, mechanical (structural / abrasion resistance), fouling resistance, and thermal performance.

Inert POSS compounds, added as flow aids, allow more robust plastics such as cyclic olefin copolymers (COCs) to replace the polypropylene base material without sacrificing the ease of flow that facilitates ease of manufacturing. The high thermal stability and ~1 nm size of the POSS molecules provide the best available flow-enhancing characteristics and could also aid fouling resistance.

The traditional material is a polypropylene that is highly filled to provide the required performance. The high filler loading makes manufacturing difficult due to the low thickness of part features (needed to save weight) that must be molded using a high viscosity material.
Bulk Interactions Can Be Quantified through Hansen Solubility Parameters

- Hansen parameters developed in late 1960s / early 1970s enabled development of a solvent mixture (n-butanol / nitroethane) for removal of “insoluble” epoxy primers from metal surfaces
- Hansen Solubility Parameters became widely used in the coatings industry, including for systems containing inorganic pigments – they remain the only successful approach for achieving miscibility via mixed solvents
- Solubility parameters for POSS compounds studied since ~2010 by numerous groups (Morgan-USM, Schiraldi-CWRU, AFRL)
Relation Between HSP and Phase Separation Dynamics

Knowledge of Hansen Solubility Parameters enables the computation of the enthalpy of mixing between two components. For polymers, the value of the enthalpy of mixing controls the rate and extent of phase separation.

When plotted in a 3-dimensional “solubility parameter space”, good solvents (an indication of low enthalpy of mixing) tend to lie within a “sphere of solubility” centered on co-ordinates that correspond to the HSP of the solute. This “spherical rule” results from the similarity of the above equation to a geometric distance formula.

\[ \Delta H_{\text{mix}} = \phi_1 \phi_2 V_{\text{ref}} [(\delta_{D_1} - \delta_{D_2})^2 + (1/4)(\delta_{P_1} - \delta_{P_2})^2 + (1/4)(\delta_{H_1} - \delta_{H_2})^2] \]

\[ \delta^2 = (\Delta H_{\text{vap}} - RT) / V \]

\[ \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \]

Hansen Solubility Parameter diagram for CO₂

Solubility parameter
Enthalpy of mixing
Molar enthalpy of vaporization
Molar volume
Dispersive, polar, and H-bonding components
Volume fractions
Hansen Solubility Parameters for Polymer Systems

**Experimental method for determining HSP**

1. Determine solubility (or affinity) in a large set of trial solvents.
2. Plot the HSP of “good” and “poor” solvents in a “solubility parameter space” as shown.
3. “Good” solvents normally lie near one another in a “region of solubility”.
4. When $2\delta_D$ is used as an axis, the region of solubility is typically bounded by a sphere.
5. The center coordinates of the sphere mark the newly determined HSP.
6. With knowledge of the HSP and “radius of interaction” (test dependent), test results for any subsequent solvent (or mixture) are reliably predicted.

The traditional approach to estimating Hansen solubility parameters requires trials of typically 30 or 50 different solvents, but is straightforward to carry out. “Good” typically is indicated by >5% or 10% solubility, or by swelling, ESC, etc.

Quantitative Interaction Parameters for Surfaces: Girifalco-Good Approach

- Measurement of contact angles for several probe liquids is used to determine the component values using linear regression.

\[ W_{sl} = \gamma_{lv}(1 + \cos \theta_E) = 2[\sqrt{\gamma_d^d} \sqrt{\gamma_d^d} + \sqrt{\gamma^+} \sqrt{\gamma^+} + \sqrt{\gamma^-} \sqrt{\gamma^-}] \]

Equilibrium contact angle

- Dispersive components

- Work of adhesion between solid and liquid

- Acid (+) / base (-) component interaction terms

- Measurement of contact angles for several probe liquids is used to determine the component values using linear regression.
Relationships Between Surface and Bulk Properties

\[ \gamma = 0.75 \delta^{4/3} \]

\[ \gamma = \left[ \frac{P_s}{V(T)} \right]^4; \ P_s \sim V_w \]

\[ \gamma_D = 4.79 \delta_D - 51.87 \]

- These relationships predict the properties of liquid surfaces, however, most fluorosilicates are solids at room temperature.
- Even in liquids, molecular order at the surface is not taken into account by the predicted values.
- To date, no widely known correlations exist for polar and hydrogen bonding components.
- In general, hydrogen bonding is much stronger in bulk than at the surface (perhaps due to fewer constraints on interlocking in the bulk).


Fluoro-POSS and Related Fluoro-alkyl Silicate Compounds

- T and Q compounds are crystalline at room temperature
- M compound is liquid at room temperature
- Q compound can be thought of as roughly half a POSS cage; M compound as roughly one-fourth a POSS cage
HSP Data for Fluoroalkyl Silicate Compounds

Octa-hexafluoroisobutyl-POSS

Octa-trifluoropropyl-POSS

Octa-fluorohexyl-POSS

Fluorodecyl-M2

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Comparison of Hansen Solubility Parameters for POSS Compounds

HSP trends do reflect the qualitative features expected on the basis on the peripheral chemical structure, such as:

- Smaller $\delta_D$ for fluorocarbons
- Larger $\delta_P$ for fluorocarbons

HSP for multiple POSS types provide an estimate of the HSP for a T8 cage

<table>
<thead>
<tr>
<th>POSS / Silicate Type</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$R_0$</th>
<th>#Exceptions / #Good</th>
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<tr>
<td>Octa-isobutyl</td>
<td>18.0</td>
<td>2.1</td>
<td>2.7</td>
<td>4.5</td>
<td>6 / 8</td>
</tr>
<tr>
<td>Octa-hexafluoroisobutyl</td>
<td>15.3</td>
<td>9.3</td>
<td>11.0</td>
<td>7.3</td>
<td>2 / 10</td>
</tr>
<tr>
<td>Octa-fluorohexyl</td>
<td>16.3*</td>
<td>6.8*</td>
<td>6.7*</td>
<td>2*</td>
<td>n/a</td>
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<tr>
<td>Octa-trifluoropropyl</td>
<td>16.8</td>
<td>9.1</td>
<td>8.9</td>
<td>4.5</td>
<td>0 / 5</td>
</tr>
<tr>
<td>Fluorodecyl-M2</td>
<td>16.0*</td>
<td>5.4*</td>
<td>5.3*</td>
<td>5*</td>
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All units (J/cc)$^{1/2}$

*estimated
Comparison of Surface Energy Parameters for POSS Compounds

Predicted values based on Hansen Solubility Parameters (for “liquid” surfaces)

<table>
<thead>
<tr>
<th>alkane (Zisman analysis)</th>
<th>all liquids$^b$ (eq 1 with $q_{al}=1$)</th>
<th>diiodomethane, dimethyl sulfoxide and water (eq 5)</th>
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<tbody>
<tr>
<td></td>
<td>$\gamma_c$</td>
<td>$\gamma_{sv}$</td>
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<tr>
<td>fluorodecyl T8</td>
<td>5.5</td>
<td>9.3</td>
</tr>
<tr>
<td>fluoroctyl T8</td>
<td>7.4</td>
<td>10.6</td>
</tr>
<tr>
<td>fluorohexyl T8</td>
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</tr>
<tr>
<td>fluoroisopropyl T8</td>
<td>19.7</td>
<td>18.7</td>
</tr>
<tr>
<td>hexafluoro-i-butyl T8</td>
<td>17.7</td>
<td>19.1</td>
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<td>fluorodecyl T8</td>
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<td>9.3</td>
</tr>
<tr>
<td>fluorodecyl Q4</td>
<td>14.5</td>
<td>14.3</td>
</tr>
<tr>
<td>fluorodecyl M2</td>
<td>19.6</td>
<td>26.8</td>
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- For perfluorohexane, the predicted value of $\gamma_{lv}$ of 21 dyn/cm is close to expectations
- Agreement for the dispersive component is better, but $\gamma_{lv}^d$ < $\gamma_{lv}$ without rearrangement
Application to Miscibility and Phase Separation

The Time-Dependent Ginzburg-Landau equation (linearized to Cahn-Hilliard equation) represents the established mathematical framework for predicting phase separation, if you know the “χ” parameter

\[
\chi = V_{\text{ref}} [(\delta_D - \delta_D^2)^2 + \frac{1}{4} (\delta_P - \delta_P^2)^2 + \frac{1}{4} (\delta_H^2 - \delta_H^2)^2]
\]

As an example, for octa-phenethyl-POSS in PEI:
Phenethyl-POSS: \((J/cc)^{1/2}\)
\(\delta_D = 19.7; \ \delta_P^2 = 8.0; \ \delta_H = 5.6\);
PEI: \((J/cc)^{1/2}\)
\(\delta_D = 19.6; \ \delta_P^2 = 7.6; \ \delta_H = 9.0\);
\(V_{\text{ref}} = 100 \text{ cc/mol} \ : \chi = 0.12\)
\(N_1 = 10; N_2 = 100\)
Predicted miscibility: 10-20%
Actual miscibility: 2.6%
Surface Migration of 5 wt% Octa-Phenethyl POSS in PEI

Films annealed at 180°C show effects that are not significantly different from those seen in pure PEI. At 210°C, fine aggregates and, later, a phase separated texture appear. The insets show the autocovariance (same length scale as main figure, red = high) of the pattern for annealing at 210°C, indicating periodicity.
Future Work

• Determine Hansen solubility parameters for additional silicate types ("D" is available from polysiloxanes, "T" from POSS, more "M" and "Q" examples needed)

• Improve precision of group contribution values for POSS cages and other silicate structures, as well as for fluorocarbons

• Generate additional predictions of miscibility and develop a spatio-temporal model for surface migration of silicate additives

• Use controlled migration to design organic / inorganic hybrids with optimal liquid repellence and other desirable properties
Summary

• Controlling the liquid repellence characteristics of polymer / silicate nanocomposites requires quantitative knowledge of both bulk and surface thermodynamic parameters.

• Quantitative surface and bulk thermodynamic data for polymer / silicate nanocomposites (including fluorinated polymers and fluoro-POSS) has recently become available.

• Comparisons of surface and bulk thermodynamic parameters provide insight into the nature of the silicate / polymer nanocomposite surface.

• Application of the thermodynamic data to investigate miscibility and phase separation in polymer / silicate nanocomposites is underway.
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