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HANSEN SOLUBILITY PARAMETERS OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS) COMPOUNDS

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Abstract

The Hansen Solubility Parameters (HSP) of three different octafunctional POSS compounds (octaphenethyl, octastyrenyl, and 1-naphthyl-heptaphenyl) were successfully determined using the traditional Hansen approach with a set of 45 test solvents. The data suggest that HSP are likely to be as valid for simple inert POSS compounds as for any organic oligomer. In the case of phenethylPOSS, there is at least some extant experimental data on polymer blend compatibility that suggests the HSP approach may offer more insight than simple "like dissolves like" heuristics.

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Introduction

The Hansen Solubility Parameter (HSP) approach has proven highly successful for predicting miscibility and phase separation phenomena in the realms of organic polymers and (mainly) organic coatings, and as an aid to understanding related phenomena such as wetting, permeation, and dispersion in systems containing polymers and organic molecules.¹ To date, however, the HSP approach has not been widely used and is often regarded as unsuitable for inorganic small molecules or even for inorganic polymers, despite the fact that HSP values are readily available for polydimethylsiloxane, and have been used, for example, in separation membrane studies.² Since organosilicon materials, such as polyhedral oligomeric silsesquioxane (POSS)³ share many characteristics with common organic oligomers, and given that HSP parameters are easily computed for materials spanning a wide range of molecular weights and are known for at least one high molecular weight organosiloxane, there is good reason to believe that the HSP approach can be applied successfully to POSS compounds as well. The aforementioned reasoning should apply particularly to stable, discrete, well-defined POSS, such as those based on attachment of relatively small organic fragments to octameric silsesquioxane cages.

Experimental

Materials. Octa(phenethyl)POSS, octa(styrenyl)POSS, and the 1-naphthylheptaphenylPOSS were synthesized at AFRL. Previously reported synthesis and characterization data are available for the octaphenethyl and octastyrenyl compounds,⁴ and, more recently, the 1-naphthylheptaphenyl compound.⁵ The set of 45 solvents used in the study were obtained from a variety of commercial sources based on laboratory availability.

Test Procedures. For each of the tests reported herein, 50 mg of the POSS compound was placed in a clean 5 mL glass vial along with 0.5 mL of the selected solvent. The tightly closed vials were then stirred for two minutes and checked for dissolution. When complete dissolution did not occur, the vials were allowed to stand for up to one hour. The tests were then rated as follows: "Pass" indicated complete dissolution within two minutes; "Pass -" indicated complete dissolution within one hour but not within two minutes (in these cases, most of the solute dissolved initially and extra time was required to achieve complete dissolution, an indication of near saturation given the low molecular weight of the POSS compounds); "Fail +" indicated that significant but incomplete dissolution occurred; "Fail" indicated that little or no dissolution was observed. Note that the "+" and "-" designations were retained for documentation purposes only, with subsequent analysis treating "Pass -" as "Pass" and "Fail +" as "Fail".

Analysis Procedures. The main analytical problem was the determination of the HSP (δ_{D-POSS} , δ_{P-POSS} , δ_{H-POSS}) of the POSS compound based on the pass / fail ratings (here denoted as "test," and the associated HSP (δ_{D-S_i} , δ_{P-S_i} , δ_{H-S_i}) of each solvent tested. The basic approach to solving the problem was to maximize the goodness of fit of the data set to the criteria described by Hansen,¹ namely, for each instance i , define a characteristic distance $R_{a,i}$ such that

$$R_{a,i} = 4 * (\delta_{D-POSS} - \delta_{D-S_i})^2 + (\delta_{P-POSS} - \delta_{P-S_i})^2 + (\delta_{H-POSS} - \delta_{H-S_i})^2$$

With the criteria being

$$\text{If } R_{a,i} < R_0, \text{ then test}_i = \text{"Pass"}, \text{ else test}_i = \text{"Fail"}$$

in which δ_{D-POSS} , δ_{P-POSS} , δ_{H-POSS} , and R_0 are adjustable parameters. The goodness of fit was determined by means of a χ^2 test, using the total fraction of tests rates as "Pass" and the total fraction of solvents for which $R_{a,i} < R_0$ to determine the distribution of expected occurrences in each category (i.e. " $R_{a,i}$

$< R_0$, test _{i} = "Pass"; " $R_{a,i} \geq R_0$, test _{i} = "Pass"; " $R_{a,i} < R_0$, test _{i} = "Fail"; and " $R_{a,i} \geq R_0$, test _{i} = "Fail"). The procedure described above was the computational equivalent of attempting to identify the central co-ordinates and radius of a sphere that included all solvents with a "pass" rating but excluded all solvents with a "fail" rating, in a Cartesian space with axes given by $2 \delta_D$, δ_P , and δ_H .

To locate the optimal values of δ_{D-POSS} , δ_{P-POSS} , δ_{H-POSS} , and R_0 , a brute force method based on an iteratively refined search space was employed. In the first iteration, δ_{D-POSS} was varied from 15 to 20 in increments of 0.5, while δ_{P-POSS} and δ_{H-POSS} were varied from 0 to 10 in increments of 1, and while R_0 was varied from 0 to 20 in increments of 0.25. The initial range represented a compromise between comprehensiveness and the need to minimize computation time, and was based on the range of the HSP noted for solvents with a rating of "pass". For every possible combination of the four parameters given the ranges and increments listed above, the χ^2 parameter was then computed and the absolute maximum recorded. For the second iteration, the search grid was centered on the point having maximum χ^2 (with the lowest value of all other parameters used to break ties) found in the previous iteration, with the increments reduced to 0.4 for δ_{D-POSS} , and 0.8 for δ_{P-POSS} and δ_{H-POSS} while the increment was maintained at 0.25 for R_0 . The process was repeated two additional times, centering the grid as described previously and reducing the increment for δ_{D-POSS} , δ_{P-POSS} , and δ_{H-POSS} by a factor of 4 each time while maintaining the increment for R_0 . The method provided a final search resolution of 0.025 for δ_{D-POSS} , 0.05 for δ_{P-POSS} and δ_{H-POSS} , and 0.25 for R_0 . Note that the finer spacing for δ_{D-POSS} was used to compensate for the factor of 4 in the Hansen expression (effectively, the parameter $2 \delta_{D-POSS}$ was used as a dimension along with δ_{P-POSS} and δ_{H-POSS} in a uniformly gridded Cartesian search space that shrank with each iteration until the optimal center co-ordinates were identified).

An additional analytical issue is the estimation of uncertainty, since, due to the highly non-linear nature of the optimization problem, many possible locations in "HSP space" bounded by an irregular and even non-contiguous region can be of equal or nearly equal goodness of fit. To address this issue, we again employed a brute force method, calculating the χ^2 value for all combinations of δ_{D-POSS} , δ_{P-POSS} , δ_{H-POSS} , and R_0 with increments of 0.05, 0.1, 0.1, and 0.25, respectively, around the optimal point identified in the final search iteration with a span of 11 increments for δ_{D-POSS} , δ_{P-POSS} , and δ_{H-POSS} and 41 increments for R_0 . We considered χ^2 values that differed from the previously determined optimum by less than one to be representative of equivalent goodness of fit, a practice originally suggested to us by E. von Meerwaal of the University of Akron and found to work quite well in this situation. The values of every combination of δ_{D-POSS} , δ_{P-POSS} , and δ_{H-POSS} for which at least one value of R_0 enabled the condition for equivalent goodness of fit to be met were logged. If any of these coordinates fell on the boundary of the search region, the increments of δ_{D-POSS} , δ_{P-POSS} , and δ_{H-POSS} were increased in linear steps of 100% (i.e. they were first doubled from their original values, then tripled from their original values, etc.), and the entire process repeated, until no co-ordinates on the boundary of the search region met the criteria. We then computed the centroid and radii of gyration (in each dimension) of the set of all co-ordinates that met the goodness of fit criteria, using the centroid for the finally determined values of the HSP for the given POSS compound. Using these centroid co-ordinates, the smallest value of R_0 that gave the maximum χ^2 was determined (by checking all R_0 values from 0 to 20 with an interval of 0.25) and reported as the final R_0 value for the POSS compound. The radii of gyration were then reported as the "characteristic uncertainty" of the measurement.

Results and Discussion

(Figures 1-3) show the test results (filled circles equate to "Pass" or "Pass -", unfilled circles to "Fail" or "Fail +") in HSP space for octa(phenethyl)POSS (Figure 1), octa(styrenyl)POSS (Figure 2), and 1-naphthylheptaphenylPOSS (Figure 3), with the HSP solubility sphere superimposed. Table 1 provides tabulations of the computed HSP values, χ^2 values, R_0 values, and the characteristic uncertainties for each of the five compounds. The χ^2 values obtained were similar to those reported for many polymers¹ (taking into account the number of tests), with the traditional HSP solubility criteria giving correct predictions about 80% of the time on average. Hence, there is no basis in the experimental data to suggest that HSP are any less valid for POSS compounds than for any type of organic oligomer.

A wide variety of POSS solubility characteristics were observed, ranging from the highly soluble octa(phenethyl)POSS to the barely soluble 1-naphthylheptaphenylPOSS. Further examination of **Table 1** shows that, despite the non-polar nature of the peripheral groups on many of the POSS compounds, significant components of polarity and "hydrogen bonding" were found. It should be noted that "hydrogen bonding" character, as it relates to HSP, can be the result of a wide variety of different chemical interactions. Essentially, the HSP studies show that POSS compounds tend to have a greater affinity for strongly polar and strongly hydrogen bonding solvents than would be expected on the basis of their peripheral groups.

These HSP values suggest that POSS / polymer blends should be readily achievable with perhaps a different set of polymers than might be expected based on simple considerations of matching peripheral groups to polymer functionality. For instance, phenethylPOSS (the cage mixture, not purely octafunctional), has been shown to be compatible at over 20 vol% in polyvinyl chloride (PVC).⁶ Although originally attributed to a specific aromatic-halide interaction, in fact, the high compatibility likely simply reflects the similarity in HSP of PVC and phenethylPOSS. In fact, the "distance" in "HSP space" between octa(phenethyl)POSS and PVC is similar to the distance between octa(phenethyl)POSS and polystyrene. Both polymers exhibit a similar level of phenethylPOSS solubility,⁷ despite the fact that polystyrene is chemically similar to the peripheral group whereas PVC is chemically quite different.

Conclusions

The Hansen Solubility Parameters (HSP) of three different octafunctional POSS compounds were successfully determined using the traditional Hansen approach. The data suggest that HSP are likely to be as valid for simple inert POSS compounds as for any organic oligomer. In the case of phenethylPOSS, there is at least some extant experimental data on polymer blend compatibility that suggests the HSP approach may offer more insight than simple "like dissolves like" heuristics.

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Table 1. HSP Data for Selected POSS Compounds

Name	δ_D -POSS	δ_P -POSS	δ_H -POSS	R_0	χ^2
Octa(phenethyl)POSS	19.9 ± 0.4	7.4 ± 0.4	6.3 ± 0.6	9.5	37 (N=45)
Octa(styrenyl)POSS	18.1 ± 0.2	7.6 ± 0.4	3.6 ± 0.9	6.5	24 (N=45)
1-naphthylheptaphenylPOSS	16.9 ± 0.1	4.2 ± 0.2	6.4 ± 0.2	2.25	29 (N=45)

Note: the values listed after the ± sign are "characteristic uncertainties" (see the Experimental section for details) for comparison purposes. Actual confidence intervals are likely to be significantly larger.

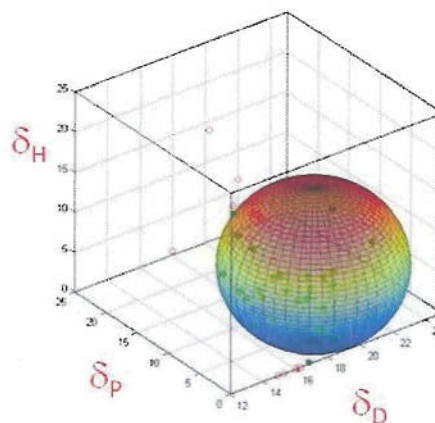


Figure 1. Hansen Solubility Parameter diagram for octa(phenethyl)POSS. Filled green circles represent solvents in which the POSS compound was soluble at 100 mg/mL or more. Unfilled red circles represent solvents in which the POSS compound was insoluble at 100 mg/mL.

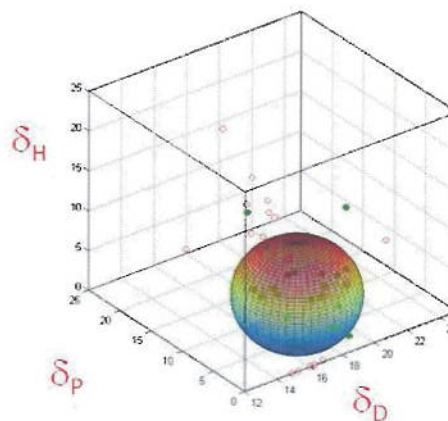


Figure 2. Hansen Solubility Parameter diagram for octa(styrenyl)POSS (see **Figure 1** for an explanation of symbols).

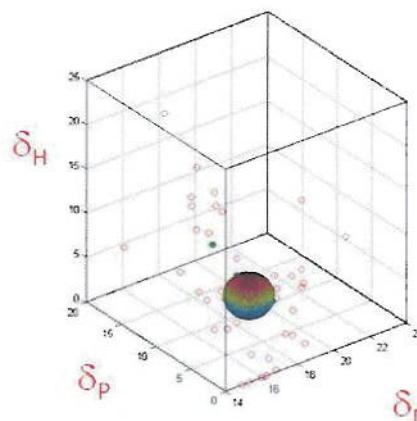


Figure 3. Hansen Solubility Parameter diagram for 1-naphthylheptaphenylPOSS (see **Figure 1** for an explanation of symbols).