# Experimental Determination of Hansen Solubility Parameters for Select POSS and Polymer Compounds as a Guide to POSS–Polymer Interaction Potentials

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ABSTRACT: Polyhedral oligomeric silsesquioxanes (POSS) have been incorporated into a wide range of polymers over the past two decades in an attempt to enhance their thermal and mechanical properties. Properties of POSS/polymer blends/composites are highly dependent on the uniformity of POSS dispersion and thus are particularly sensitive to the magnitude of interaction between POSS and added fillers/polymers. Methods to characterize these interactions in terms of solubility parameters have been recently examined in the literature using group contribution calculations. The present work presents a method for measuring three-dimensional Hansen solubility parameters for polymers and POSS which allows for the direct calculation of interaction potentials. These measured solubility parameters predict POSS/polymer interactions more accurately than group contribution calculations and accurately predict the uniformity of POSS dispersion and the resultant property enhancements.
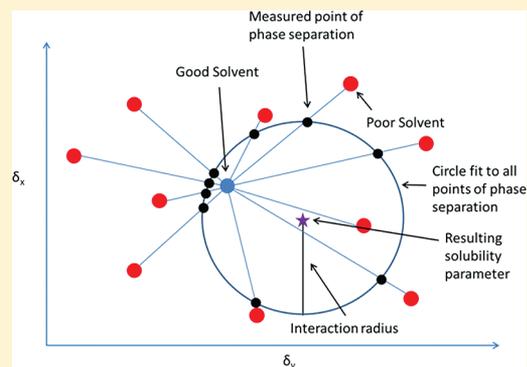
INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are a class of hybrid molecules which consist of an inorganic siloxane core which is functionalized with any of a number of organic substituents. POSS has been incorporated into polymers though copolymerization,[1,2] grafting,[3] and blending[4−7] over the past two decades in hopes of providing property enhancements similar to that seen in the traditional composite field in which rigid inorganic particles are incorporated into polymers to provide thermal and mechanical reinforcement.[8,9] Early research in the field of nanocomposites indicated that inorganic particles require compatibilization to produce strong interactions with a polymer, resulting in reinforcement and a strong interface.[10,11] This compatibilization is generally accomplished by modifying the surface of the particles with an organic moiety to closely match the chemical structure of the polymer. POSS molecules have attracted attention as molecular-scale equivalents to organically modified particles because they are hybrid materials containing rigid inorganic cores modified by a huge variety of pendant group functionalities. Over 100 different POSS molecules are commercially available with different organic functionalities for matching and blending with desired matrix polymer. The challenge is to predict which POSS functionality will enhance properties when incorporated into a given polymer. In the case of copolymerization or grafting of a POSS material to a polymer, the choice of modifier will be based on the specific chemistry needed for a given reaction scheme. In the case of melt-blending though, a different set of criteria must be met. In a melt blend POSS behaves as a large molecule, and can exist in

a number of states once incorporated into a polymer. In many cases the POSS will simply phase separate due to a lack of compatibility with the polymer. If a high degree of attractive interaction is present, the POSS can be dispersed on the nanometer scale or even in a completely dissolved state.[12,13] In the case of molecular dispersion it can act as a plasticizer.[14] If there are specific interactions (hydrogen bonding), the system can behave similarly to that of a copolymer or grafted system.[15]

If the desired system is one in which a high degree of POSS/polymer interaction is present, how does one go about selecting an optimal POSS additive for a specific polymeric matrix? A simple examination of the chemical structure is not sufficient as it is difficult to ascertain what the effects the silicate core and molecular geometry will have on the interaction potential of POSS. For this reason several researchers have turned to evaluating POSS/polymer combinations in terms of solubility parameters.[16−18] By assigning solubility parameter values to different POSS and polymer species, predictions about dispersion and compatibility can be made. If the difference in solubility parameters between the POSS and polymer is very low, it is expected that there will be a high degree of POSS polymer interaction, yielding favorable results similar to a graft or copolymer system, while if the difference is very high it is assumed that the system would phase separate yielding a decrease in the desired physical properties.

Work from Morgan et al. describes interaction potentials as calculated using the Hoy method of group contribution calculation.[16] These calculations result in a single parameter value for the square root of cohesive energy density. Chin et al. also relate the level of dispersion of POSS to solubility parameters in terms of the three-dimensional Hansen solubility parameter which contains separate terms for the contribution of dispersion, polar, and hydrogen bonding forces.[16−18] The contribution of hydrogen bonding is ignored in that work though, as is the contribution of the core silicate to the calculated solubility parameter.

To obtain accurate solubility parameters, it was our goal to independently and directly measure the Hansen solubility parameters of a variety of polymers and POSS grades. These experimental results can then be used to test the assumptions used for group contribution or other calculation methods.

Solubility of a given solvent−solute pair is governed by the free energy of mixing

$$\Delta G_M = \Delta H_M - T\Delta S_M \tag{1}$$

where ΔG_M is the Gibbs free energy of mixing, ΔH_M is the enthalpy of mixing, T is the absolute temperature, and ΔS_M is the entropy of mixing.[19] In order for spontaneous mixing to occur, $\Delta G_M \leq 0$. In the case of high molecular weight species, dissolution is accompanied by a relatively small positive change in entropy, and thus the enthalpy of mixing is the dominant term. Hildebrand and Scott[20] proposed that enthalpy of mixing could be described as

$$\Delta H_M = V_{mix}[(\Delta E_1^V/V_1)^{1/2} - (\Delta E_2^V/V_2)^{1/2}]^2 \Phi_1\Phi_2 \tag{2}$$

where V_{mix} is the volume of the mixture, ΔE_i^V is the energy of vaporization of species i, V_i is the molar volume, and Φ_i is the molar volume. The cohesive energy, E, of a material is the energy required to break all intermolecular forces. When divided per unit volume the value for cohesive energy density is obtained:

$$CED = \frac{E}{V} = (\Delta H_{vap} - RT)/V \tag{3}$$

The Hildebrand solubility parameter then is defined as the square root of cohesive energy density:

$$\delta = \left(\frac{E}{V}\right)^{1/2} \tag{4}$$

Equation 2 can be rewritten in terms of the Hildebrand solubility parameter (eq 4) to give the heat of mixing per unit volume of a two part mixture:

$$\frac{\Delta H_M}{V} = (\delta_1 - \delta_2)^2 \Phi_1\Phi_2 \tag{5}$$

In order for $\Delta G_M \leq 0$, the heat of mixing must be smaller than the entropic term in eq 1; therefore, the difference in solubility parameters $(\delta_1 - \delta_2)$ must remain small. The major shortcoming of the Hildebrand method, though, is that it does not take into account specific interactions between molecules, like hydrogen bonding. To expand on this idea, Hansen proposed breaking the cohesive energy into three parts, corresponding to three types of interactions:[21]

$$E = E_D + E_P + E_H \tag{6}$$

where the total cohesive energy (E) is composed of individual terms for contributions from dispersion (D), polar−polar (P), and hydrogen bonding (H) forces. Dividing this equation by the molar volume gives the square of the total (Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components.

$$\frac{E}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V} \tag{7}$$

$$\delta^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2 \tag{8}$$

These three parameters can be measured experimentally (as will be described later) such that solubility "distance" (Ra) can be calculated for any polymer−solvent (and POSS/polymer) combination. In order to maximize POSS/polymer interactions, one must simply choose a filler/matrix combination which minimizes this distance.

$$(Ra)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \tag{9}$$

In this equation, the factor of "4" is predicted by the Prigogine corresponding states theory of polymer solutions when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules and has been found to be convenient when plotting solubility data as a sphere.[22]

Conceptually, the method for determining Hansen solubility parameters (HSP) is to define a sphere in three-dimensional Hansen space (with dispersion, polar, and hydrogen bonding forces as the three axes) in which all of the good solvents (including solvent mixtures) for the solute exist inside the sphere while all of the poor solvents are excluded from the sphere. The three component values for HSP are well-known for a large number of common solvents, and thus each solvent is represented by a point in a Hansen three-dimensional space. By replacing some of the good solvent with a poor solvent (creating a mixture), we move along the line connecting the good solvent solubility parameter to the poor solvent solubility parameter. At some point the polymer or solute will phase separate, which defines a boundary on that line. By repeating this process with a number of poor solvents, a sphere can be fit in which all of the soluble mixture (points) are within the sphere while all of the nonsoluble mixtures are outside of it. The center of this sphere is then the three-dimensional solubility parameter of the solute with the radius of the sphere defined as the radius of interaction. Figure 1 represents this concept in two dimensions.

Once solubility parameters have been determined for different POSS and polymer combinations the distance between these two compounds in Hansen space can be calculated by eq 9. The distance defines how far separated two components are in solubility space. Dividing the solubility distance by the minimum interaction radius (smaller of the two) one arrives with a value of "relative energy distance" (RED), which in effect measures the mutual compatibility of the two materials. If the RED is 0, then the solubility parameters are exactly matched and the materials are soluble with no energy difference. If the RED is less than 1, then the two compounds are strongly compatible and predicted to be mutually soluble. A value at or close to 1 is a boundary condition, and progressively higher values indicate lower affinities. If the distance is greater than the larger of the interaction radii, then the blend should phase separate. These values will be used
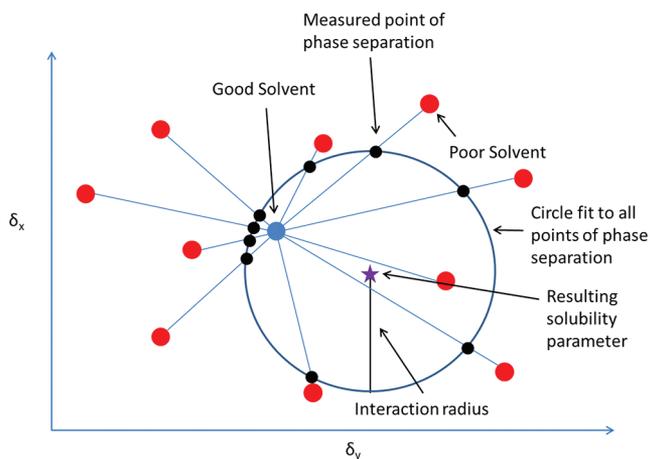
Figure 1. Graph showing conceptual method for solubility parameter determination. For ease of viewing only two dimensions are shown.

to predict when certain POSS–polymer combinations will show a high degree of interaction, with lower values predicting high interactions and higher values predicting little to no interaction and phase separation.

The present work will serve to show how well POSS dispersion, interaction potential, and phase separation can be predicted with this method as well as show the deficiencies of other methods which make use of calculations with problematic assumptions. Specifically, a previous study by the Schiraldi group[15] will be analyzed in terms of solubility parameter. In this work it was found that a high degree of POSS/polymer interactions (and associated property enhancements) were found for a blend of phenoxy resin and trisilanolphenyl POSS while the same POSS blended with polycarbonate (PC) showed phase separation and decreased properties. For the comparison to other methods, the work of Morgan[16] and Chin[17,18] will also be examined to show how the direct measurement of three-dimensional solubility parameters can lead to a better understanding of the phase behavior of these blends without the need for assumptions.

■ EXPERIMENTAL SECTION

Materials. The following solvents were used, either as good or poor solvents, and were all obtained from Fisher with 99% or higher purity, free of inhibitors and dried over molecular sieves before use: dichloromethane, tetrahydrofuran, hexane, toluene, methyl ethyle ketone, 1-propanol, cyclohexane, acetonitrile, methanol, *N,N*-dimethylformamide, ethanol, dimethyl sulfoxide, heptane, propylene glycol, hexafluoroisopropanol, and triethylene glycol. Hansen solubility parameters for these solvents were obtained from ref 21.

Aminopropylisobutyl POSS (AM0265), phenylisobutyl POSS (MS0813), phenylisooctyl POSS (MS0814), and trisilanolphenyl POSS (SO1458) were purchased from Hybrid Plastics Inc. and used as received. Polysulfone was obtained from Solvay Advanced Polymers (Udel P-1700 NT 11) with a reported melt flow index of 6.5 g/10 min at 343 °C and 2.16 kg. PKFE phenoxy resin was obtained from InChem Resins Inc. (Rock Hill, SC), with reported number-average and weight-average molecular weights of 16 000 and 60 000 g/mol, respectively. Calibre 200-14 an unstabilized polycarbonate resin was supplied by Styron LLC.

Solution Preparation. Initially, good and poor solvents for each of the seven analytes were determined qualitatively by making ca. 1% weight solutions in a variety of solvents. The data needed to construct a sphere in three-dimensional Hansen space consists of a series of volume fraction values of good/poor mixtures where the last clear solution and first visibly phase separated solution is noted. Here is the

procedure: Once a good solvent had been determined a standard solution of the polymer/POSS of interest was prepared such that 1 mL of this solution would contain 50 mg of the compound of interest (2.5 g in 50 mL). Using an autopipet, 1 mL of solution was added to each of 50 glass vials. The solvent was then removed by vacuum leaving 50 mg of polymer/POSS in the vial. The initial series consisted of volume ratios of (good solvent:poor solvent) 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90, with a total volume of 5 mL. The appropriate volume of good solvent was added to each of the vials and left overnight to allow complete dissolution. Next, the appropriate volume of each of 6–10 bad solvents was added to each series of solutions. The vials were shaken to ensure complete mixing and left for 1 week to equilibrate, reducing any kinetic effects of dissolution. Once equilibrated a record was made for each series of which solutions remained clear and which showed signs of phase separation. These values were then used to build models for each of the compounds.

The models were constructed using a Microsoft Excel solving routine in which the boundary conditions were defined such that the last condition of solubility would be contained within a sphere while the first condition of insolubility would be contained outside of said sphere. The model contained as many parameters as solvent series were prepared for a particular compound. Since there are four parameters (dispersion, polar, hydrogen bonding, and interaction radius), the minimum number of inputs is four, though in many cases 6–7 data series were used. The model was optimized by minimizing the average distance between the radius as defined by the boundary condition recorded and the radius predicted by the model. In this way the three-dimensional Hansen solubility parameters (with interaction radius) were measured and modeled for a variety of POSS molecules and polymers.

■ RESULTS AND DISCUSSION

In total, three polymers and four POSS grades were measured and modeled. The structures and short names of these compounds are listed in Figure 2. The initial results for solubility parameters are listed in Table 1. Values are given for each of the three parameters (in units of $MPa^{1/2}$), interaction radius (unitless), and total solubility parameter (in units of $MPa^{1/2}$ and $(cal/cm^3)^{1/2}$), as calculated from eq 8. It should be noted that two different approaches were taken to calculate these values. The first approach solved for the model points in a way to minimize the deviation from the measured boundary points (best fit). The second solved for the model points in such a way as to minimize the total interaction radius. In most cases the values given by either approach were quite similar, and so values shown in Table 1 are produced using the best fit model

To gauge how well these values predict POSS–polymer interactions, the work of Schiraldi and Iyer[15] was analyzed in terms of solubility parameters. In that work it was found that a blend of trisilanolphenyl POSS (SO1458) and polycarbonate showed a lack of POSS–polymer interactions and therefore phase separated, yielding decreased physical properties. By blending the same POSS with PKFE phenoxy resin, though, a different trend was found. In that system an increase in modulus and glass transition temperature was noted and explained by the presence of hydrogen bonding and $\pi-\pi$ stacking which resulted in a pseudografted POSS structure. Now knowing the experimental solubility parameter values for each of these compounds calculations can be carried out (using eq 9) which will provide the relative energy difference between each of the polymers and the POSS grade which was used. The results from these calculations are listed in Table 2. From these calculations it is clear that trisilanolphenyl POSS has a significantly smaller relative energy difference to PKFE (1.11) than to PC (1.87) and therefore a higher interaction potential.
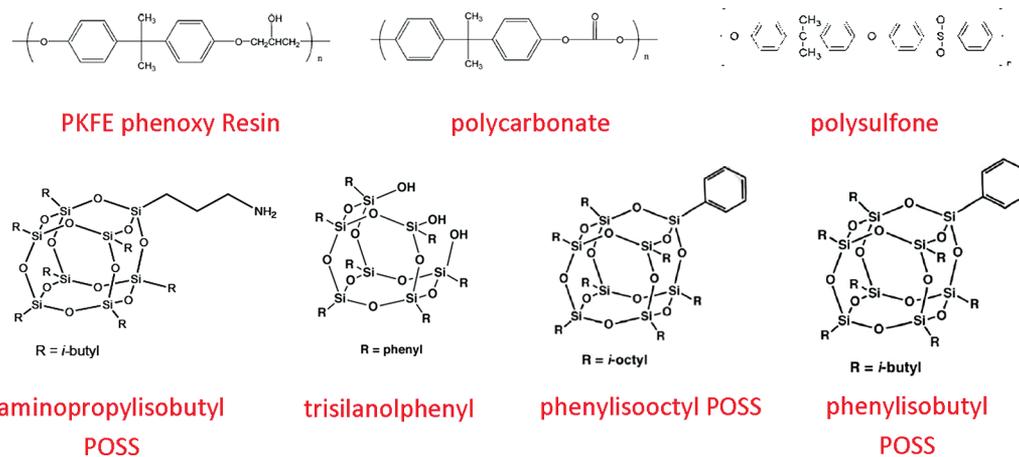
Figure 2. Structures and short names for polymers and POSS grades tested.

Table 1. Solubility Parameters for Select Compounds

compd	δ_D	δ_P	δ_H	r	δ_T, MPa$^{1/2}$	δ_T, (cal/cm^3)$^{1/2}$
PC	19.35	6.43	5.80	6.23	21.20	10.36
PKFE	22.05	9.06	9.58	12.62	25.69	12.56
PSF	19.02	5.90	6.13	4.29	20.84	10.18
SO1458	16.60	16.72	5.23	15.07	24.14	11.80
AM0265	16.85	0.00	11.83	10.83	20.58	10.06
MS0813	16.93	5.69	7.23	4.30	19.30	9.43
MS0814	16.31	8.32	8.75	7.00	20.29	9.92

Table 2. Calculation of Relative Energy Difference (RED) for POSS−Polymer Combinations

	δ_D	δ_P	δ_H	r	RED (SO1458)
PC	19.35	6.43	5.80	6.23	1.87
PKFE	22.05	9.06	9.58	12.62	1.11
PSF	19.02	5.90	6.13	4.29	2.77
SO1458	16.60	16.72	5.23	15.07	0.00

The value of 1.11 for the SO1458−PKFE combination predicts that the two are almost soluble. In this case the results are clearly predicted by use of solubility parameters. While this model does not take into account the processing and thermal history of the blends, the results are consistent with the predicted values. These Hansen solubility parameters were developed using a solution technique and are most accurate when comparing to solution blended systems. The predicted results for dispersion and reinforcement in this study, however, are confirmed through this method.

It was this previous work which led to additional research by Schiraldi et al. which incorrectly predicted that similarities in chemical structure between polysulfone (PSF) and trisilanol-phenyl POSS would lead to a high degree of interaction between blend components resulting in polymer properties enhancements.[23] It was assumed that polysulfone would behave more similarly to phenoxy resin than polycarbonate due to its polarity and the potential for hydrogen bonding to sulfone groups. The calculation of "RED" for SO1458 and PSF though yields a result of 2.77; this large difference means that PSF has a significantly lower interaction potential than PC which is why a highly phase-separated morphology and decreased mechanical properties were observed in these blends. This example

illustrates the futility in predicting POSS/polymer interactions based on chemical structures alone. While polysulfone could be assumed to behave in a similar manner as phenoxy resin in POSS blends, it exhibited lower compatibility than was previously observed with the poorly matched polycarbonate polymer. By measuring values for solubility parameters of POSS−polymer combinations, the nature and the magnitude of the interactions can be understood and predictions can be made about whether a phase separated or dispersed blend will result without the need to perform experiments.

The values determined herein were then used to revisit other examples from the literature. As was mentioned previously, a number of workers in the field have begun to try to correlate solubility parameters to POSS−polymer interactions, though they are using different techniques to find the solubility parameters which may lead to inaccurate determinations. Morgan et al.[16] tried to use the Hoy solubility parameters of nylon-6, with calculated values for octaisobutyl POSS and trisilanolphenyl POSS. The Hoy method of group contribution calculations were used to determine single value solubility parameters, generating the listed in Table 3. Since values were

Table 3. Solubility Parameters As Calculated Using the Hoy Method[16]

	$\sum G_i$ (kcal cm^3/mol)$^{1/2}$	δ (cal/cm^3)$^{1/2}$
PA6	1.10	11.0
octaisobutyl-POSS	7.43	7.8
trisilanolphenyl-POSS	7.93	9.8

not determined for octaisobutyl POSS in the present work, only the values for nylon-6 (provided by ref 21) and trisilanolphenyl POSS (SO1458) will be considered.

From these values the authors hypothesize that the nylon-6 will have a higher degree of interaction with trisilanolphenyl POSS because the values for solubility parameter are closer than that of octaisobutyl POSS. While this may be true there is no discussion of how close those values need to be to produce a strong interaction. With a single value solubility parameter there is no way of taking into account interaction radius or understanding how the different component contributions of solubility parameter affect the real difference in interaction potential. If those same materials are considered using the Hansen method to calculate a "RED", a much different result is

Table 4. Hansen Solubility Values and RED Calculation for PA6−SO1458 Combination

	δ_D	δ_P	δ_H	r	RED (SO1458)
PA6	17.00	10.6	3.4	5.10	2.82
SO1458	16.60	16.72	5.23	15.07	0.00

noted (Table 4). Using this approach, a RED value of 2.82 is determined which would suggest that there is actually a very large difference in solubility parameters and that the nylon-6-SO1458 blend should show a phase-separated morphology, which indeed is the result which was reported.

This example shows that solubility parameters can be effectively used to predict POSS/polymer interactions, but it is necessary to use a more sophisticated model which takes into account each of the interaction forces independently and which does not rely on the calculation of single values based on group contribution methods.

Other recent work has also highlighted how solubility parameter could be useful for understanding POSS−polymer interactions. Work by Chin et al. also uses group contribution calculations to make estimations of interaction potentials.[17,18] The importance of using three parameter Hansen solubility parameters is stressed by Chin; however, assumptions were then made which could lead to errors in accurately predicting interaction potentials. In order to perform the calculations using the Hoftyzer and van Krevelen method, two assumptions were made: (1) hydrogen bonding was assumed to have no impact based on the symmetry of the molecule, and (2) the core POSS cage's contribution to the overall solubility parameter was neglected. The results of these calculations are listed in Table 5. In that work aminopropylisobutyl POSS is the

Table 5. Calculated Solubility Parameters for Select Compounds[17]

	δ_d ($J^{1/2}$ cm$^{-3/2}$)	δ_P	δ_h	δ
PA6	15.9	34.6	13.4	18.0
aminopropylisbutyl-POSS	17.5	0	0	17.5
aminopropylisooctyl-POSS	18.6	0	0	18.6
aminopropylphenyl-POSS	19.2	1.5	0	19.3

only POSS used which has been measured and modeled so it will be discussed here.

As stated earlier, the authors have made the assumption that there is no hydrogen bonding contribution and that the POSS cage has no contribution. This however is refuted by the results shown previously (Table 1) which show that indeed hydrogen bonding has a large contribution to the total solubility parameter. In the case of aminopropylisobutyl POSS (AM0265/AB POSS) hydrogen bonding plays a significant role in the solubility behavior of the compound (δ_H = 11.83). The authors have presented the total solubility parameters for nylon-6 and a series of POSS types without explaining the connection between the difference in solubility parameter and the resultant interaction potential. The authors state that since the value for nylon-6 is closest to aminopropylisobutyl POSS, it has the highest degree of interaction and therefore the best dispersion; however, the difference between nylon-6 and aminopropylisobutyl POSS is 0.5, while the difference between nylon-6 and aminopropylisooctyl POSS is negligibly different at 0.6. Using the Hansen value for nylon-6 and the measured value for AM0265, a relative energy difference calculation can be carried out (Table 6), which shows a

Table 6. Hansen Solubility Values and RED Calculation for PA6−AM0265 Combination

	δ_D	δ_P	δ_H	r	RED (AM0265)
PA6	17.00	10.6	3.4	5.10	0.71
AM0265	16.85	0.00	11.83	10.83	0.00

distance of 0.71. This RED predicts that the POSS would be soluble in the nylon matrix which is indeed the result that is reported. In this case our conclusions are consistent with what the author reports, but our method of prediction is more advanced and we contend considerably more accurate.

It is not our goal to treat the previous work as incorrect or insubstantial. On the contrary, their work correctly anticipates the need for an accurate method for predicting and interpreting POSS/polymer interactions, and the proposed group contribution calculations are one method to move in that direction. Unfortunately, though, in order to perform those calculations, unnecessary assumptions are made which can lead to misleading results. By using the experimental determination of Hansen solubility parameter as described here, direct measurements can be made which separate the contributions from the many forces which determine interaction potentials between molecules. Using this information, relative energy difference calculations can be made which can quantitatively determine the degree of interaction between polymer and POSS.

CONCLUSIONS

In this work an experimental method for the determination of Hansen solubility parameters was presented and used to determine solubility parameter values for a number of polymers and POSS grades. Using these solubility parameters, it was then possible to carry out relative energy distance calculations for various POSS−polymer combinations. The results from these calculations accurately predict the solubility, the POSS−polymer interactions and resultant POSS−dispersion uniformity compared to reported experimental results in the literature. Specifically, the behavior of POSS/phenoxy resin and POSS/polycarbonate blends was examined, and it was shown that the solubility parameter values for the POSS/polymer combinations used in that work accurately predict the very different observed behaviors in these blends. It was also shown that more recent work on POSS/polysulfone blends that showed a phase-separated morphology can be explained due to a high relative energy difference which was not predicted by simple evaluation of the chemical structures of the POSS and polymer used.

Examples of solubility parameter estimations using group contribution calculations were also examined and compared to the values which had been determined using the Hansen method. It was determined that these calculation methods are inaccurate and specifically make unjustifiable assumptions. By experimentally determining the Hansen solubility parameters for a given POSS−polymer combination without any a priori assumptions, we get accurate prediction of POSS−polymer interactions and therefore POSS dispersion uniformity. These works did, however, highlight the need for these types of experimental evaluations to understand and predict POSS dispersion. Future work in this area will determine to what degree processing and thermal history affect the accurate prediction of these values. The current model has no way to account for the degree of mixing achieved by blending or differences in cooling rates from the melted state. These factors

may affect the ability of the POSS and polymer to associate in an ideal manner. In some cases these factors may have an effect which may be greater than the interaction potentials which would be present in a solution blended system.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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