White Paper: Utilizing Hansen Solubility Parameters for Formulation Optimization using PixClear® Zirconia Nanocrystals

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September 2017

Abstract

Hansen Solubility Parameters are a quantifiable measure of compatibility that aid in the optimization of formulations for a variety of applications. The HSP values have been determined for Pixelligent's PixClear® PCPR zirconia nanocrystals. From these tests, PixClear® is shown to have excellent compatibility with a broad range of components that may be used in complex formulations. The basic test approach for determining the parameters is reviewed. The method by which these results can be utilized to choose compatible components is then demonstrated. Future directions for additional testing are also discussed.

Introduction

The ability of Pixelligent's PixClear® nanocrystals to deliver high performance nanocomposites with the desired properties (higher refractive index, optical transparency, physical cohesion, etc.) is dependent upon uniformly distributing the nanocrystals throughout the nanocomposite. Uneven distribution of the nanocrystals (aggregation of nanocrystals being an extreme case of this) can lead to performance issues, including reduced transparency and poor mechanical strength. While it is the zirconia core of Pixelligent's nanocrystals which deliver the desired improvements in refractive index to the nanocomposite, it is the chemistry of the capping agents at the surface of the nanocrystals which control the compatibility, and thus dispersibility, of the nanocrystals in solvents, monomers, and polymers. Pixelligent offers products with surface chemistry tailored to deliver compatibility with different ranges of nanocomposite components. Full optimization of these formulations requires a strong understanding of how the chemistry of the components controls compatibility. Hansen solubility

parameters (HSP) are one such way to understand, communicate, and optimize compatibility between the various components (solvent, monomer, polymer, and nanocrystals) of a formulation.

The HSP approach builds upon the general concept of like dissolves/disperses like by quantifying the interfacial interactions between component molecules in a mixture or formulation.[1] This quantification is accomplished by considering the cohesive energies (i.e. the energy needed to break all the inter-molecular bonds/attractions between one molecule and its surroundings) in a dispersion. In the HSP approach, this cohesive energy is broken down into three components (dispersion, polar, and hydrogen bonding). Finally, these component energies must be converted to energy densities to correct for molar volume differences. These component energy densities are known as the Hansen solubility parameters and are denoted as δD (for the dispersion parameter), δP (for the polar parameter), and δH (for the hydrogen-bonding parameter). Each different molecule has specific HSP values, which can be looked up, calculated, or determined experimentally. Geometrically these 3 values can be thought of as describing a locus in 3-dimension Hansen space. The closer in proximity that two molecules are in the 3-d Hansen space, the more compatible they are.

The Hansen Solubility Parameters for a nanocrystal can be experimentally determined by dispersing the nanocrystals into a variety of screening solvents with known HSP values. These test solvents should be chosen to cover a wide range of Hansen space so that the location of the capped nanocrystals can be accurately determined. The test solvents which yield good dispersions (stable, low scattering) will tend to be grouped together in 3-d Hansen space. Instead of visualizing the nanocrystal as having a single locus in 3-d Hansen space, it is often more useful to visualize a solubility sphere for the nanocrystal. The surface of the sphere is the shell which separates compatible and non-compatible solvents within 3-d Hansen space, with the group of compatible solvents contained within the sphere.

In this paper we present the results of the experimental determinations of HSP values for PixClear® PCPR nanocrystals as well as the theoretical calculation of HSP values for bisphenol A glycerolate dimethacrylate (BPA), a high refractive index monomer.

Experimental

Pixelligent Technologies contracted with Agfa Labs in Belgium to have the Hansen solubility parameters for three PCPR nanocrystal batches measured. Agfa Labs used reference liquids as screening

solvents in a high throughput formulation technique. Test dispersions which were transparent with no visible sedimentation result in a solvent being scored as "1", while a rating of "0" was given to solvents used to make screening dispersions which resulted in obvious scattering due to aggregates. These scores were entered into HSPiP software (5th Edition) to calculate the location and radius of the solubility sphere for each nanocrystal dispersion. The software plots the location of each screening solvent in 3-d Hansen space, then assigns the corresponding dispersion score. A genetic fitting algorithm is then used to determine a solvation sphere with the smallest possible radius that can contain all the "good" solvents (solvents scored as "1"), while containing the least number of "bad" solvents (solvents scored a "0").

Theoretical calculation of the HSP values for bisphenol A glycerolate dimethacrylate (BPA) was also carried out by Agfa labs utilizing the Conductor like Screening Model for Real Solvents (COSMO-RS).[2]

Results and Discussion

Three separate manufacturing runs of PCPR were chosen for this study. The objective of these measurements was to determine the Hansen Solubility Parameters for our nanocrystals to help us better understand and communicate the compatibility of our nanocrystals with polymers and solvents. The different batches were chosen to help determine how sensitive the HSP values were to batch-to-batch variations as well as changes made as part of manufacturing process optimization. The experimentally determined HSP values, the interaction radius (R), and the quality of the fit for the 3 batches of PCPR nanocrystals are shown in table 1. The δD, δP, and δH values determine the location of the solubility sphere in 3-d Hansen space, while the value for R defines its radius. A high value for R means that the volume of Hansen space in which the good solvents reside is relatively large and thus the PCPR nanocrystal is relatively insensitive to the choice of solvent, while a small value indicates that the nanocrystals are highly sensitive to the dispersion environment.n`

Sample name	Sample Notes	δD	δP	δH	R	fit
PCPR Batch #1	original process	18.61	8.71	5.64	8.8	0.966
PCPR Batch #2	modified process	18.36	8.93	5.58	8.6	0.966
PCPR Batch #3	original process	18.54	8.69	5.76	8.7	0.931

Table 1. *Experimental results of HSP measurements*

The similarity of the HSP and R values for the three samples suggests that the change made as part of manufacturing process optimization had minimal effect on the compatibility of the final product. The similarity of data for the modified batch to data from the original process proved to be a vital tool in ultimately adopting the final manufacturing process for PCPR. When combined with other key data, it gave us good confidence that the process change had no discernable effect on the compatibility of the PCPR nanocrystals.

One potential target for refinement of the HSP determination method is the way in which the ratings for individual screening dispersions are determined. Currently operator judgement is required to determine the rating for the test dispersions. Small amounts of scattered light can be interpreted as either due to the presence of large aggregated particles or as light scattered due to the index mismatch between the solvent and the nanocrystals. This judgment may lead to false ratings and ultimately inaccurate determinations of the HSP values. The introduction of a tool, such as a dynamic light scattering (DLS) instrument, to quantitatively measure aggregation would improve the confidence in the ratings. However, as can be seen from the following discussion, the current values lead to many correct predictions of compatibility with our nanocrystals.

Using the experimentally determined HSP values, along with the value of R, a knowledgeable formulator can mathematically predict which potential components of a formulation will be compatible with the PCPR nanocrystals. As stated in the introduction, the distance between two molecules in Hansen space can be used to quantify the degree of compatibility of those two molecules. Mathematically, the distance between two different molecules (denoted by subscripts “a” and “b”) in HSP space can be calculated with the following formula:

$$(\text{Distance})^2 = 4*(\delta D_a - \delta D_b)^2 + (\delta P_a - \delta P_b)^2 + (\delta H_a - \delta H_b)^2$$

This distance between the different components in the mixture, say the PCPR capped nanocrystals and the solvent, can then be scaled to the sensitivity of the nanocrystals to the solvent by dividing the calculated distance by the interaction radius (R) of the nanocrystal. This yields the relative energy difference (RED) between the two components. If RED is less than 1, the molecules are compatible and mixing will lead to a good solution/dispersion. For RED values larger than 1, the solvent will not dissolve/disperse the nanocrystals and the nanocrystals will eventually settle out of the

dispersion. Table 2 shows the Hansen solubility parameters of several molecules of interest, including the values for BPA that were calculated at Agfa labs. The table also includes calculated RED values between the different batches of nanocrystals and these molecules.

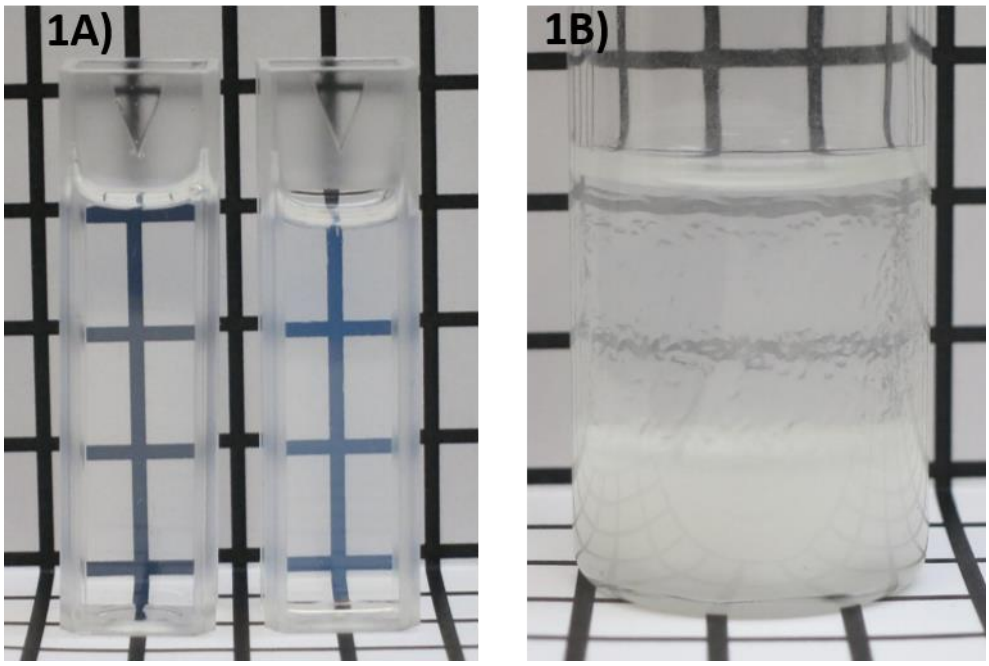
Solvents and Monomers of Interest	δD	δP	δH	Calculated RED values		
				PCPR Batch #1	PCPR Batch #2	PCPR Batch #3
Bisphenol A Glycerolate Dimethacrylate (BPA)	18.14	5.80	12.54	0.86	0.89	0.85
PGMEA (PGA)	15.60	5.60	9.80	0.90	0.90	0.89
Ethyl acetate (ETA)	15.80	5.30	7.20	0.77	0.75	0.76
n-Hexane	14.90	0.00	0.00	1.45	1.47	1.46
Benzyl Alcohol	18.40	6.30	13.70	0.96	0.99	0.95
Acetonitrile	15.30	18.00	6.10	1.30	1.27	1.30
Benzyl Alcohol/Acetonitrile Mix {50/50 (vol%/vol%)}	16.90	12.20	9.90	0.74	0.72	0.73

Table 2. *HSP values for solvents and monomers of interest. Also shown are the distances between molecules of interest and the different batches of PCPR capped nanocrystals, expressed as RED values. (The HSP values were taken from Ref. 1, with the exception of the values calculated for BPA at Agfa Labs.)*

From the RED values shown in table 2, we can see that the BPA monomer, PGA, ETA, and benzyl alcohol all have RED values of less than 1, and thus are all predicted to be compatible with PCPR nanocrystals. This is in good agreement with our experience, as PCPR dispersions in these materials show excellent shelf life stability. On the other hand, hexane and acetonitrile are predicted to be, and indeed are, poor solvents for the dispersion of PCPR nanocrystals.

A 50/50 (vol%/vol%) mixture of benzyl alcohol and acetonitrile (HSP and RED values shown in table 2) demonstrates a couple of the interesting features of the HSP method. Firstly, the HSP value for a mixture of solvents can simply be arrived at by calculating the volume-weighted average HSP values for the individual components. The ease of this calculation proves useful when one wants to determine how the HSP values change as the ratio of solvents change (for example, during solvent evaporation). The second principle is that it is possible to make a good solvent out of a bad solvent simply by mixing the bad solvent with the proper choice of co-solvent. As one can determine from the low RED values, the 50/50 (vol%/vol%) mixture of Benzyl alcohol and acetonitrile is predicted to act as a good solvent for Pixelligent's PCPR nanocrystals, even though acetonitrile is a poor solvent. Experimentally this was

proven to be the case, as can be seen in figure 1. The three mixtures in figure 1 were all made by adding an amount of solvent equal to the weight of the dried nanocrystals, in an attempt to make 50 wt% dispersions. The addition of benzyl alcohol to the nanocrystals results in a good dispersion (figure 1A, left) while the dispersion in acetonitrile (shown in figure 1B) is clearly not good. Even after thorough mixing, the nanocrystal/acetonitrile mixture evolves into a two phase system with the nanocrystal rich



phase at the bottom and an acetonitrile rich supernatant. Thermogravimetric Analysis (TGA) of the supernatant shows less than 3 wt% loading of PCPR nanocrystals. However, when 50 vol% of the acetonitrile is replaced with benzyl alcohol, the mixture of benzyl alcohol and acetonitrile behave as a solvent for PCPR, as can be seen in the right hand side of Figure 1A.

Figure 1. *Pictures displaying dispersion quality for experiments with PCPR, benzyl alcohol, and acetonitrile. Figure 1A shows 1 cm cuvettes filled with 50 wt% dispersions of PCPR nanocrystals in benzyl alcohol (left) and a 50 wt% dispersion of PCPR nanocrystals in 50/50 (vol%/vol%) mixture of benzyl alcohol and acetonitrile (right). Figure 2 shows the attempted dispersion of PCPR in pure acetonitrile.*

Conclusions

The experimentally determined Hansen solubility parameters have been reported for three batches of Pixelligent's PixClear® PCPR nanocrystals. The three different batches yield similar HSP values, demonstrating good batch to batch repeatability. These parameters make finding compatible

components for a fully formulated nanocomposites more straight-forward. Future work will focus on making improvements to the scoring of the screening dispersions as well as extending the measurements to nanocrystal systems beyond PCPR.

Literature Cited:

1. Charles M. Hansen, *Hansen Solubility Parameters: A User's Handbook, Second Edition* (Boca Raton FL: CRC Press, Inc., 2007)
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