



OPTIMIZE THE COMPATIBILITY BETWEEN GRAPHENE AND TiO₂ PARTICLES USING THE HANSEN APPROACH

APPLICATION TO THE PAINT & INK INDUSTRY

Context

Formulating stable particle suspensions is of great interest for industrials as it allows to enhance the properties and the lifetime of their products. This is particularly true for the Paint & Inks products in which complex additives can be added to the initial formulation to reinforce define properties. One current tendency for such products is the addition of Graphene which allows to reinforce among others, their anticorrosion and thermal-resistance properties. However, single and few-layers Graphene can present quite important aggregation behavior due to π -stacking as well as destabilizing the formulated product after addition. One way to reduce the additive impact on the product stability is to play on the choice of the dispersion medium, which is often a key parameter to avoid particle agglomeration when adding additives. Indeed, using a solvent which ensures a good Graphene stability and which is compatible also with the initial paint formulation can greatly tackle destabilization. Finding such appropriate solvent is not an easy task as it depends both on the Graphene used and the initial paint formulation. In that way, methods have been already developed to predict this dispersion medium such as the Hansen Parameters (HP).

The aim of this note is to demonstrate that accurate compatibilization of Graphene in a model paint formulation (dispersion of Titanium dioxide TiO₂ P25 in various aqueous mixtures) can be realized by applying the Hansen theory.

Definiton

The semi-empirical Hansen's approach, which has been historically developed to predict the solubility of molecules, can be adapted to describe the particles stability in various solvents. This approach is based on the decomposition of the Hildebrand parameter $\bar{\delta}$,

linked to the binding energy between two particles, into three different parameters δ_D , δ_P and δ_H describing respectively non-polar, polar and hydrogen interactions between the particle surface and the dispersion media as follow:

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

Considering these non-polar, polar and hydrogen components, each particle or solvent can be represented by a point in a 3D-space with these components as coordinate values named HP coordinates. The stability of the particle under study is evaluated considering a range of solvents exhibiting large variation in these 3D-space followed by a ranking of the tested solvents as good or poor stabilizing media. The border between good and poor solvents allows to build a sphere with a center corresponding to the HP coordinates of the particle and a radius R_0 . Actually, if a solvent is situated inside the sphere of the particle, it can be considered as a good stabilizing media. Inversely, a solvent situated outside the sphere should poorly stabilize the suspension. Considering the distance R_a between the HP coordinates of the particle ($\delta_{D,p}$; $\delta_{P,p}$; $\delta_{H,p}$) with the one of the solvent ($\delta_{D,s}$; $\delta_{P,s}$; $\delta_{H,s}$), it is quite easy to estimate the Relative Energy Difference, named RED, which indicates if the chosen solvent should give a stable ($RED < 1$) or an unstable suspension ($RED \geq 1$) as follow:

$$RED = \frac{R_a}{R_0} \quad \text{with}$$

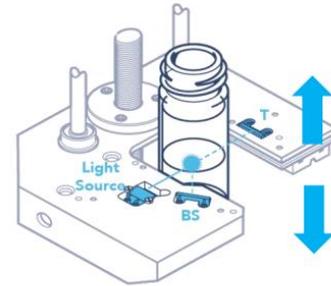
$$R_a = \sqrt{4 \cdot (\delta_{D,p} - \delta_{D,s})^2 + (\delta_{P,p} - \delta_{P,s})^2 + (\delta_{H,p} - \delta_{H,s})^2}$$

By definition, the lower is the RED, the more stable the suspension should be. The particular case for which the RED is equal to 0 signify that the studied solvent is at the same position than the center of the sphere (i.e. the position of the particle).

TURBISCAN: How it works

TURBISCAN technology, based on Static Multiple Light Scattering, consists on sending a light source (880 nm) on a sample and acquiring backscattered (BS) and transmitted (T) signal all over the height of a sample in its native state. By repeating this measurement over time at adapted frequency, the instrument enables to monitor physical stability of a sample without dilution. The signal is directly linked to the particle concentration (φ) and size (d) according to the

Mie theory knowing refractive index of continuous (nf) and dispersed phase (np):



BS and T = f(φ , d, np, nf)

At a concentration typically used in a paint formulation, the Graphene dispersions have a low concentration (0.01 and 0.0625 g.L-1), samples are reaching quite high level of transmission which are closed to the one of the solvent taken alone. In such cases, the transmission level of the solvent impacts a lot on the transmission fluctuations used to quantify the stability of the Graphene dispersion and must be considered. In that way, the mean free path (noted L) can be used as it is representative of the dispersed phase evolution with consideration of the environment (i.e. the continuous phase nature). The mean free path represents the average distance over which an emitted photon travels before substantially changing its direction or energy as a result of one or more successive collisions with scatters (i.e. few-layers Graphene flakes here). The mean free path is directly related to the mean diameter and the volume fraction of scatters according to the following relation:

$$L = \frac{2d}{3\varphi Q_e}$$

with d the mean diameter, φ the volume fraction and Q_e the extinction factor obtained from Mie theory.

Using the mean free path L, it is quite easy to define a stability ratio, noted RS, which is representative of the variation of mean diameter (i.e. the colloidal stability) of the Graphene sheets. Such ratio can be defined as follow:

$$R_s = \frac{\Delta L}{L_{av}} = \frac{|L_{min} - L_{max}|}{L_{av}} = \frac{2}{3\varphi} \frac{|d_{min} - d_{max}|}{Q_e^{min} - Q_e^{max}}$$

$$R_s \approx \frac{|d_{min} - d_{max}|}{d_{av}} = \frac{\Delta d}{d_{av}} \text{ as } Q_e^{min} \approx Q_e^{max} \approx Q_e^{av}$$

With ΔL and Lav respectively the standard deviation and the arithmetic mean of the mean free path variations in function of time. According to this definition, the lower is the RS value, the better will be the colloidal stability of the sample (with a RS value of 0 indicating a perfect colloidal stability, i.e. no diameter variation vs time).

Evaluation of Graphene dispersion stability

Macroscopically stable Graphene dispersed in water obtained from Carbon Waters® (at a concentration of 0.1 or 0.25 g.L-1) has been diluted with a miscible solvent to obtained 20mL of Graphene dispersion respectively at 0.01 and 0.0625 g.L-1. Each Graphene sample obtained has been dispersed according to the mechanical stirrer of a TURBISCAN DnS at 1000rpm during 15 minutes to ensure a same dispersibility procedure before stability analysis.

The same TURBISCAN DnS has been used to record the evolution of the transmission signal in function of time. The stability of Graphene dispersion is then quantified according to the calculation of the stability ratio RS from the transmission variations. The following table 1 indicates the Hansen parameters used for each mixture of solvents calculated by averaging the Hansen parameters of the individual solvents by volume.

The different Graphene dispersions have been classified according to their colloidal stability through their RS values. Results are displayed for 0.01 and 0.0625 g.L-1 Graphene dispersions by the following Figures 1 and 2 respectively.

The RS values borders between good and bad aqueous mixtures (i.e. green colored mixtures vs others ones) have been established according to the most representative Hansen sphere obtained (see explications below). The other RS values borders between aqueous mixtures with a moderate and bad colloidal stability (yellow vs orange) as well as between bad and completely unstable ones (orange vs red) have been determined arbitrarily.

Table 1: List of the 26 aqueous mixtures tested to build the Graphene Hansen Sphere

Solvents	δ _d	δ _p	δ _h
25%v H ₂ O/75%v 1-Propanol	15.88	9.10	23.63
25%v H ₂ O/75%v 2-Butoxyethanol	15.88	7.83	19.80
25%v H ₂ O/75%v Acetone	15.50	11.80	15.83
25%v H ₂ O/75%v DMF	16.93	14.28	19.05
25%v H ₂ O/75%v DMSO	17.68	16.30	18.23
25%v H ₂ O/75%v Ethylene glycol	16.63	12.25	30.08
25%v H ₂ O/75%v EtOH	15.73	10.60	25.13
25%v H ₂ O/75%v Formamide	15.93	18.55	36.48
25%v H ₂ O/75%v Isopropanol	15.73	8.58	22.88
25%v H ₂ O/75%v MeOH	14.90	13.23	27.30
25%v H ₂ O/75%v NMP	17.38	13.23	15.98
25%v H ₂ O/75%v Propylene glycol	16.48	11.05	28.05
75%v H ₂ O/25%v 1-Propanol	15.63	13.70	36.08
75%v H ₂ O/25%v 2-Butoxyethanol	15.63	13.28	34.80
75%v H ₂ O/25%v Acetone	15.50	14.60	33.48
75%v H ₂ O/25%v DMF	15.98	15.43	34.55
75%v H ₂ O/25%v DMSO	16.23	16.10	34.28
75%v H ₂ O/25%v Ethylene glycol	15.88	14.75	38.23
75%v H ₂ O/25%v EtOH	15.58	14.20	36.58
75%v H ₂ O/25%v Formamide	15.93	18.55	36.48
75%v H ₂ O/25%v Glycerol	15.98	15.03	39.05
75%v H ₂ O/25%v Isopropanol	15.58	13.53	35.83
75%v H ₂ O/25%v MeOH	15.30	15.08	37.30
75%v H ₂ O/25%v NMP	16.13	15.08	33.53
75%v H ₂ O/25%v Propylene glycol	15.83	14.35	37.55
H ₂ O	15.50	16.00	42.30

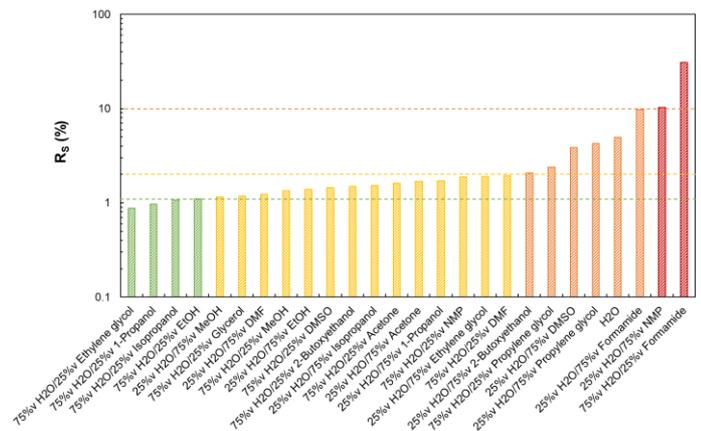


Figure 1: Colloidal stability classification of the 26 aqueous mixtures tested with 0.01 g.L-1 few-layers Graphene according to their RS values obtained after 2 hours of analysis

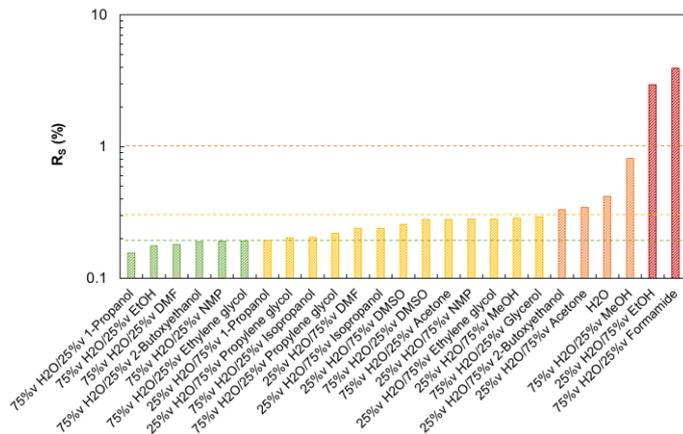


Figure 1: Colloidal stability classification of the 26 aqueous mixtures tested with 0.0625 g.L⁻¹ few-layers Graphene according to their R_s values obtained after 2 hours of analysis

According to these results, three solvents seems to have quite good stabilizing abilities regarding 0.01 and 0.0625 g.L⁻¹ Graphene concentrations such as mixtures of Water with 1-Propanol, Ethylene glycol and Ethanol. On the other side, the mixture of 75%v Water with Formamide appears to have quite bad stabilizing properties regarding the Graphene studied. The other aqueous mixtures tested exhibit different R_s values according to the Graphene concentration indicating fluctuations in the colloidal stabilization properties.

Calculation of HP Stability Sphere

Using previously determined classifications, it is quite easy to score each aqueous mixtures toward their abilities to stabilize Graphene particles and so building the corresponding Hansen sphere by repeated calculation and iteration using an adapted software like HSPiP as highlighted by Figure 3. The number of good aqueous mixtures are chosen according to the previous determined classification and in order to maximize the determined Hansen sphere representativity (i.e. maximization of the FIT). The Figure 3 presents two different spheres corresponding to a 0.01 and 0.0625 g.L⁻¹ Graphene concentration in the various aqueous mixtures tested. The sphere obtained from the 0.01 g.L⁻¹ Graphene concentration appears to be less representative compared to the more concentrated one with a lower number of good solvent situated inside (4 against 6) and also a lower FIT value (0.965 against 0.981).

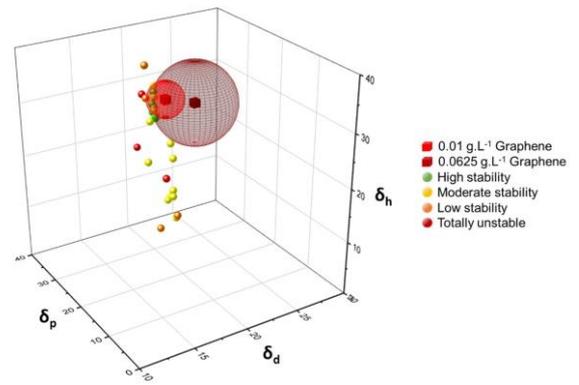


Figure 2: Hansen spheres obtained for Graphene in various aqueous mixtures at a concentration of 0.01 g.L⁻¹ (FIT=0.965, 1 solvent wrong in, no solvent wrong out) and 0.0625 g.L⁻¹ (FIT=0.981, 3 solvents wrong in, no solvent wrong out)

From the localization of the sphere center by the software, the Hansen parameters at the two concentrations for Graphene molecules are easily obtained as well as the stability sphere radius. Values obtained are the following ones:

- For the 0.01 g.L⁻¹ : $\delta_D = 16.31 \text{ MPa}^{1/2}$, $\delta_P = 12.54 \text{ MPa}^{1/2}$, $\delta_H = 37.53 \text{ MPa}^{1/2}$, $R_0 = 2.99 \text{ MPa}^{1/2}$
- For the 0.0625 g.L⁻¹ : $\delta_D = 18.79 \text{ MPa}^{1/2}$, $\delta_P = 12.03 \text{ MPa}^{1/2}$, $\delta_H = 36.06 \text{ MPa}^{1/2}$, $R_0 = 6.79 \text{ MPa}^{1/2}$

According to these results, the position of the Graphene dispersion in the Hansen 3D-space (i.e. the center of the sphere) appears quite close to each other for the two series of experiments at different concentration, indicating the reliability of the stability analysis realized. In the next section, only the sphere of the more concentrated Graphene will be considered as it is more representative of experimental stability data obtained due to a better FIT value.

From the determination of the Graphene position in the Hansen space, it is quite easy to calculate the RED and evaluate how far another solvent is from the Graphene position, and so if it will be a good or a poor stabilization media (i.e. inside or outside the stability Graphene sphere) according to its own Hansen parameters. A such prediction can be also done regarding another type of interest chemical as TiO₂ P25 particles which are massively used in paint formulations. The Figure 4 presents the position of the Graphene and TiO₂ spheres in the Hansen space (the determination of TiO₂ P25 sphere is available in application note TS_STAB_63).

Compatibilization of the Graphene in a Model Paint Formulation

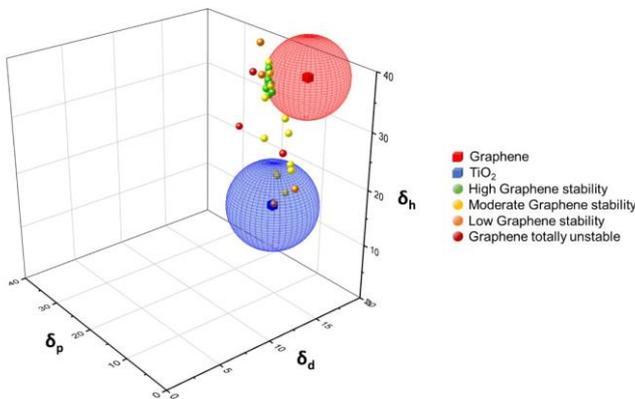


Figure 4: Hansen sphere positions obtained for Graphene using 26 aqueous mixtures (FIT=0.981, 3 solvents wrong in, no solvent wrong out) and TiO₂ P25 using 18 solvents (FIT=1, no solvent wrong in, no solvent wrong out)

As highlighted by Figure 4, the TiO₂ and Graphene spheres are clearly separated, indicating that no ideal solvent can be found in the Hansen space as no overlapping is present between these two spheres. However, if the determination of an ideal solvent remains not possible, evaluating one presenting a good compromise in the stabilization of Graphene and TiO₂ can be inferred from the sphere positions. Indeed, a such solvent can be found by minimizing the REDmix toward Graphene and TiO₂. The REDmix value of a defined solvent can be calculated from the individual RED value of this solvent related to Graphene and TiO₂ as follow:

$$RED_{mix} = \sqrt{RED_{Graphene}^2 + RED_{TiO_2}^2}$$

To validate this method, 6 different aqueous mixtures situated between the Graphene and TiO₂ spheres in the Hansen 3D space were chosen. The chosen mixtures are the following ones:

- 25%v H₂O/75%v 1-Propanol ($\delta_D = 15.88, \delta_P = 9.10, \delta_H = 23.63$)

- 25%v H₂O/75%v Ethylene glycol ($\delta_D = 16.63, \delta_P = 12.25, \delta_H = 30.08$)
- 25%v H₂O/75%v Ethanol ($\delta_D = 15.73, \delta_P = 10.60, \delta_H = 25.13$)
- 25%v H₂O/75%v Methanol ($\delta_D = 14.90, \delta_P = 13.23, \delta_H = 27.30$)
- 25%v H₂O/75%v Propylene glycol ($\delta_D = 16.48, \delta_P = 11.05, \delta_H = 28.05$)
- 75%v H₂O/25%v Acetone ($\delta_D = 15.50, \delta_P = 14.60, \delta_H = 33.48$)

REDmix values of each mixture has been calculated and the stability of 0.031 g.L⁻¹ Graphene with 0.031 g.L⁻¹ TiO₂ P25 in each mixture has been determined thanks to the stability ratio RS. Results are gathered in the following Figure 5 which presents the evolution of the experimental RS value in function of the calculated REDmix parameter. According to Figure 5, the lower is the REDmix value of the solvent, lower is the RS value, and so better will be its colloidal stabilization properties regarding few-layers Graphene and TiO₂ P25. Among the 6 promising aqueous mixtures tested, the ones with Water and Ethylene glycol or Propylene glycol appears to be the best candidates to compatibilize Graphene and TiO₂ P25. In that way, formulating such Graphene additives in these mixtures should increase the compatibility and reduce destabilization effects occurring after its incorporation in aqueous paints formulations containing large amount of TiO₂.

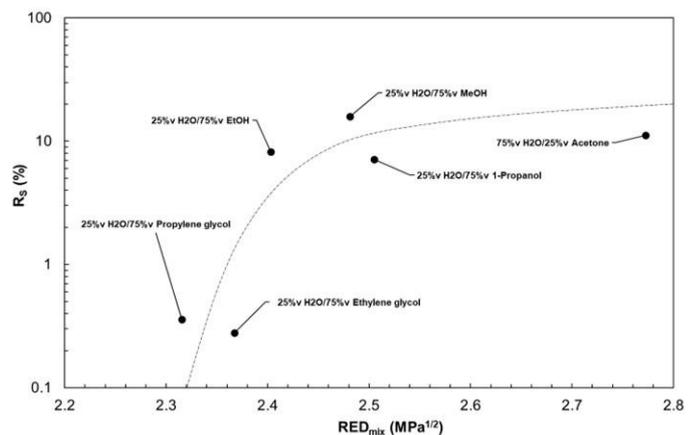


Figure 3: Evolution of the stability ratio *R_s* in function of REDmix for 6 aqueous mixtures regarding simultaneous stabilization of Graphene and TiO₂ P25

Conclusion

TURBISCAN technology experiments have been performed to quantify and compare the effect of the dispersion media on the stability of few-layers Graphene in various aqueous mixtures. TURBISCAN technology, through the calculation of the stability ratio RS, allows classifying the different aqueous mixtures tested and is well adapted to the Hansen approach for predicting an optimum dispersion media. Using this predictive approach to represent simultaneously Graphene and TiO₂ spheres can be a great help in finding solvents that compatibilize both Graphene flakes and TiO₂ particles to considerably reduce destabilization. Such study finds a direct application in the paint & inks industry in which complex and numerous additives are often used to reinforce texture, application or the final properties of the formulation.



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