



HAL
open science

Stability parameters for mineral suspensions: Improving the dispersion of fillers in thermoplastics

Arnaud Lafaurie, Nathalie Azéma, Laurent Ferry, José-Marie Lopez-Cuesta

► To cite this version:

Arnaud Lafaurie, Nathalie Azéma, Laurent Ferry, José-Marie Lopez-Cuesta. Stability parameters for mineral suspensions: Improving the dispersion of fillers in thermoplastics. *Powder Technology*, 2009, 192 (1), pp.92-98. 10.1016/j.powtec.2008.11.018 . hal-03181081

HAL Id: hal-03181081

<https://imt-mines-ales.hal.science/hal-03181081v1>

Submitted on 1 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Stability parameters for mineral suspensions: Improving the dispersion of fillers in thermoplastics

Arnaud Lafaurie ^a, Nathalie Azema ^{b,*}, Laurent Ferry ^b, José-Marie Lopez-Cuesta ^b

^a Rio Tinto Alcan, Usine Vaudreuil-UPCH, Bat 301D, 1955 Boulevard Mellon, Jonquière (QC), Canada G7S 4L2

^b Centre des Matériaux de Grande Diffusion, Ecole des Mines d'Alès, 6, Avenue de Clavières, 30319 Alès Cedex France

A B S T R A C T

The study of the stability of mineral suspensions using Hansen solubility parameters (HSP) has been developed to predict and optimize the dispersion of mineral particles in thermoplastics, in order to prevent the agglomeration of particles leading to a decrease in polymer performances. In our study, this approach was applied to an innovative approach for the management of silica fume (SF) waste, consisting in using this by-product as a filler for polypropylene. The determination of the stability coefficient took into account the main dispersion parameters, which thus also provided a stability map, enabling a surface modification of the SF to be defined that makes it highly suitable for incorporation in polypropylene. We present chemical surface treatments with octadecylamine to illustrate this approach.

Keywords:

Suspension
Interface characterization
Hansen parameters
Stability
Mineral fillers
Silica fumes
Filled polymer

1. Introduction

Silica fume (SF) is a by-product of the reduction of high-purity quartz by coal or wood in electric furnaces for the production of silicon and ferrosilicon alloys. Before the mid-1970s, nearly all silica fume was discharged into the atmosphere. As a result of environmental concerns regarding the collection and landfilling of silica fume, it has now become economically viable to use silica fume in various applications.

One of the most beneficial uses for silica fume is as concrete reinforcement. Because of its small particle size, large specific surface area and high SiO₂ content, silica fume acts as a filler, improving the physical structure by occupying the spaces between the cement particles, and reacting chemically to impart far greater strength and durability to the concrete [1,2]. However, when used as a concrete additive, SF remains a rather low-added-value product.

SF producers are therefore trying to find new ways to valorise the material, as mineral fillers in thermoplastic polymers. These systems are complex, involving various interactions, such as filler-polymer, filler-filler, surfactant-filler, leading in many cases to the agglomeration of particles. The result is in a decrease in material performance (such as mechanical properties). There are therefore many studies dealing with the use of particle surface treatments to improve dispersion.

During the last decade, many studies have been carried out to develop experimental techniques enabling the analysis of filler

dispersion. Characterization can be performed off-line using image analysis methods [3] or in-line during processing using spectroscopic techniques such as infrared or ultrasonic measurement [4,5]. A more unusual approach is the development of methods for predicting filler dispersion prior to their incorporation in the polymer matrix. These methods involve the determination of filler surface characteristics and the use of specific experimental techniques such as Inverse Gas Chromatography (IGC) [6].

For many years, solubility parameters have been used to estimate the affinities between polymers and solvents. Hansen [7,8] proposed extending the concept of solubility parameters in order to characterize the surface properties of pigments, fillers or fibers and to determine their affinity for solvents or polymers. These characterizations are based on simple tests consisting in observing the suspension and/or sedimentation behavior of particles in various liquids, and defining subjective criteria for determining the “good solvents” for stable dispersions and “bad solvents” for instable dispersions. The use of Hansen solubility parameters (HSP) enables suitable surface modification of inorganic materials to optimize or improve their compatibility with organic polymers.

In this paper, we propose using Hansen cohesion parameters to predict and optimize the dispersion of SF particles, with or without chemical treatment, in a polypropylene matrix. The work focused on filler/polymer interactions, considering that filler/filler interactions are also consequently modified by the surface treatment. In a first stage, the HSP of silica fume were determined by evaluating the stability of twenty SF suspensions using a binary characterization (stable or

* Corresponding author. Tel.: +33 4 66 78 53 56; fax: +33 4 66 78 53 65.
E-mail address: nathalie.azema@ema.fr (N. Azema).

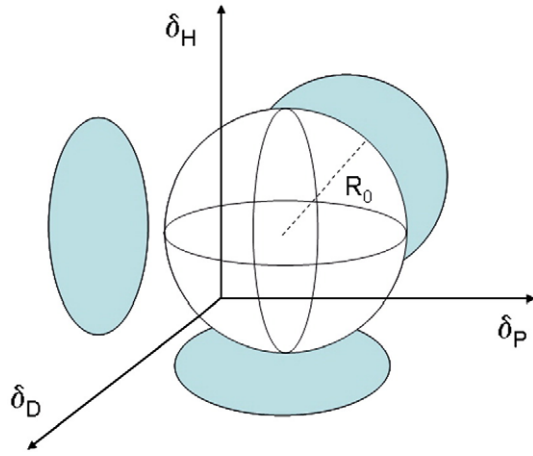


Fig. 1. A schematic representation of HSP sphere in the 3 dimensional diagram.

instable) as in the Hansen approach. In a second stage, we suggest using the speed of sediment formation and the relative terminal sediment height to obtain a continuous quantification of suspension stability. This method determined a stability map, which enabled a surface modification of the SF to be defined that made it highly suitable for incorporation in polypropylene.

2. Hansen solubility parameters

The total cohesion energy of a liquid, E , can be divided into at least three separate parts. In the three-parameter Hansen approach these parts quantitatively describe the nonpolar, atomic (dispersion) interactions, E_D , the permanent dipole–permanent dipole interactions, E_P , and the hydrogen bonding interactions, E_H (Eq. (1)):

$$E = E_D + E_P + E_H. \quad (1)$$

E can be experimentally measured by determining the energy required to evaporate the liquid, thus breaking all of its cohesion bonds in the process (Eq. (2)):

$$E = \Delta H - RT \quad (2)$$

where ΔH is the measured (or predicted) latent heat of vaporization, R is the universal gas constant, and T is the absolute temperature.

Dividing Eq. (1) by the molar volume, V , gives the respective Hansen cohesion energy (solubility) parameters (Eq. (3)):

$$E/V = E_D/V + E_P/V + E_H/V. \quad (3)$$

Since the Hildebrand solubility parameter δ ($J^{1/2} cm^{1/2}$ or $MPa^{1/2}$) is defined by $\delta = (E/V)^{1/2}$, its generalization, the Hansen solubility parameter, is obtained from Eq. (3) by Eq. (4):

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2. \quad (4)$$

Liquids with similar HSP will be miscible, and polymers will dissolve in solvents whose HSP are not too different from their own. HSP can be readily measured or calculated for liquids or polymers using different techniques.

Solubility properties can be conveniently visualized using HSP with a three-dimensional coordinate system with axes δ_D , δ_P and δ_H as shown in Fig. 1. The HSP coordinates of the solute are at the center of a sphere (spheroid) and the radius of the sphere, R_0 , indicates the maximum difference in affinity tolerable for complete solution (or other given interaction criteria) to take place. Good solvents are within the sphere, and bad ones are outside it. A simple composite affinity

parameter, the RED (Relative Energy Difference) number, has been defined according to Eqs. (5) and (6):

$$(Ra)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (5)$$

$$RED = Ra/R_0. \quad (6)$$

The subscripts are 1 for the solute and 2 for solvent, respectively. Good solvents will have RED less than 1.0. Less good solvents will have increasingly higher RED numbers because Ra will have progressively higher value than R_0 . The factor 4 in Eq. (5) in effect expands the smallest dimension of the spheroid making the figure a sphere, which improves clarity when making plots.

It has been recognized that solubility parameters can also be used to characterize many surfaces including substrates, coatings, filled polymers, pigments and fillers [9]. In this case, the term cohesion energy parameter is more appropriate than solubility parameter. There are few papers dealing with the characterization of filler surface using HSP. Shareef et al. [10] characterized the surface of metal oxide particles. Inorganic fibers have also been studied. More recently HSP have been used to probe the behavior of organophilic layered silicates [11] or fullerene [12] in a variety of solvents. The results have been used to successfully predict behavior with mixtures of solvents and polymer systems. Solubility parameters are also useful for optimizing the dispersion state of suspension by assessing the efficiency of surface treatments [13] or surfactants. Ham et al. studied the dispersion of carbon nanotubes in various solvents and aqueous surfactant emulsions using HSP [14].

3. Experimental

3.1. Materials

Polypropylene PP3400MA1 was supplied by APPRYL (France), in the form of pellets. The molecular weight of this polymer is about 250 000 g/mol and the melt flow index is 40 g/10mn.

Raw SF waste from a silicon plant (Péchiney Electrometallurgie-France) was used as filler. A TEM micrograph (Fig. 2), performed by Voreppe Research Center (France), shows the spherical shape of individual particles. The SF has a median individual particle size of 0.5 μm and a specific surface area of 20 m^2/g . Nevertheless in liquid media, particles are agglomerated, and the particle size distribution obtained, for example in water (Fig. 3), by a laser granulometer (LS230 – Beckman Coulter) presents a principal mode of about 22 μm and a maximum diameter of about 200 μm , whether or not the suspensions are ultrasonically dispersed. Obviously, the agglomeration phenomena

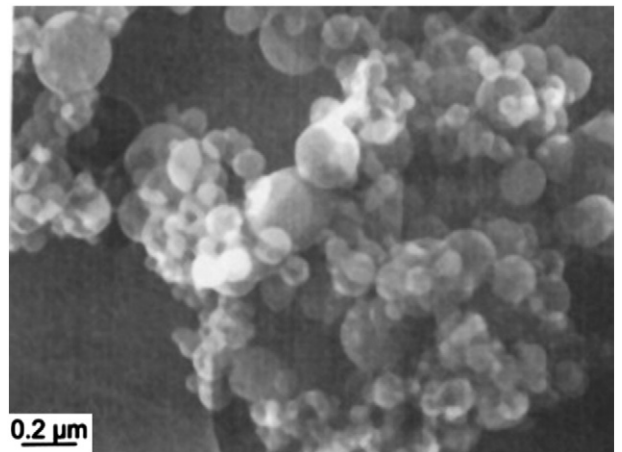


Fig. 2. Transmission electronic micrograph of silica fume.

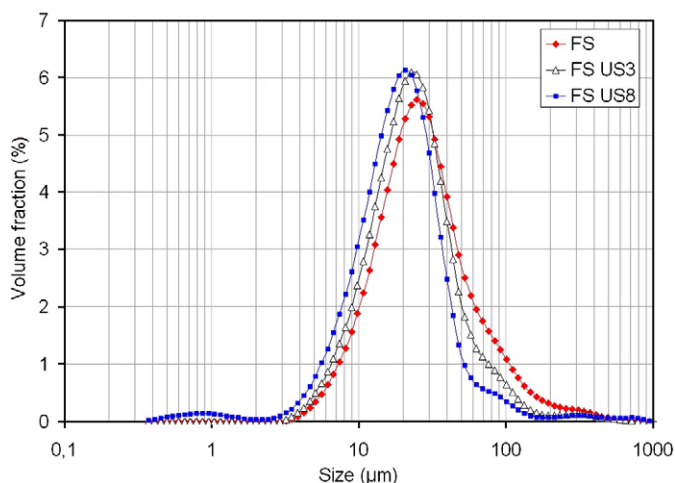


Fig. 3. Granulometric distributions of silica fume (FS) with and without ultrasonic procedure applied (US3 and US8) before analysis.

observed are highly dependent on specific interactions between liquid and silica fumes, which can vary with the chemical nature of the liquid.

Chemical treatments of the SF surface were performed using stearic acid, octadecanol (Sigma-Aldrich) and octadecylamine (Armeen® HT from Akzo Nobel). Surface treatments were carried out at 120 °C for 1 h by dry blending in a high speed mixer (DRAIS EIRICH).

3.2. Suspensions

Suspensions were prepared to obtain a weight percentage of 3% and mixed for 15 min before the sedimentation behavior was analyzed to determine the suspension stability. Various liquids were used in order to obtain sufficient variations of the Hansen solubility parameters (Table 1).

3.3. Dispersion optical analyzer

An optical analyzer (Turbiscan MA 2000) was used to determine the stability parameters of the suspensions. This instrument detects and measures modifications of concentrated and opaque suspensions. The Turbiscan carries out step-by-step vertical scanning (for 1 min) of the whole sample by a pulsed near-infrared light source ($\lambda=850$ nm) and converts the macroscopic aspects of the mixtures into two graphics [15]. Transmission and back-scattering data come respectively from the transmission detector which receives the light going across the sample (at 180° from the incident beam), and from the backscattering detector which receives the light scattered backward by the sample at 135° from the incident beam.

4. Results and discussion

4.1. Characterization and modification of surface of SF particles

The technique of diffuse reflectance infrared Fourier transform spectroscopy (DRIFT-BRUKER IFS66) was used to characterize the surface of the SF and compare it to the surface of a commercial fumed silica (Aerosil OX50) obtained by pyrogenation. DRIFT is a powerful technique for studying the vibrations of silanols at the surface of silica. Fig. 4 shows that the commercial silica exhibits a broad absorption band in the range 3000–3720 cm^{-1} , corresponding to hydrogen bonded silanols or chemically bonded water. Moreover, we observed a sharp band at 3750 cm^{-1} that can be attributed to free silanols, which predominate in this kind of silica. The presence of free silanols was correlated to the low surface roughness of fumed silica or silica fumes that prevents hydrogen bonding between neighbors' silanol groups [16].

Table 1
Hansen parameters, density and viscosity of different solvents used

Solvents (number)	Total $\langle\Delta\rangle$ (MPa ^{1/2})	$\langle\Delta\rangle_D$ (MPa ^{1/2})	$\langle\Delta\rangle_P$ (MPa ^{1/2})	$\langle\Delta\rangle_H$ (MPa ^{1/2})	Density	Viscosity (cP)
Hexane (1)	14.9	14.9	0	0	0.66	0.33
Butyl acetate (2)	17.4	15.8	3.7	6.3	0.87	0.74
Toluene (3)	18.2	18	1.4	2	0.87	0.59
Chloroform (4)	18.9	17.8	3.1	5.7	1.48	0.37
Methyl Ethyl Ketone (5) (MEK)	19.1	16	9	5.1	0.96	0.59
Tetrahydrofurane (6) (THF)	19.5	16.8	5.7	8	0.89	0.55
Chlorobenzene (7)	19.6	19	4.3	2	1.1	0.8
Acetone (8)	19.9	15.5	10.4	7	0.79	0.35
Isophorone (9)	19.9	16.6	8.2	7.4	0.92	2.6
Dioxane (10)	20.5	19	1.8	7.4	1.04	1.31
Octanol (11)	21.0	17	3.3	11.9	0.83	7.21
Butanol (12)	23.2	16	5.7	15.8	0.81	4
Nitromethane (13)	25.1	15.8	18.8	5.1	1.13	0.62
Butyrolactone (14)	26.3	19	16.6	7.4	1.29	1.92
Dimethyl sulfoxide (15) (DMSO)	26.7	18.4	16.4	10.2	1.1	1.98
Propylene carbonate (16)	27.2	20	18	4.1	1.2	2.8
Methanol (17)	29.6	15.1	12.3	22.3	0.79	0.59
Aminoethanol (18)	31.3	17	15.5	21.2	0.91	24.1
Formamide (19)	36.7	17.2	26.2	19	1.13	3.3
Water (20)	47.8	15.5	16	42.3	1	1

When analyzing the spectrum of the SF, we observed that the sharp band at 3750 cm^{-1} is also present. Therefore we concluded that the surface of SF must be close to that of fumed silica probably due to somewhat similar process conditions. The presence of free silanols, which are highly polar, at the surface of the SF indicates poor dispersability in non-polar polymers such as polypropylene. On the other hand, the presence of silanols also means that the possibility of surface modification by chemical treatment can be considered.

Taking into account the discrepancy in polarity between filler and matrix, three amphiphilic molecules were selected to modify the SF surface. The three molecules are analogous and differ only in their terminal function. The hydrophobic side of the molecules consists of a hydrocarbon chain with 18 carbon atoms whereas the hydrophilic side successively consists of alcohol, amine or carboxylic acid groups. These groups were chosen with respect to their reactivity with silanols.

Alcohols are expected to react with silanols by etherification, and this method is used to quantify silanol density [17]. However, the grafting of alcohols depends on their steric hindering, thus on the length of the alkyl chain. Amines are also likely to interact with silanols. According to Iler [16], amines and weak bases interact via hydrogen bonds whereas amines and strong bases lead to the formation of an ammonium salt. Finally, carboxylic acid can also be adsorbed on the silica surface by hydrogen bonding. However, in the case of fatty acids, dimerisation may occur, leading to a decrease in the grafting efficiency.

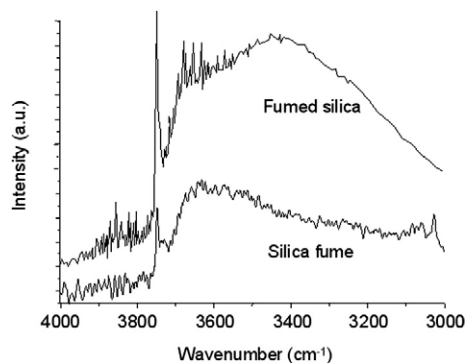


Fig. 4. Diffuse reflectance infrared spectra of silica fume and industrial fumed silica.

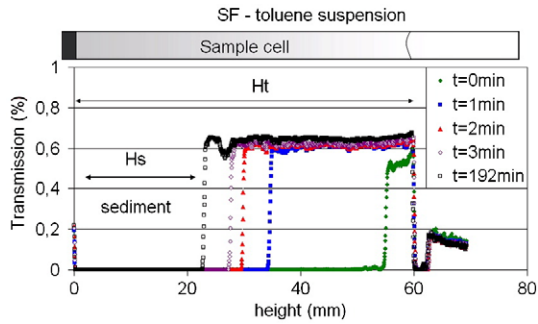


Fig. 5. Example of transmission spectra in the clarifying zone.

If we consider that the intensity of the 3750 cm^{-1} band, in the DRIFT spectrum, is proportional to the free silanol content, we can thus calculate the free silanol density at the surface of the SF. The free silanol density of fumed silica, determined by the supplier, is 2.4 nm^{-2} , therefore, according to the infrared peak ratio, the free silanol density of the SF should be 1 nm^{-2} .

If we assume that surfactant molecules are attached to SF by interaction between the free silanols and the functional groups (amine – 255 g/mol , alcohol – 256 g/mol , acid – 270 g/mol) we can then estimate the minimal surfactant content necessary to involve all the free silanols using the relation:

$$\text{surfactant content} = \frac{S_{\text{BET}} d_{\text{OH}} M_{\text{surf}}}{N_A} \quad (7)$$

where S_{BET} is the specific surface area of SF (m^2/g), d_{OH} is the free silanol density (m^{-2}), M_{surf} the molar mass of the surfactant (g/mol) and N_A Avogadro's number. Since the molar mass of the 3 surfactants are very close, the surfactant contents are very similar, close to $0.85\text{ wt.}\%$.

If we now assume that the whole SF surface can be covered by surfactant molecules, whatever the free silanol density, the minimal surfactant content w_{surf} thus becomes:

$$w_{\text{surf}} = \frac{S_{\text{BET}} M_{\text{surf}}}{S_{\text{surf}} N_A},$$

where S_{surf} is the surface occupied by a surfactant molecule when disposed perpendicular to the surface of the particle (0.219 nm^2) [18,19]. This last calculation leads to a surfactant content of ca. $4\text{ wt.}\%$. Considering both hypotheses, the surfactant content was varied from 0.5 to $4\text{ wt.}\%$ in the subsequent experimental steps.

4.2. Study of suspension stability

The suspension stability was studied in organic and aqueous media (Table 1) in order to determine the compatibility of the SF surface with organic polymers, in particular polypropylene, using Hansen cohesion parameters. The stability can be evaluated correctly by two parameters: the relative terminal sediment height or the speed of sediment formation. The interest of studying the resulting sediment rather than clarification or sedimentation speed is conditioned by the extent of variations in the density and viscosity of the solvents used (respectively from 0.66 to 1.48 and from 0.33 to 24.11 cP) which could consequently influence the sedimentation speed of particles in suspension. It should be specified that there was no adherence of particles to the glass surface of the analysis cell, and that no gel formation was observed.

The Turbiscan optical analyzer (MA 2000) was used to measure these parameters and track the destabilization process of the concentrated suspensions. A volume of about 7 ml of suspension, prepared beforehand, was introduced in the sample cell.

Fig. 5 shows an example of a transmission graph corresponding to the sedimentation process in function of time of the SF suspension in

toluene. The sediment height (H_s) is clearly identified at the bottom of the sample cell (represented on the top of Fig. 5), and in the same way, the total height of the suspension (H_t) can be determined at the meniscus. The relative terminal sediment height (TSH) can be estimate using the following relation:

$$\text{TSH} = (H_s/H_t) * 100. \quad (9)$$

4.2.1. Liquid/solid interactions in suspensions: the Hansen solubility parameter (HSP) method and its limitations

As mentioned above all solvents presented in Table 1 can be located on a three dimensional diagram with axes δ_D , δ_P , δ_H but the more usual representation is a two dimensional plot (δ_H versus δ_P , because δ_D is high and almost constant – 15 to 20) as shown on Fig. 6 for the solvents used in this study.

The HSP of silica fumes can also be determined by qualitative sedimentation experiments and presented using the same two dimensional plots. The methodology is based on the binary classification of suspensions created in various liquid media: stable dispersion (take value 1) or instable dispersion (take value 0). According to this classification, the HSP sphere of the powder, with minimal radius and containing a maximum of good solvents (1) and a minimum of bad solvents (0), is searched using an iterative method developed by Hansen (described p19–20 in reference [7]). Fig. 7 was plotted in this way for untreated silica fume (including or not including the point for sedimentation in water) and silica fume treated with 1 or $2\text{ wt.}\%$ of octadecylamine.

It can be noticed that considering water as a polar liquid in the choice of solvents, increase the characteristics of the HSP sphere of the silica fumes because of the particularly high value of δ_H ($\delta_H = 42.3\text{ MPa}^{1/2}$) compared to other solvents. This high value of δ_H leads to high radius values as it's shown in Fig. 7, and by consequence leads to Hansen parameter values (Table 2). Nevertheless, independently of the case selected (considering water or not) we can conclude that silica fumes present high δ_D and δ_H parameters, which indicates high surface polarity and the affinity to create hydrogen bonds with the suspension liquid due to the presence of free silanols (see paragraph 4.1). Moreover, these surface properties lead to low compatibility with organic solvents such as hydrocarbons or chlorinated solvents with low hydrogen contributions (chloroform and chlorobenzene).

Finally, the octadecylamine surface treatments lead to a significant decrease in the polar and hydrogen interactions of the silica fumes (Table 2) indicating a hydrophobic property. This surface reactivity is explained by the capacity of silanol groups to create hydrogen or covalent bonds with the surfactant.

The methodology used in the above section highlights the influence of the treatment but cannot quantify it and does not reveal different sedimentation behaviors. We therefore also aimed to develop a new quantitative approach taking into account two parameters describing

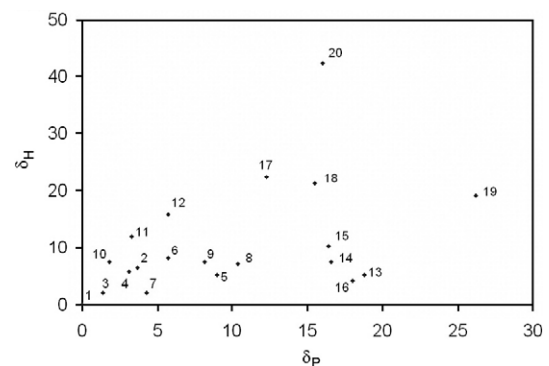


Fig. 6. Solvents (the corresponding numbers are indicated in Table 1) studied in the δ_H ($\text{MPa}^{1/2}$) versus δ_P ($\text{MPa}^{1/2}$) plot.

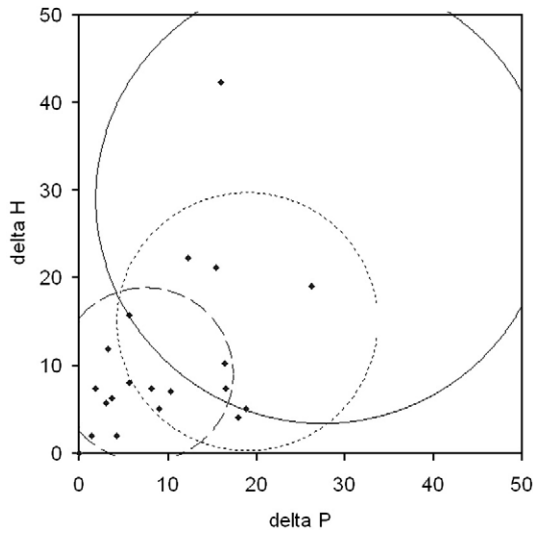


Fig. 7. Representation in the δ_H (MPa^{1/2}) versus δ_P (MPa^{1/2}) plot, of Hansen parameters of silica fumes, untreated (dotted line), untreated including water (continuous line) and treated by octadecylamine at 1 and 2 wt.% (broken line).

the sedimentation behavior and the dispersion state of the suspension studied: the clarifying speed and the relative terminal sediment height.

4.2.2. A quantitative approach to suspension stability

This new approach consists in obtaining a stability coefficient broadly taking into account all the parameters of the suspension such as solvent density, solvent viscosity, particle/liquid interactions, agglomeration state of particles, concentration of solid, etc. This stability characterization is not simply a binary characterization with a qualitative criterion (0 or 1). It determines a quantitative stability coefficient (S_i) which can take any value ranging between 0 and 1 (relation 10). This methodology is described in the following paragraphs and based on the measure of destabilization kinetic of each suspension used for the silica fume HSP determination.

The aim is not only to quantify the dispersion of silica fumes treated in different ways but also to show the interest of this original approach. Only the chemical surface treatments with octadecylamine are presented in this study.

Starting from the clarifying speed, which is obtained from the transmission profiles (Fig. 5) during the sediment formation process as shown in Fig. 8, an angle α can be determined from the variation of sediment height versus time (Fig. 8).

The stability coefficient values are calculated by the relation:

$$S_i = \sin\left(\alpha \frac{d_{SF} - d_L}{\eta}\right) \quad (10)$$

with

$$\alpha = \arctan\left(\frac{t}{100 - TSH}\right) \quad (11)$$

where η is the solvent viscosity, d_{SF} and d_L respectively the silica fumes and liquid densities.

Table 2
Hansen parameters of silica fume treated or not by octadecylamine

Silica fume	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})
FS (with water considered)	18	27.5	29
FS (without water considered)	17	19	15
FS treated with octadecylamine (1 or 2 wt.%)	18.5	7.5	9

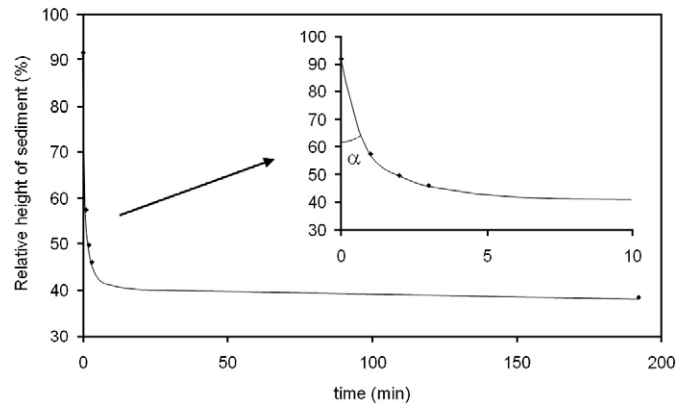


Fig. 8. Determination of angle α from the curve of sediment formation.

In consequence, the S_i coefficient tends respectively towards 0 or 1 when α tends towards 0 or 1, corresponding to an unstable or stable suspension.

These data can be clearly resumed on a stability map with isoproperty lines. This concept enables several stability zones to be obtained, rather than a single sphere.

Fig. 9 shows stability maps for SF in two dimensional plots, δ_H versus δ_P . These results are in good agreement with the previous results. The stability of suspensions is obtained for values of δ_H and δ_P higher than 15 and 10 MPa^{1/2} respectively, showing the high reactivity and polarity of the silica fume surface.

In order to estimate the HSP of silica fumes, the average localization (center of gravity) of each HSP of every solvent used was calculated as follows:

$$\frac{\sum S_i \times \delta_i}{\sum S_i} \quad (12)$$

S_i is the stability coefficient of SF in the solvent i , and δ_i the HSP components of solvent i . These three values are taken as the HSP of the silica fumes and represented by the red point on the stability map (Fig. 9). For the silica fumes, if the water is not taken into account, the results obtained are: $\delta_D = 17$, $\delta_P = 12.5$ and $\delta_H = 15$ MPa^{1/2} (Table 3). As mentioned above, these values can be higher if water is taken into consideration.

Independently of the method, we can note, as mentioned in Hansen works [8], that it is necessary not only to use good solvents but also a sufficient number of solvents in order to obtain a good estimate of the stability parameters of a given solid. Conversely, the method may determine erroneous values.

Fig. 10 shows the influence of 0.5, 1 and 4 wt.% of octadecylamine on the stability map. The evolution of the shape of stability zones in

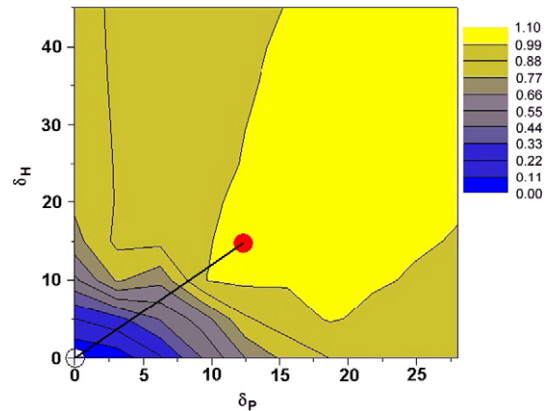


Fig. 9. Stability map for SF in the two dimensional plot δ_H (MPa^{1/2}) versus δ_P (MPa^{1/2}).

Table 3
Hansen parameters of silica fume treated or not by octadecylamine

	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})
FS (without water considered)	17	12.5	15
FS+0.5%	17.1	10.3	10.3
FS+1%	17	6.9	7.3
FS+4%	17	7.9	8.9

function of percentage of surfactant clearly exhibits the hydrophobic behavior obtained, since the hydrogen and polar contributions of the Hansen parameters decrease sharply. So, the optimum treatment is about 1 or 2 wt.% of octadecylamine. If this percentage increases, the amines are free in solution with amine groups oriented towards the liquid phase, leading to the increase in the δ_H of the silica fumes.

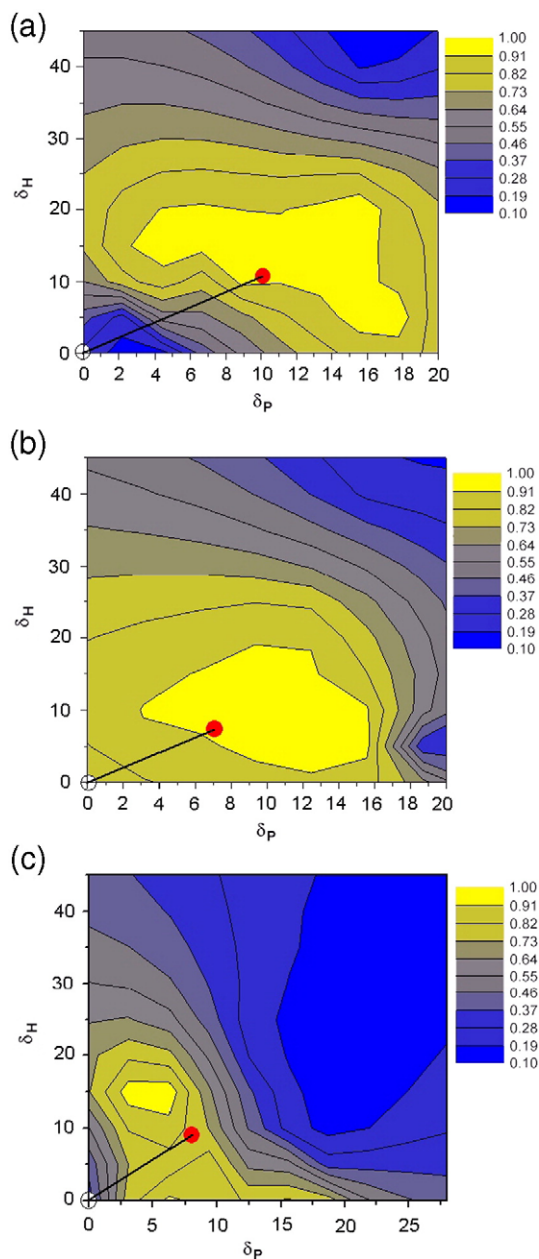


Fig. 10. Stability maps for SF treated with 0.5 (a), 1 (b), 4 (c) wt.% of octadecylamine. At zero the barycentre of PP Hansen sphere and the other points (red) the barycentre of stability zone of SF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

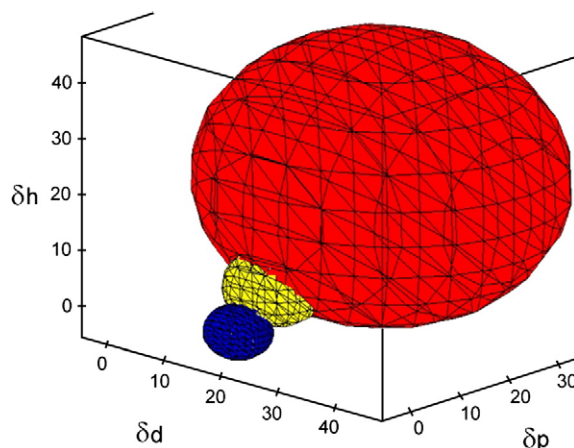


Fig. 11. HSP of PP (small sphere), of silica fume with octadecylamine treatment (medium sphere), and without treatment (big sphere).

The values of Hansen solubility parameters obtained are summarized in Table 3. They show that the results for the treated and untreated SF are in good agreement with the previous data (Table 2) obtained by a qualitative approach and one can conclude that this new quantitative approach correctly accounts for the modifications of the silica fume surface.

4.2.3. Formulation of a filled thermoplastic polymer using Hansen solubility parameters

The study of the dispersion silica fume in various liquids provided indirect information concerning surface properties and their modifications. One application is to predict filler dispersion in a polymer matrix, polypropylene, to be precise, with the aim of improving its mechanical properties, this increase being principally due to increased compatibility of the SF surface with the polypropylene.

One method of predicting compatibility consists in comparing the Hansen parameters of SF to those of the polymer matrix. Fig. 11 shows the Hansen spheres of silica fume with and without octadecylamine treatments, together with that of polypropylene. On the one hand, one can note that there is no overlap between the polypropylene and SF spheres, indicating the incompatibility of the SF with this matrix. On the other hand, the sphere of the SF treated with octadecylamine intersects the PP sphere, which indicates compatibility between the filler surface and the matrix.

The two dimensional plane stability maps (δ_H versus δ_P) represented in Figs. 9 and 10, show two barycenters: for polypropylene (at

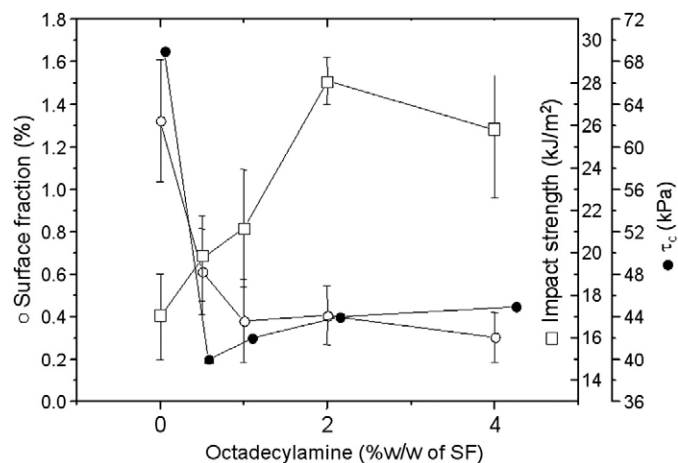


Fig. 12. Correlation of filler dispersion in polypropylene with impact resistance and image analysis.

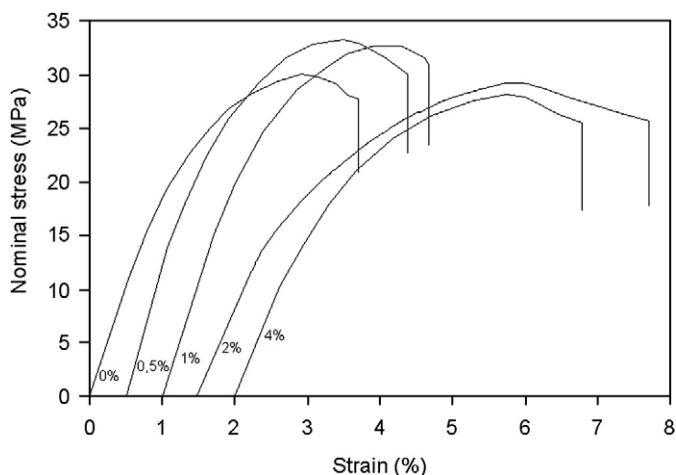


Fig. 13. Influence of SF surface modification by octadecylamine on stress-strain curves of PP-SF (70/30) composites. Curves were shifted along the strain axis (increments 0.5%) for clarity.

zero) and the other corresponding to the treated or untreated SF. The distance between these two points can be correlated to the degree of filler/matrix compatibility. The lowest distance is obtained for the 1% octadecylamine surface treatment.

The dispersion of the chemically modified SF in the PP was assessed by image analysis and ultrasonic characterization. The SEM images show that there is an improvement in dispersion whatever the treatment. Fig. 12 represents the fraction of particles or aggregates larger than 3 μm in function of octadecylamine content. It should be noted that the size of the aggregates decreases very rapidly with surfactant content. Above 1% octadecylamine, there is no further improvement in the dispersion state of the particles in the matrix taking into account the accuracy of the measurement method.

Complementary characterization of the dispersion was performed using in-line ultrasonic measurements. The results, presented in a previous paper [7], showed that the attenuation of the ultrasonic waves decreases with increasing surfactant content, highlighting the reduction of aggregate size in the polymer. A minimal value is obtained with 2% octadecylamine. In the dynamic mode, it was noted that the evolution of attenuation of composites containing SF treated with various amounts of surfactant depends on the applied shear stress τ . This result reveals that the size of interacting aggregates is modified by octadecylamine. The critical disaggregation shear stress τ_c is considerably reduced compared to untreated SF-PP composites. From 2% of fatty amine coating, τ_c is almost constant (Fig. 12). Results of ultrasonic characterization are in good agreement with those of image analysis.

Fig. 13 shows the evolution of tensile curves of PP-SF (70/30) composites when the SF surface is chemically modified by various contents of octadecylamine. The results indicate that at low surfactant content (0.5 and 1%) the yield stress is increased, suggesting that filler-matrix interactions are enhanced and dispersion is improved. Above 1%, addition of fatty amine leads to no further increase in the yield stress. Elongation at break increases but, in parallel, the Young modulus decreases. These results are corroborated by impact resistance values (Fig. 12). The toughness increases by a factor of 2 when octadecylamine content increases from 0 to 2%. Above 2%, we observe stagnation and even a slight decrease in toughness.

Above 2%, the SF surface is assumed to be entirely covered by a monolayer of surfactant. The excess of surface modifier may form a second layer with opposite orientation of molecules (polar end turned to the outside). This effect is likely to reduce the dispersive efficiency of the chemical treatment. Increasing surfactant content may result in a multilayer coating that will create a soft interface between SF and PP. This phenomenon could be the cause of the decrease in rigidity

observed at high surfactant content. Another hypothesis could be the migration of excess surfactant through the polymer matrix, inducing a plasticizing effect.

5. Conclusion

The re-use of silica fumes as fillers in polypropylene requires surface treatments to modify the surface, which presents highly polar free silanols possibly leading to poor dispersability in non-polar polymers. It has been shown in this study that Hansen solubility parameters could be highly interesting for predicting the possible dispersion through the polymer of fillers with or without surface treatments. Moreover, the definition of a stability coefficient (S_i) which can take any value ranging between 0 and 1 enables a quantitative approach to be developed, based on solvent viscosity, and particle and liquid densities. As an illustration, treatments with octadecylamine to improve the dispersion of silica fumes in polypropylene were investigated using this approach. Comparison between the Hansen solubility parameters of the treated silica fumes and those of the polymer matrix showed that compatibilization had been achieved.

The improved impact resistance of the filled polypropylene due to the surface treatment confirmed the appropriate selection of the surface agent as well as the interest of this new quantitative approach.

References

- [1] M. Mazloom, A.A. Ramezani-pour, J.J. Brooks, Effect of silica fume on mechanical properties of high-strength concrete, *Cement and Concrete Research* 26 (2004) 347–357.
- [2] G.A. Rao, Investigations on the performance of silica fume-incorporated cement pastes and mortars, *Cement and Concrete Research* 33 (2003) 1765–1770.
- [3] L. Avérous, J.C. Quantin, A. Crespy, Determination of the microtexture of reinforced thermoplastics by image analysis, *Composites Science and Technology* 58 (1998) 377–387.
- [4] T. Rohe, W. Becker, S. Kölle, N. Eisenreich, P. Eyerer, Near infrared (NIR) spectroscopy for in-line monitoring of polymer extrusion processes, *Talanta* 50 (1999) 283–290.
- [5] L. Häider, J. Tatibouët, A. Lafaurie, L. Ferry, In-line ultrasonic characterization of shear dispersion processes of polydisperse fillers in polymer melts, *Journal of Physics: Condensed Matter* 14 (2002) 4943–4961.
- [6] E. Fekete, J. Móczó, B. Pukánszky, Determination of the surface characteristics of particulate fillers by inverse gas chromatography at infinite dilution: a critical approach, *Journal of Colloid and Interface Science* 269 (1) (2004) 143–152.
- [7] C.M. Hansen, *Hansen Solubility Parameters: A User's Handbook*, CRC Press, Boca Raton, 2000.
- [8] C.M. Hansen, *Hansen Solubility Parameters: A User's Handbook (2nd Ed.)*, Lavoisier, 2007.
- [9] C.M. Hansen, Polymer additives and solubility parameters, *Progress in Organic Coatings* 51 (2004) 109–112.
- [10] K.M.A. Shareef, M. Yaseen, M. Mahmood Ali, P.J. reddy, Suspension interaction of pigments in solvents: characterization of pigment surfaces in terms of three-dimensional solubility parameters of solvents, *Journal of Coatings Technology* 58 (35) (1986) 733–737.
- [11] Burnside S.D., "Synthesis and characterisation of polymer matrix nanocomposites and their components", PhD thesis, Cornell University, (1997).
- [12] C.M. Hansen, A.L. Smith, Using Hansen solubility parameters to correlate solubility of C60 fullerene in organic solvents and in polymers, *Carbon* 42 (2004) 1591–1597.
- [13] J.L. Gardon, J.P. Teas, Solubility parameters, in treatise on coatings, in: R.R. Myers, J.S. Long (Eds.), *Characterisation of Coatings: Physical Techniques, Part III, vol. 2*, Marcel Dekker, New York, 1976, chap. 8.
- [14] H.T. Ham, Y.S. Choi, I.J. Chung, An explanation of dispersion states of single-walled carbon nanotubes in solvents and aqueous surfactant solutions using solubility parameters, *Journal of Colloid and Interface Science* 286 (2005) 216–223.
- [15] O. Mengual, G. Meunier, I. Cayre, K. Puech, P. Snabre, Characterisation of instability of concentrated dispersions by a new optical analyser: the Turbiscan MA 1000, *Colloids and surfaces – A: Physicochemical and Engineering Aspects* 152 (1999) 111–123.
- [16] R.K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, 1979.
- [17] J.B. Donnet, A. Vidal, E. Papirer, M.J. Wang, Modification of silica surfaces by grafting of alkyl chains. I. Characterization of silica surfaces by inverse gas-solid chromatography at zero surface coverage, *Chromatographia* 23 (1987) 121–128.
- [18] S. Acharya, D. Bhattacharjee, G.B. Talapatra, Monolayer characteristics and spectroscopic study of benz(b)fluoranthene assembled in Langmuir Blodgett films mixed with stearic acid, *Journal of Physics and Chemistry of Solids* 64 (2003) 651–657.
- [19] Glenn O. Rubel, Dependence of hexadecanol monolayer cohesion on subphase acidity, *Journal of Physical Chemistry* 91 (1987) 2103–2106.