Quantifying Surface Properties of Silica Particles by Combining Hansen Parameters and Reichardt’s Dye Indicator Data

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To obtain quantitative understanding of the effects of a chemisorbed organic modification on the surface of particles, the use of Reichardt’s dye (RD) and Hansen solubility parameter (HSP) is discussed, whereby the S should be understood in terms of “similarity” rather than solubility as dispersibility is in focus. Silica nanoparticles modified to different extents with a medium chain silane including completely hydrophilic and hydrophobic particles are chosen. During spray-drying such particles form fully dispersible micro-raspberry superstructures. After qualitative estimations of the particles’ polarity based on measuring both immersion time and ability of modified particles to stabilize oil–water emulsions, surface properties are quantified by HSP and RD. With increasing hydrophobicity, i.e., increasing amount of silane at the surface, all three contributions to HSP change. At the same time, RD analysis reveals that the normalized solvent polarity parameter decreases progressively. HSP and RD analysis are in good agreement, giving strong confidence on each method applied individually. This work demonstrates that after noticeable attempts for combined solubility parameters in case of molecules, carbon allotropes, and gelators, such studies can be extended toward functional (nano)particles and that a full picture of particle surface properties is possible via the combination of different, quantitative techniques.

1. Introduction

Despite decades of progress in nanoparticle research, in particular the characterization of nanoparticle surfaces remains a major challenge today. For many applications, it is essential to modify nanoparticle surfaces with functional groups to render their compatibility with their environment, e.g., with polymer matrices in the case of polymer nanocomposite materials.[1–3] Nanoparticles in such polymers act as reinforcing fillers,[3–5] which play an important role in for example vehicle tyre technology. However, the well-controlled modification of nanoparticle surfaces is not only very beneficial for polymer composites, it is also crucial for the stabilization of suspensions and emulsions. For the latter, silica nanoparticles are particularly suitable to stabilize so-called Pickering emulsions.[9,10] The stability as well as the type of the formed emulsion (oil-in-water (o/w) or water-in-oil o/w) depends crucially on the polarity of the nanoparticles.[11–15]

To quantify the surface polarity of functional nanoparticles, advanced characterization is indispensable. Analytical techniques such as infrared spectroscopy or Raman spectroscopy are used to determine the presence of organic groups in general.[16,17] To quantify the amount of organic moieties in a nanoparticle sample, differential thermogravimetric analysis (TGA), ideally coupled to mass spectrometry, can be applied.[1,4] Furthermore, (solid state) nuclear magnetic resonance (NMR) spectroscopy is a powerful method, which is most often used to add information on the mode of bonding of molecules on nanoparticle surfaces,[18–21] although it should be noted that beyond obtaining only this, it was also demonstrated that NMR is capable of acting as a tool to quantify functional groups[22,23] or even to estimate particle size.[24] The combination of small angle X-ray and neutron scattering could become an important link between the molecular picture and wetting/dispersibility, as it allows to analyze organic ligand shells around nanoparticles in situ.[25] However, such knowledge on surface chemistry on the molecular level cannot
Herein, we demonstrate how the combination of two quantitative methods for surface modified inorganic nanoparticles, namely Hansen parameters and RD, can be combined with each other and how studying both approaches enables a mutual validation of each individual approach. To show the strength of this combination for the resolution of surface functionalities, we chose so-called nanostructured silica-based micro-raspberry particles as an interesting model system. It can be tuned over a wide range of polarity and obtained by spray-drying in large quantity with the resulting micrometer sized powder composed of modified nanoparticles being easy to handle and readily redispersible by mechanical activation.\(^{[40]}\)

## 2. Surface Property Quantification

### 2.1. Hansen Parameters

A frequently used approach to assess the compatibility between different molecular compounds, in particular polymers and solvents, is the so-called HSP.\(^{[41]}\) Historically, Hansen divided another solubility parameter, the Hildebrand parameter (HP), which goes back to the energy of vaporization and thus to the integral amount of all interactions within a molecule, into three parts. These are dispersion interactions, \(\delta_D\), describing the contribution of nonpolar London interactions, polar interactions, \(\delta_p\), describing the interactions of two permanent dipoles, and hydrogen bonds, \(\delta_H\), accounting for the ability of electron exchange based on the acid and base concept of Lewis. This allows creation of a 3D parameter space with three distinct coordinates. Then, like in any approach dealing with solubility parameters, HSP are based on the paradigm “like dissolves like,” i.e., the solubility of the substance of interest is investigated in a defined set of probe liquids with known HSP. Thus, by challenging the target molecule in question with different probe liquids with known HSP coordinates and distinguishing them into “good” (dissolves the target molecule) and “poor” (does not dissolve the target molecule), solubility regions within the 3D interaction space are identified. Finally, by drawing a sphere around all “good probe liquids,” the center of the sphere gives the HSP of the unknown target molecule. Once determined, suitable solvents are identified based on their HSP coordinates. The closer the HSP of the chosen solvent and the examined compound, the higher the solubility and vice versa.

In principle, as shown by others and Süß et al.\(^{[42–50]}\) the approach is transferable to (nano)particles although at this point it has to be mentioned that when moving from molecules to disperse systems, a boundary is crossed. Particulates are usually thermodynamically unstable because of the inherent phase boundary, i.e., interface. Only for distinct cases of small nanoparticles with hard sphere behavior, the integral Gibbs energy of solvation can become \(<0\) \(\text{kJ}\).\(^{[51]}\) Hence, as the thermodynamic basis of HP is left when transferring the approach to colloidal systems, the term Hansen dispersibility parameter (HDP) was suggested whenever particles are discussed,\(^{[47]}\) or, at least the \(S\) in HSP should be understood in terms of “similarity” instead of solubility.\(^{[52]}\)

Regarding the measurement of nanoparticles, Süß et al.\(^{[47]}\) introduced recently a new, completely objective determination...
of HDP.[53] In brief, a standardized measurement and evaluation procedure for discrimination of probe liquids into "good" (i.e., is a suitable dispersion medium) and "poor" (i.e., is not a suitable dispersion medium) was developed using analytical centrifugation (AC) and an algorithm that is based on the step-wise switch on of good liquids. Validation was done by predicting the dispersibility of carbon black in untested liquids and liquid mixtures. Thus, by combining HDP with a standardized determination procedure, the surface properties of particles become quantitatively accessible by distinct values of $\delta_D$, $\delta_I$, and $\delta_H$ in an easy and accurate way.[47] Once determined properly, these could be potentially linked to the previously discussed surface chemistry on the molecular level allowing to address formulation as the true multiscale issue it is. Although this is highly challenging, recent developments on intensely studied model systems like ZnO do give some hope that this can be realized.[54–60]

2.2. Reichardt’s Dye

For liquids, another method to determine polarity exists, namely, the employment of solvatochromic indicators.[61–64] The working principle is as follows: The indicator, usually a dye, changes its color depending on the polarity of its immediate molecular environment. The solvatochromic effect, which is for some dyes still in the focus of nowadays research,[65,66] can be observed with increasing polarity, or as positive solvatochromism with a bathochromic shift (red shift). A widely used indicator is Reichardt’s dye, RD (Figure S1a, Supporting Information). RD exhibits a medium-dependent charge transfer transition in the visible region of the light spectrum. Polar liquids like methanol (MeOH) stabilize the molecular electronic ground state more than the excited state leading to an increased transition energy.[67] The RD exhibits one of the largest known negative solvatochromic effects (a blue shift with increasing polarity). The color of this dye ranges from green in nonpolar liquids (acetone) to red in polar liquids (methanol) (Figure S1b, Supporting Information). RD is defined as the molar electronic transition energy of the betaine dye 30 in accordance with the longest-wavelength UV/Vis absorption maximum of RD. The molar electronic transition energy of the betaine dye 30 ($E_{\text{T}}(30)$) is defined as the molar electronic transition energy of the betaine dye 30 in accordance with the longest-wavelength UV/Vis absorption maximum of RD under standard conditions (Equation (1)).[67]

$$E_{\text{T}}(30) = \frac{hc\tilde{v}_{\text{max}}N_A}{28591/\lambda_{\text{max}}(\text{nm})^4}$$

For a much easier handling, the normalized $E_{\text{T}}^N$ value was introduced (Equation (2)).[67] Herein, tetramethyilsilane (TMS) ($E_{\text{T}}(\text{TMS}) = 30.7$) was used as an extreme nonpolar reference liquid and water ($E_{\text{T}}(\text{water}) = 63.1$) was used as the extreme polar reference liquid. With these limits the polarity scale ranges from 0 for TMS to 1 for water

$$E_{\text{T}}(\text{solvent}) = \frac{E_{\text{T}}(\text{solvent}) - E_{\text{T}}(\text{water}) - 30.7}{E_{\text{T}}(\text{water}) - E_{\text{T}}(\text{TMS})} = 32.4$$

where $h$ is Planck constant, $c$ is the speed of light, $N_A$ is Avogadro constant, $\tilde{v}_{\text{max}}$ is the frequency, and $\lambda_{\text{max}}$ the wavelength of the maximum of the longest wavelength, intramolecular charge transfer $\pi-\pi^*$ absorption band of RD.

In fact, RD was already further developed from molecules to determine the surface polarity of particles,[68–72] but it is still far from being a standard method for the general characterization of particles, especially for particles with different modification degrees. Thus, proving its applicability to complex nanoparticles and comparing the results to another, independent technique is seen as a major step forward in accessing particulate surface properties.

2.3. Micro-raspberry Particles as Model System

The idea of using the silica micro-raspberries was to create a nanoparticle system with adjustable properties, which is very easy to handle and could be used for different applications. Starting with silica nanoparticles in suspension, the particles were modified with silane and afterward spray-dried to an easy to handle powder (Figure S2, Supporting Information). This system is ideal to study the characterization potential of a combined HDP and RD analysis: Starting with the surface modification at single nanoparticle level, the approach first allows for a careful tuning of the degree of silanisation on the nanoparticle surfaces. Second, the drying approach gives a powder at hand which makes studies of dispersion behavior in different solvents easy. Without drying, one would always face the problem of remaining traces of solvents when particles are transferred from one solvent to another. Using a powder as starting point overcomes this problem. The silane modification prevents irreversible hard agglomeration as demonstrated earlier.[48] We chose silane octyltriethoxysilane (OCTEO) as ligand which is able to gradually change the polarity of the nanoparticle surfaces from hydrophobic to hydrophilic (with increasing amounts of silane). Despite OCTEO being a rather “simple” surface modifying agent, it has a great impact on the later properties of the modified particles regarding dispersibility or reinforcement of a matrix such as in an elastomer composite.[73] Here, the octyl groups transform the hydrophilic Si-OH groups on the surface of the primary silica nanoparticles into hydrophobic, hydrocarbon covered surfaces. Thus, by controlling the degree of silane coverage, the polarity of the primary particles can be gradually adjusted.[40] It should be noted that this study was carried out using a triethoxysilane, despite being aware that these silanes might undergo mutual condensation among each other and to some extent might complicate the analyses and interpretation. However, we think that for application relevance, it is important to try to establish a holistic picture for nanoparticles modified with commonly used silanes. To the best of our knowledge, the overwhelming majority of research and also development and application is done with silanes which have three reactive groups (triethoxy or trimethoxy). Moreover, for the time being any particle surface is ill-defined due to the inherent complexity of multiple functionalities, (surface) ions and atoms and adsorbed solvent molecules which are all interacting i) amongst each other, ii) with the particle core and iii) with the continuous phase. Therefore,
we selected such a well-explored silane for our studies and did not choose, e.g., monoalkoxysilanes.

Herein, with the combination of HDP and RD, two approaches are at hand that potentially allow for a quantitative determination of the nanoparticles’ surface polarity across different laboratories. To the best of our knowledge this is the first time this was done for complex, spray-dried particulates and could, ultimately and on the long-term run, pave the way for predictions on the dispersibility of nanoparticles in solvents or polymer matrices.

3. Results and Discussion

3.1. Strategy

In this work, an approach for characterizing the particulate surface properties of silica-based nanostructured micro-raspberry particles is developed by combining different analytic methods. Starting with simple characterization methods like Fourier-transform infrared spectroscopy (FTIR) and TGA, which can provide a first positive indication of surface modification in general, liquid tests follow. Then, to get a much deeper understanding of the surface modification of the particles, advanced methods like HDP and RD are considered in combination. Finally, these two methods are validated against each other to gain the best possible insights regarding the changes in surface properties upon modification.

3.2. Simple Methods

3.2.1. Liquid Tests

The degree of redispersibility strongly depends on the polarity of the nanoparticle surface and thus on the degree of silane modification relative to the type of liquid or matrix the particles are dispersed in. In this study, silica nanoparticles with different degrees of OCTE0 surface modification (completely modified 1, partly modified 2/3, 1/2, 1/3, 1/5, 1/10 of the surface of the primary nanoparticles compared to completely modified and nonmodified, i.e., 0) were used. The silane is hydrolyzed and can subsequently covalently bind to the silica surface via condensation. Qualitative evidence of silane on the nanoparticle surfaces was conducted by FTIR measurements and reported before by Stauch et al. (Figure S3, Supporting Information).[

Compared to nonmodified particles, new peaks between 3000 and 2800 cm$^{-1}$ were found for modified particles, which can be assigned to the CH$_2$ and CH$_3$- stretching modes from the OCTE0 molecules bound to the silica surface. These peaks are more pronounced for larger amounts of OCTE0 at the nanoparticle surface, which was also confirmed from the results of TGA, also reported before by Stauch et al. (Figure S4, Supporting Information).[73]

For all systems with silane modification, two main stages of weight loss were observed. The weight loss at low temperatures up to 250 °C is attributed to the evaporation of water physically adsorbed to the particle surface. The second weight loss region in the temperature range 250–900 °C results from the condensation of silanol groups to siloxane groups and the decomposition of organic moieties. Additionally, the weight loss of organic moieties increases with the amount of OCTE0. These measurements give a first insight to the extent of surface modifications of the silica nanoparticles which will affect their surface properties.

To obtain further information especially on the behavior of the surface polarity, liquid tests were conducted (Figure S5, Supporting Information). In a first test series, the modified nanoparticles were dispersed in water and toluene separately. Completely (1) and also partly modified (2/3, 1/2, 1/3, 1/5, 1/10) particles could not be dispersed well in water, but dispersed well in toluene (Figure S5a,b, Supporting Information, top row). This can be explained by the increase in hydrophobicity of the primary nanoparticles with increasing silane coverage and vice versa. After spray-drying of the nanoparticles, the effect becomes even more pronounced, since the hydrophobic nanostructured micro-raspberry particle powders float on the water surface, whereas the hydrophilic particles enter water spontaneously (Figure S5a, Supporting Information, middle row). Subsequently, the particles were additionally treated with ultrasound to test the surface modification under mechanical stress (Figure S5a,b, Supporting Information, upper row). Particularly the micro-raspberries consisting of partly modified nanoparticles show differences compared to the picture obtained after having only shaken the samples. In case of 1/3-modified nanoparticles, the powder can be partly dispersed in water, due to bursting of the micro-raspberries during ultrasonic treatment. This indicates that the individual nanoparticles apparently behave more hydrophilic than the micro-raspberry particles, which could be also seen from Figure S5a,b top row (Supporting Information). In the case of 1/3-modification there should be 33% octyl groups and 66% silanol groups on the nanoparticle surfaces. The validity of the assumption that the silane modifies each individual nanoparticle to the same degree and not a fraction of nanoparticles completely and another fraction not at all was confirmed in another, recent work.[74] Therein we transferred the modification principles to super-paramagnetic particles with which we were able to clearly demonstrate that all nanoparticles are partly modified in the same way. As the details of this finding are very complex and as a repetition would be way too exhaustive in this current work, the reader is referred to this recent reference for a detailed information.[74] Therefore, the particles should show a more hydrophilic than hydrophobic behavior. In the case of the micro-raspberry particles the solid–liquid interface area (raspberry to solvent interface) is very small compared to individual nanoparticles (where liquid would need to cover every single nanoparticle surface). Therefore, the interaction of particle surfaces with liquid is significantly higher for nanoparticles after raspberries are broken upon sonication. Ultimately, the tendency in a rather amphiphilic system toward being either a tiny bit more hydrophilic or hydrophobic starts to matter. Thus, in the system here, the hydrophilic character is apparently slightly more pronounced. The result is that nanoparticles from bursted raspberry particles are obtained which tend to disperse slightly better in polar liquids.
To test the surface properties of the nanostructured micro-raspberry particles in more detail, in a second test series two-phase liquid tests based on an emulsification step were carried out (Figure 1). For this purpose, the particles were added to a toluene–water mixture and treated with an ultrasonic finger. For the particles with average silane coverage of 1/2, 1/3, or 1/5 stable emulsions (Figure 1b) were observed. To test the stability of these emulsions, the mixture was centrifuged. Only for samples consisting of 1/2-modified nanoparticles, the emulsions were stable after centrifugation. This correlates well with the finding of Binks and Lumsdon who state that slightly hydrophobic/hydrophilic particles form more stable emulsions than strongly hydrophobic/hydrophilic particles. Examination of the emulsion type reveals that the emulsion is water-in-oil (w/o). This finding also fits well with reports in the literature, according to which w/o emulsions are mostly formed by more hydrophobic particles (and herein, our particle system in the region of 2/3 to 1/3 modification turned out to have a slightly more pronounced tendency of hydrophobicity), whereas more hydrophilic particles prefer to stabilize o/w emulsions.

Additionally, wettability tests with different water/methanol mixtures (0:100, 25:75, 50:50, 75:50, 100:0) were carried out to examine the surface polarity more precisely (Table S1 and Figure S6, Supporting Information). The wettability of all particle powders increases with increasing methanol content, whereby the particles with lower silane coverage could be wetted quicker. In pure methanol, the wettability of the particle samples modified to different degrees with silane is complete and happens very quickly, while it takes days to wet partly hydrophobic particles in pure water. This behavior of silica particles modified with alkyl groups was also reported before by Li et al. and Binks and Lumsdon. In general, the more hydrophilic the particles are, the better is the wetting behavior into water/methanol. Noteworthily, this was confirmed for every water:methanol ratio.

Although the above experiments are only qualitative in nature, they provide very important information. As the behavior of all nanoparticles in each batch was the same, it can be qualitatively concluded that within a batch, at least globally, a high homogeneity is achieved. This means, in line with our recent findings, that a partly modified system is exclusively composed of nanoparticles that are all partly modified and is not a mixture of fully and barely modified nanoparticles. However, determination of surface polarity of the nanostructured micro-raspberry particle system is quite challenging because of the various chemical groups on the particle surfaces. As already mentioned, there are approaches to examine the situation on a molecular level, however, this ultimate endeavor is very complex and challenging and thus clearly beyond the scope of this work.

Thus, so far it can only be stated that in the partly modified case, mixtures of alkyl groups and also OH groups are located on the particle surfaces, which apparently lead to enhanced interface-activity of the particles. Obviously, the above experiments yield a quick visual impression of the behavior of the nanoparticles. However, it remains a purely phenomenological, thus, a qualitative observation. To pave the way for reliable predictions, quantitative results would be desirable to classify the polarity of particles. Thus, advanced techniques for quantification are needed and in the following the combination of HDP and RD methods is described.

### 3.3. Advanced Methods

#### 3.3.1. Determination of HDP

To get a better understanding of the surface modification, we carried out a HDP analysis as described in Experimental section 5 (for the calculated distance plot and the 2D projections, the reader is referred to Figure S7 of the Supporting Information and our previous work). In brief, the powders were dispersed in a set of defined liquids with known HSP (indicated by blue...
tetrahedra and red cubes in Figure 2) and measured by AC. Then, the measurements were evaluated resulting into an order of liquids, i.e., from the best to the poorest liquid as described in the Experimental Section. Based on an evaluation algorithm developed in our previous work, liquids are step-wise switched on, i.e., ranked as good. By looking for the minimum “hop” of the HDP of the particles under investigation in 3D Hansen space as distinct point for the discrimination into “good” (i.e., blue tetrahedra) and “poor” (i.e., red cube), the 0/1-scoring into good liquids and poor liquids was obtained. The finally obtained HDP plot calculated via HSPiP (Hansen Solubility Parameters in Practice, 4th edition, version 4.1.07) software is exemplarily shown for nonmodified micro-raspberry particles in Figure 2. The small blue tetrahedra inside and red cubes outside the green transparent dispersibility sphere indicate good and poor-ranked liquids, respectively. Its center represents the distinct HDP coordinates of nonmodified nanostructured micro-raspberry particles. The three contributions of HDP and the radius of the sphere were determined to $\delta_D = 15.5 \text{ MPa}^{1/2}$, $\delta_P = 22.7 \text{ MPa}^{1/2}$, $\delta_H = 23.4 \text{ MPa}^{1/2}$, and $R = 19.9 \text{ MPa}^{1/2}$.

In line with the structure and surface functionalities of the nonmodified nanostructured micro-raspberry particles, a relatively low dispersion contribution and high polar and H-bond contributions were obtained, emanating from the hydrophilic Si-OH groups on native particle surfaces. Next, we investigated the differently OCTEO-modified nanostructured micro-raspberry particles. Already from the good ranked liquids it became clear that with the herein applied liquid list given in Table 1 three kinds of surfaces could be detected. For 0 and 1/10 surface modified raspberry particles, liquids 3, 6, 9, 10, 12, 13 were ranked good, for 1/5–2/3 surface modified raspberry particles liquids 3, 10, 12, and finally for 7/10-1 modified raspberry particles liquids 3, 5, 6, 9, 10, 12 were ranked good. Noteworthily, absolute relative sedimentation times (RSTs), which were derived using the integral extinction determined by AC,[47] did change gradually for every surface modification. However, due to the fact that the ranking, i.e., the order of good liquids sorted from the best to the worst liquid within regions I, II, and III, was constant, the resulting HDP did not change. Accordingly, Figure 3 depicts the evolution of the individual HDP contributions, namely, dispersion (Figure 3a), polar (Figure 3b), and H-bond (Figure 3c) with increasing silane coverage for regions I (0-1/10), II (1/5-2/3), and III (7/10-1). The dispersion contribution first increases followed by a plateau and then decreases starting from a silane coverage of 7/10. This is explained by the replacement of Si-OH groups by OCTEO molecules on the one hand, while at the same time additional carbon atoms are

![Figure 2. HDP sphere of nonmodified nanostructured micro-raspberry particles derived from HSPiP software. The large green sphere indicates the dispersibility sphere of the particles with its distinct coordinates represented by the small green center in the middle. The blue triangles indicate the positions of good-ranked liquids, while the red cubes indicate the positions of poor-ranked liquids.](image)

![Figure 3. Evolution of single HDP contributions depending on OCTEO surface coverage of SiO2-NPs. a) $\delta_D$, b) $\delta_P$, c) $\delta_H$.](image)

| Table 1. Liquids used for HDP determination. |
|---------------------------------------------|
| Liquid | Dielectric constant | Purity [%] | Supplier          |
|--------|----------------------|------------|-------------------|
| 1. n-hexane (Hex) | 1.9 | $\geq 95$ | C. Roth, Germany |
| 2. Toluene (Tol) | 2.4 | $\geq 99.5$ | C. Roth, Germany |
| 3. n-methyl-2-pyrrolidone (NMP) | 32.6 | $\geq 99.8$ | C. Roth, Germany |
| 4. 1,4-dioxane (Diox) | 2.2 | $\geq 99.5$ | C. Roth, Germany |
| 5. Ethyl acetate (EA) | 6.1 | $\geq 99.5$ | C. Roth, Germany |
| 6. Acetone (Act) | 21.0 | $\geq 99.8$ | C. Roth, Germany |
| 7. Diacetone alcohol (DAA) | 18.2 | $\geq 98$ | Merck, Germany |
| 8. Tetrahydrofuran (THF) | 7.5 | $\geq 99.5$ | C. Roth, Germany |
| 9. Isopropyl alcohol (IPA) | 20.2 | $\geq 99.8$ | C. Roth, Germany |
| 10. Dimethyl sulfoxide (DMSO) | 27.2 | $\geq 99.5$ | C. Roth, Germany |
| 11. Propylene carbonate (PC) | 66.1 | $\geq 99.7$ | C. Roth, Germany |
| 12. Methanol (MeOH) | 33.0 | $\geq 99.9$ | C. Roth, Germany |
| 13. Millipore water (H2O) | 80.1 | - | - |
introduced. However, starting from a silane coverage of 7/10 to 1, the dispersion part of the OCTEO modified particles is quite low. This at first glance surprising evolution shows the complex interplay of ligand mixtures at particulate interfaces, which are for the time being not sufficiently understood. Here we believe that quantification of such phenomena in combination with complementary solubility parameters like $E_T(30)$ and an in-depth understanding of the molecular level will shed light on these interesting effects. However, for the time being the latter would be far beyond the scope of this work which focuses on the quantification of particle surface properties rather than the in-depth understanding of the underlying molecular features.

Regarding $\delta_i$ and $\delta_4$ shown in Figure 3b,c, high values for both the polar and H-bond contributions for 0 and 1/10 modified particles are recognized. This is ascribed to the Si-OH groups at the surface, which are still dominant at 1/10 OCTEO coverage. Starting from 1/5 OCTEO coverage, the polar and H-bond contributions decrease, indicating the increasing influence of OCTEO that is replacing the OH groups on particle surface (Figure S8, Supporting Information). Starting from 7/10 to full OCTEO coverage, the H-bond contribution steeply decreases while the polar contribution remains unchanged. Due to the replacement of Si-OH groups by OCTEO, more organic molecules are introduced and the particle surface becomes less polar. This leads to an overall decrease in the polar and H-bond contributions. Again, the reason why in region III the polar contribution is not affected, while the H-bond parameter is significantly reduced, cannot be explained without more detailed information of the molecules (re)organization at the molecular level.

Thus, from Figure 3 we can draw two conclusions. First, we note that three major regions I–III are identified where we expect pronounced changes of HDP of the raspberry particles. Second, it becomes clear that for a more detailed resolution of the changes within I–III, a refinement of the liquid list in the regions of interest or an additional, complementary technique making the gradual changes accessible would be required. For instance, in future work, similar to the convex solubility parameter (CSP) approach of Boucher and Howell,[32] also the nonbinary RST values as direct outcome of AC analysis could be processed.

Finally, we calculated the Hildebrand parameter $\delta$ as the sum of the single HDP contributions as reference quantity (note that in case of molecules $\delta$ would be the heat of evaporation relative to the molecular volume which is linked to the integral sum of all interactions, i.e., not clearly defined in case of particles)[47]

$$\delta = \sqrt{\delta_0^2 + \delta_1^2 + \delta_4^2}$$  \hspace{1cm} (3)

Noteworthily, the evolution of $\delta$ should follow the analogue trend as polarity, as is depicted in the dependence of the silane coverage in Figure 4 (details on $\delta$ and $R_i$ can be found in Table S2, Supporting Information). As expected, first, $\delta$ is high in region I for nonmodified and 1/10 modified nanostructured micro-raspberry particles, then decreases to a plateau in region II (1/5–2/3 modified samples) followed by a final noticeable decrease to region III with 7/10 to fully OCTEO modified micro-raspberry particles.

Thus, our results show the strength of the HDP approach, as they quantitatively depict the decrease of polarity with increasing OCTEO coverage of surface-modified micro-raspberry particles. However, to better resolve the gradual change of the surface during OCTEO modification and for comparing HDP results with another independent and complementary method, RD studies were performed to investigate global polarity in more detail.

3.3.2. Reichardts’s Dye and Comparison to HDP Results

RD is a very useful indicator for the nature of silica particle surfaces,[69] thus it can be compared and correlated with the results from HDP. Other particle systems may be explored with the method as well, although certainly not all as for instance in case of iron oxide nanoparticles the magnetic character would destroy the coloration of dyes due to quenching. The choice of suitable liquids for the adsorption process of the dye on the particle surfaces is very important. The solubility of RD is good in very polar liquids like methanol and therefore the dye molecules might not be completely adsorbed onto the silica particles. Depending on the adsorption–desorption equilibrium, most of them will remain in the liquid. To examine the influence of liquids on the $E_T(30)$ value of the silica particles in more detail, a slightly nonpolar liquid, dichloromethane (DCM), and the nonpolar liquids $n$-octane and toluene were compared. In DCM, RD is highly soluble in contrast to $n$-octane where RD cannot be dissolved. Thus, in the latter solvent, the dye cannot be adsorbed on the silica surface. The reason is that for an adsorption process of the dye onto the nanoparticles, a minimum solubility in the liquid environment, i.e., in the solvent, has to be attained. In the case of DCM as liquid, RD could be adsorbed almost completely on the more hydrophilic micro-raspberry particles, whereas a residue of unbound dye remains in the supernatant after centrifugation of the more hydrophobic particles. In toluene, the affinity of RD toward going in solution is less pronounced. As a consequence, in this liquid, the driving force for RD adsorption onto the nanoparticle surfaces is enhanced. This can also be confirmed from visual inspection of the supernatant after the nanoparticles have been centrifuged following the adsorption process: What remains is a liquid which is hardly colored anymore. For this reason, toluene was chosen as the main liquid to conduct the dye adsorption on all silica nanoparticles.

The nanostructured micro-raspberry particle powders, modified to different degrees with silane, were therefore mixed with the RD-toluene solution to adsorb RD on the particle surfaces by the negatively charged oxygen atoms (Figure 5a). RD is adsorbed on nonmodified silica particle surfaces (0), appearing red, which becomes purple when adsorbed to partly modified particles, and blue in the case of fully modified particles. These findings correlate well with the findings from the liquid tests described above as well as with the HDP study, by which also three main regions were identified. As expected, the polarity degree of the particles decreases with increasing silane coverage. To calculate the $E_T(30)$ value of the particle samples as a quantitative measure for polarity, the $\pi \rightarrow \pi^*$ transition energy of the adsorbed dye was monitored by diffuse reflectance UV/Vis spectroscopy. For this purpose, the particles were carefully dried (Figure 5b). The colors of the adsorbed dye on the particle surfaces became brighter...
after drying and changed from red to orange for nonmodified particle samples, from purple to pink for partly modified particle samples and from blue to dark purple for fully modified particle samples. This is due to the absence of toluene. By visual inspection, the drying process seems to lead to a slight hypsochromic shift (blue shift), which means that the electronic ground state is better stabilized for dried particles than for particles dispersed in a nonpolar liquid like toluene.

The calculated \( E_T(30) \) values and \( E_T^{N} \) values decrease with increasing silane coverage of the nanoparticles (Table S3, Supporting Information). A dependence of the \( E_T(30) \) and \( E_T^{N} \) values on the original liquid the particles were dispersed in can be excluded by comparing values for different liquids (toluene and DCM, Table S3, Supporting Information), which indicates almost the same results. The \( E_T^{N} \) value of 0.93 for nonmodified particles fits well with findings from the literature which report 0.96 [69,71,72].

In contrast to HDP, four different regions could be observed: Two single point regions at the two extremes (unmodified (0) and completely modified (1) particles), a third region for slightly modified up to 1/3 modified particles, and a fourth region for strongly modified (2/3-9/10) particles (Figure 5c). This trend could be attributed to the arrangement of the alkyl groups of the silane on the silica nanoparticle surface: We expect that small islands/patches of alkyl groups initially form, which grow with increasing amount of silane until the surface of a nanoparticle is completely covered with silane (Figure S9 of the Supporting Information depicts a scheme for this evolution). The RD is assumed to reach the silanol groups of the nanoparticles between the silane patches, yet with more patches/islands less dye can reach the surface. Noteworthily, this is in line with the expectations from HDP analysis. However, it should be also noted that the above interpretation is one possible hypothesis, but not necessarily the only potentially correct explanation. As can be seen in Figure 5c, also a somewhat linear trend could be attributed to the data points in regions II and III. It should further be noted that Figure S9 (Supporting Information) is only one model assumption and the reader should be careful in taking this model as “the real” situation. The point we would rather focus on is that only by quantitative analysis such discussions are enabled at all and potentially hand back questions to the molecular level. This is the reason why we think that the methods presented in this work are relevant in shedding light on surface properties on the particle level.

Finally, by comparing the \( E_T^{N} \) values with the values for mass loss between 250 and 900 °C against silane coverage, two different curve shapes were found (Figure 6). The curve of mass loss is almost linear, throughout the \( E_T^{N} \) values decrease in four steps, which could be explained by the patchy like structure of the silane. Noteworthily, this finding clearly reveals that polarity of nanostructured micro-raspberry particles does not scale linearly with surface coverage but synergistic effects do occur. These were monitored by two completely independent techniques for characterization of surface properties, Hansen parameters, and RD.
4. Conclusion

Tailored surface properties of nanoparticles are of major importance for their subsequent processing in polymers to create polymer nanocomposites. A detailed understanding of the nanoparticle surface character is essential to obtain the desired dispersion results. Quick and simple dispersion tests in solvents and their subsequent inspection were demonstrated to be able to provide a first glimpse of the surface character of the particles. However, the current study went beyond and demonstrated that by more sophisticated analyses quantitative data becomes accessible that can be compared throughout different laboratories. In fact, nanoparticle systems with a distinct degree of hydrophobicity or hydrophilicity, respectively, can be well resolved with respect to their surface character in a quantitative manner using Hansen parameters and Reichardt’s dye characterization. Most importantly, our study revealed that surface properties in terms of, e.g., polarity do not scale linearly with the amount of modification bound to the particle surface but synergistic effects clearly occur.

This is not only paving the way toward giving scientists a link for connecting particulate surface properties with the molecular level, but also gives to those who apply new functional (nano) particles in industrial products standardized characterization procedures, and thus strategies for quality control, at hand.

5. Experimental Section

Materials: Silica nanoparticles were used in aqueous dispersion at pH = 9.7 (Köstrosol 2040, K2040, Chemiewerke Bad Köstritz, Germany) containing 40 wt% particles with a hydrodynamic diameter of 20 ± 2 nm (dynamic light scattering, Malvern Instruments Zetasizer, UK) without further purification. OCTEO (purity 97%) for the modification of the silica nanoparticles and n-octane (purity 98%) were purchased from abcr, Germany. Toluene (purity 99.8%), methanol (MeOH, purity 99%), and RD were purchased from Sigma-Aldrich, Germany and ethanol (EtOH, purity 99.5%) was purchased from Jäcklechemie, Germany. DCM (purity 99.9%) was purchased from Merck, Germany.

Modification of Silica Nanoparticles with OCTEO: For the modification, 375 g deionized water (H2O, conductivity 0.06 µS cm⁻¹) and 400 g ethanol (EtOH) were added within 15 min drop-wise and under stirring to 375 g silica sol K2040 (silica nanoparticles in water at pH = 9.7). Then, OCTEO was added as an ethanolic solution in the desired quantity. For a complete covering of particles with OCTEO, 45.5 g (164 mmol) was dissolved in 200 g EtOH, added to the nanoparticle dispersion via a dropping funnel with stirring over 45 min. After combining the reactants, the reaction flask was refluxed at 78 °C for 3 h under stirring. Afterwards, the obtained dispersion was centrifuged (4301 relative centrifugal acceleration (RCA)) for 60 min. Particles were washed thrice by redispersion in EtOH and subsequent centrifugation. To obtain partially silane-modified nanoparticles, the amount of silane was reduced to 2/3, 1/2, 1/3, 1/5, 1/10 of the amount above while the rest of the procedure remained unchanged.

Micro-raspberry Synthesis: To obtain nanostructured micro-raspberries, the (modified) nanoparticle dispersions were spray-dried in a B-290 mini spray-dryer (Büchi, Switzerland). The inlet air temperature was set to 120 °C and the outlet temperature was 65–75 °C. Afterward, the produced powders were dried in an oven at 110 °C for 48 h.

Liquid Tests: 50 mg of nanostructured micro-raspberry powder was mixed with either 10 g of toluene or 10 g of water and followed by shaking for a few minutes. Then, ultrasonic treatment for 5 min using an ultrasonic finger (Branson Sonifier 450, 400 W, Branson Ultrasonics, USA) was conducted with the following settings: Duty cycle = 40, output control = 3.

Two-Phase Tests: 50 mg of nanostructured micro-raspberry powder was mixed with 5 g of toluene and 5 g of water. The mixture was treated with ultrasound for 20 min (4 × 5 min) using an ultrasonic finger (Branson Sonifier 450, 400 W, Branson Ultrasonics, USA) with the following settings: Duty cycle = 40, output control = 3 with shaking in between and subsequently centrifugation at 7513 RCA for 8 min.

Wettability Tests: 50 mg of micro-raspberry powder was placed on the surface of 10 mL of pure water, on the surface of mixtures (10 mL total) of water and methanol (75:25, 50:50, 25:75) and on the surface of 10 mL of methanol.

Hansen Dispensibility Parameters: All liquids used in this study including their abbreviations and dielectric constant ε are listed in Table 1. As described in the previous work,[47] liquids were selected in such way that their HSP coordinates allow a proper scanning of a wide range of the 3D Hansen space (Figure S10, Supporting Information). In addition to the liquids used in the previous work, water was used as a probe liquid as silica nanoparticles are usually synthesized and stored in water.

Dispersion Procedure: The spray-dried powder of micro-raspberry particles was used to prepare 0.01 wt% dispersions in the respective liquids listed in Table 1. Afterward, 15 min of ultrasound was applied to all suspensions using an ultrasonic bath at 20 °C (VWR International, 30 W according to the manufacturer). Then, samples were filled into measurement cells for AC analysis.

AC Analysis: All AC measurements were carried out with a LUMiSizer LS 651 (LUM GmbH, Germany) using the blue wavelength (470 nm) to maximize the signal of small particles with low scattering intensity. The set temperature of all measurements was 20 °C. Polymide measurement cells with an optical path length of 2 mm (LUM GmbH, Germany) were used as received and filled with 430 µL of suspension. After ultrasonic treatment, the cells were inserted immediately to the rotor and centrifugation was performed with no delay at 500 rpm corresponding to a RCA of 36 at the cell bottom.

HDP Evaluation: Since the general method of HDP derivation using the AC approach is already described in the previous work, only a brief summary is given. For the detailed procedure, the reader is referred to literature.[47] In order to determine HDP, the stability of particles, i.e., the presence/absence of agglomeration/flocculation has to be evaluated in a defined set of probe liquids. Afterward, samples have to be classified into so-called “good” and “poor” ones to get a liquid ranking from the best to the worst. To visualize stability in an objective way, the sedimentation behavior was monitored in an AC experiment which is—in brief—a sedimentation experiment with optical access in time and space. As larger agglomerates/flocs sediment faster compared to smaller ones, the sedimentation time (t sed) of particles in different liquids, which can be derived from the integral extinction as measurement quantity, is a measure of their stability against agglomeration/flocculation. From t sed the so-called RST is derived after considering the density difference between the particle (ρ p) and the liquid (ρ L), the liquid viscosity (η L), the centrifugal acceleration (a), and the optical path length of the cuvette (d cell):

\[
\text{RST} = \frac{t_{\text{sed}} (\rho_p - \rho_L)}{\eta_L d_{\text{cell}}} \cdot a
\]

By comparing RST values in different probe liquids, a ranking from the best (largest RST) to the worst (smallest RST) liquid can be established. Then, using an evaluation algorithm developed by us where the number of good ranked liquids is stepwise increased according to the RST ranking, a well-defined HDP for a given material is obtained in an objective way. For more details on the standardized derivation of HDP by AC, the reader is referred to Süß et al.[11]
Analyses: Scanning electron micro-raspberry (SEM) was carried out with a Zeiss Supra 25 SEM at an acceleration voltage of 3 keV. The micro-raspberry powders were placed on a SEM sample holder equipped with a sticky carbon pad without further treatment. Differential TGA was carried out starting from 30 °C up to 900 °C (heating rate = 10 K min⁻¹) with a TG 209 F1 Libra DTA-TG (Netzsch, Germany). FTIR ( Nicolet MagnaIR 760 Spectrometer E.S.P., USA) was used to analyze the silica particles in KBr pellets. UV/Vis spectroscopy was performed using a Shimadzu UV3100 instrument (Nakagyoku, Japan). The spectrum of the solids was measured against BaSO₄ in a diffuse reflectance mode.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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analytical centrifugation, colloidal stability, interface characterization, silica particles, surface coating

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