Converting processes to Unfold the Potential of Nanoparticels

H. Näf, S. Pilotek, S. Schär, and F. Tabellion
Bühler PARTEC GmbH, Science Park 2, 66123 Saarbrücken, Germany.
nano@buhlergroup.com

SUMMARY

The huge innovation potential offered by nanoparticles (d < 100 nm) as nano-additives can usually only be utilized, if an excellent state of dispersion is accomplished. Agglomerated or even aggregated nanoparticles are widely available on the market. To produce usable nanoparticle dispersions from these, we propose our approach of tailored dispersion techniques. As important corner stone we refined nanoparticle processing in agitator bead mills comprising the concurrent utilization of chemical and mechanical action called chemomechanical processing. Agitator bead mills provide a number of advantages in the processing of nanoparticles. Most notably, the milling chamber can be understood as a reaction vessel where complex chemical reactions can be conducted under well-defined mechanical conditions in the wet phase. In consequence, nanoparticles can be dispersed, stabilized, and functionalized in one step. Using this technique, nanoparticles with d < 10 nm can be dispersed down to the primary particle size. Whereas nanoparticle technology cannot be assigned to one specific application, it is a versatile tool in various industries. As an example, the technology enables transparent UV protection with long-term stability. As another example, nanoparticles produce much interest as nanofillers in transparent coatings, e.g. to increase scratch resistance. In this application, functionalization of the nanoparticles with respect to the individual coating formulation is key.

1 NANOPARTICLES

The interest, which is generated by the subject of nanoparticles is based on their property *profile*. Firstly, nanoparticles possess intrinsic properties of the material they are made of; e.g. the hardness of ceramics, the high refractive index of titania, and the UV absorption of zincoxide. Using nanoparticles, these features can be transferred into a product formulation. This is especially interesting in combination with the most noted property of nanoparticles: Small enough particles may result in transparent materials, as light scattering is decreasing with decreasing particle size. Highly interesting are those properties of nanoparticles which arise solely from their size and may be called “dimensional properties”. As an example, one may consider the color of inorganic fluorescence pigments, which changes gradually from red to green as the particle size gets smaller[1]. The most Janus-faced property of nanoparticles is strongly related with these dimensional properties: Powders of small particles possess high specific surface areas. High surface areas are attractive in applications where contact is crucial, e.g. catalysis or storage. In product formulations “surface” translates into “interface” between particle and medium. A higher fraction of interfaces results in more interaction between matrix and particle and thus toughening of the material. On the other side, increase of such interfaces usually results in considerable alteration of viscosity, light scattering, and homogeneity of the product. Because of the immense interfacial area of nanoparticles, skilful control of the particle-medium interface is indispensable for a successful product development.

1.1 Tailored Dispersion Techniques

[1] D. Bertram, H. Weller, Phys. Journal. 1 (2002), Nr 2, 47-52.

A crucial point in employing nanoparticles in novel products is to achieve a nanoscaled state of dispersion of the particles. As the number of combinations between formulations and particles are legion, standard solutions are problematic in principle. In contrast, we propose a approach to nanoscaled dispersion using a scientific set of process parameters like building blocks. This allows easy access to tailored suspensions in industrial scale. For dispersing agglomerated powders, we propose a technique using agitator bead mills comprising the simultaneous utilization of chemical and mechanical competences called chemomechanical processing.[2] Most notably, this approach allows tailoring of specific solutions for highly different combinations of application, processing, particle, and formulation starting from commercially available nanopowders.

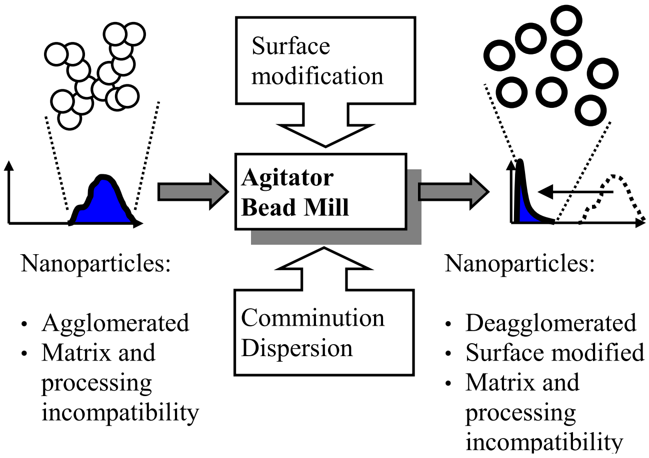

Figure 1: Scheme of chemomechanical processing.

Chemomechanical processing is based on the combination of a) the mechanical comminution of agglomerated nanopowders in agitator bead mills and b) the rules of colloidal chemistry utilizing surface modification in order to tailor the particle surface chemistry. Using this technology agglomerated nanoparticles, which are incompatible for the further processing techniques will be converted into tailor made deagglomerated and functionlized dispersions ready for further processing (fig.1). In addition, nanoparticles and nanodispersions can be produced by real comminution of larger particles. This applies also for application areas, where to-date no production technology exists.

1.2 Agitator bead mill reactor

Agitator bead mills provide a number of advantages in the processing of nanoparticles. They are devices to process suspensions with high energy at controlled conditions. Solid state nanoparticles are processed in the liquid phase, which makes their further processing into end products easy. The method itself is established, known and used for a long time. Therefore, a lot of experience is available about principles, constructive possibilities as well as about processing details. Grinding in an agitator bead mill is a scaleable process and thus industrially relevant. The large variety of available constructive details provides many possibilities for optimizing processes, e.g. different grinding chamber geometries, grinding media separation, and cladding materials. For nanoparticle processing, the milling chamber has to be understood

[2] DE 103 04 849.9 “Chemomechanical Synthesis of functional colloids.”

as a reactor where complex chemical reactions can be conducted under well-defined mechanical conditions in the wet phase. Agitator bead mills are advantageous in this respect, as they provide a defined volume and a readily controllable energy input. The energy need for nanoparticle processing is strongly dependent on starting materials and product requirements. Consequently, the mill may be operated passage-wise or in recirculation mode (fig.2).

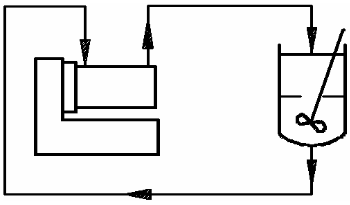

Figure 2: Flow sheet of recirculation mode operation of agitator bead mills

Experience has shown that for traditional wet grinding processes a particle size of ca. 100-200 nm seems to constitute a major barrier in comminution. In many cases, increasing the energy input does not lead to finer particles. This has to be interpreted in terms of specific surface area and Van der Waals forces, which increases rapidly by reducing the particle size and approaching the barrier of 200 nm. If no precaution for the stabilization is carried out, a balance between deagglomeration and agglomeration ariseads to a stagnation of the comminution process and the resulting particle size distribution.

1.3 Chemical surface modification

In principle suspensions can be stabilized by making use of electrostatic, steric and electrosteric stabilization techniques. Quite often in addition to stabilization, applications demand a surface modification with chemically functional groups.

We utilize the concept of *small molecule surface modification* to realize stabilization and functionalization. This concept relies on the chemical bond principles known from solution chemistry and employs them for the anchoring of the surface modifiers (small molecules) on the nanoparticle surface. The basic principle of the surface modification, using organic acids as an example, is shown in figure 3.

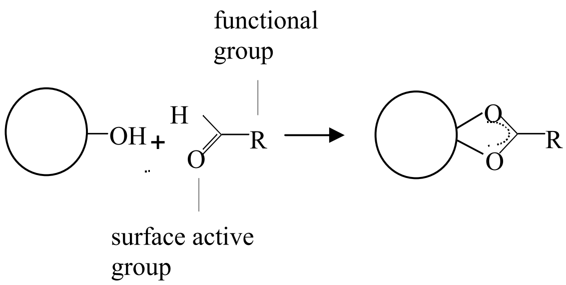

Figure 3: Basic principle of small molecule surface modification.

As surface modifiers for nanoparticles bifunctional molecules are employed. One of the groups is reactive towards the surface of the particles to form a stable connection between particle and surface modifier, whereas the other group is to be chosen in terms of the later application or the required functionality. For the stabilization of nanoscaled suspensions the surface modifier needs to be compatible with the solvent, i.e. the respective part of the surface modifier needs to be soluble. Those small molecules still provide sufficient barrier for holding nanoparticles apart, but reduce the organic content to a minimum. Moreover, molecular surface modifiers are paradigm for nanoparticles if it comes to introducing a chemical functionality. This is indispensable if specific chemical interactions are required, e.g. improvement of mechanical properties of paints and coatings. Mechanical impact like scratches leads to propagation of stress inside the coating material. At the interface of separate phases inside the material, the stress increases as it cannot be transferred. If the stress is too large, the coating breaks. As a result, a surface modifier has to chemically connect polymer and nanoparticles, such that stress can be transferred to the particles and thus be dissipated.

2 EXAMPLES

The capability of chemomechanical processing may be demonstrated using zirconia (ZrO_2) particles. Due to the high refractive index of the crystalline powder (n_D ca. 2.0) the material is used to adjust the refractive index of transparent plastics. This is only feasible if the particle size in dispersion is well below 30 nm to prevent light scattering. As one important parameter the process is dependent from the quality of the starting materials. Using zirconia synthesized via a flame-pyrolysis process (primary particle size ca. 30 nm), a suspension could be prepared, where 90 wt.-% of the particles were smaller than 100 nm (d_{90}, volume distribution). In contrast, by employing hydrothermally crystallized nanoscaled zirconia (primary particle size < 10 nm, BET: 150 m²/g) using the same process parameters, a suspension with d_{90} : 30 nm was obtained (volume distribution). Fig. 4 shows a TEM micrograph of the particles before and after chemomechanical processing. This result was achieved using a carboxylic acid and parameters of production scale. The optimization of process parameters led to a dispersion of particles down to the primary particle size. Thus, a suspension was produced where 90 wt.-% of the particles were 7 nm or smaller (d_{90}, volume distribution) using the same starting material as before. Fig. 5 shows the laser light scattering analytical data.

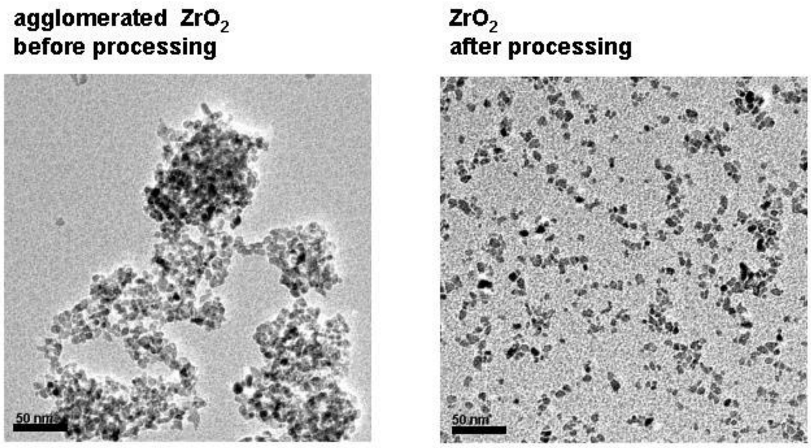

Figure 4: TEM micrograph of ZrO_2 particles before (left) and after (right) chemomechanical processing. Bar: 50 nm.

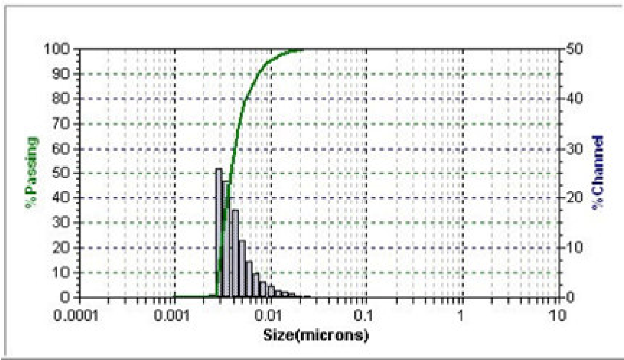

Figure 5: Particle Size Distribution of Chemomechanically processed ZrO_2 in ethanol (d_{50}: 5 nm / d_{90}: 7 nm).

The application of UV protection with transparent matrices translates into efficient light absorption at a wavelength below 400 nm but high transparency at higher wavelengths. Organic molecular absorbers are very often employed for this purpose, and transparency is obviously not an issue with these. Absorption of light transfers the molecules into a higher energetic state, though, which comes along with an increased reactivity. Consequently, the efficiency of UV absorption may decrease with time. In some practical applications the comparatively high mobility of molecular UV absorbers poses another challenge, e.g. in the packaging of food. Inorganic UV absorbers like Titania (TiO_2), Ceria (CeO_2), or Zincoxide (ZnO) are UV-stable, and particles in general posses a much lower mobility than molecules. If high transparency is needed, the particles must be nanodispersed in the matrix.

Titania is most often used when inorganic UV absorbers are employed. It has a high absorption especially in the UV-B region. TiO_2 is also photocatalytically active. In the application of UV protection, each individual nanoparticle needs to be coated for inactivation. Zincoxide has similar absorption properties, but lower photocatalytic activity has been reported.

We investigated Zincoxide produced by solid state (mechanochemical) synthesis[3]. The material has a very narrow particle distribution, especially compared to zincoxide nano-particles synthesized by other routes. The size of the particles was 25 nm as confirmed by BET, XRD, and TEM analysis. The combination of the small particle size and the narrow particle size distribution leads to a sharp band edge profile in the UV-VIS spectrum (fig. 6). This feature is highly interesting for the application of the material as UV protection agent in coatings e.g. wood coatings. The transparency is high in the visible range but low at UV wavelengths.

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[3] Advanced Nanoproducts ltd, Australia (APT).

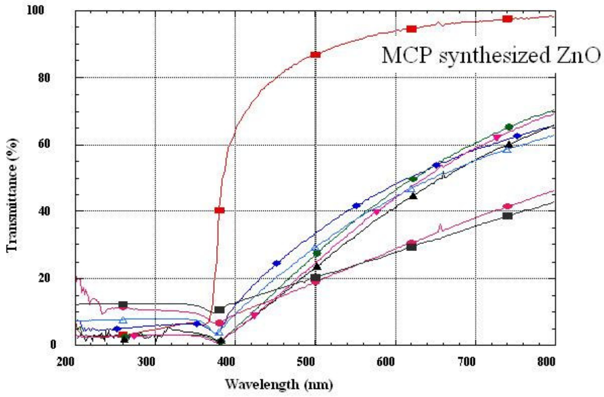

Figure 5: Absorption spectra of nanoscaled Zinkoxide synthesized by different methods. MCP: Mechanochmical synthesis (solid state reaction). Courtesy of APT.

The inorganic particles have been modified to be compatible with a highly unpolar solvent (shellsol 100). This results in a highly dispersive state in this solvent as shown in the particle size distribution (Fig. 6).

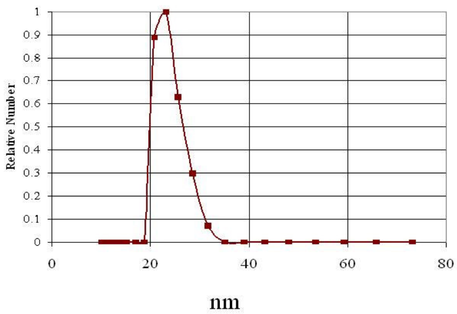

Figure 6: Particle size distibution of ZnO. Courtesy of APT.

SiO_2 particles have gained wide interest in a variety of industries. This is partly due to the price of silica and also to the favorable index matching of silica and many organic polymer coatings. Though the comminution part of the process may be skipped using a colloidal suspension as starting material, the surface modification needs to be adapted to the requirements. Fig. 7 shows the particle size distribution of the processed particles.

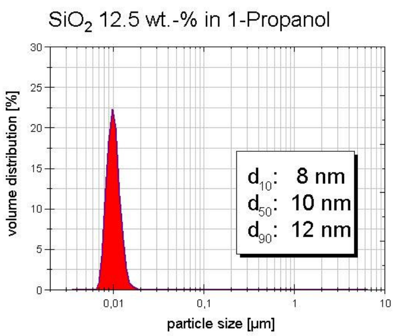

Figure 7: Particle size distribution of colloidal silica. 90% of particles are smaller than 12 nm.

The transparency of compositions containg 5 wt.-% silica nanoparticles in paint components was investigated (fig. 8). The transparency may be evaluated using the transmission coefficient γ, which summarizes effects of both particle size and differences in refractive indices. Small values of γ refer to high transparency, values of $\gamma > 100$ refer to opaque materials. Using a suitable surface modification, excellent states of dispersion were achievable. From theory, 100 nm silica particles with $\gamma > 10$ in hydroxy components and with □ $\gamma > 100$ in butyl acetate lead to opaque formulations. Using 20 nm silica particles, from theory, transparent compositions are achievable for these components. We used epoxy- and alkylsilanes to prepare a suitable surface modification of colloidal silica particles. This resulted in a highly dispersive state of the particles in the respective paint components as shown by the low values of γ.

Transparency (Transmission-coefficient) **of SiO_2- formulation**	D_{90} /nm	γ Epoxy resin	γ Polyol resin	γ Butylacetate
n_D^{20} of organic component		~1,50	~1,48	~1,39
Modification A	<20	0,5	0,8	2,0
Modification B	<20	0,2	0,6	3,1
Theory	20	0,01	0,1	2,3
Theory	100	1,5	14	290

Figure 8: Transmission coefficient of compositions of modified SiO_2 in paint components.

3 CONCLUSION

Nanoparticles offer a wide potential for materials innovations. In each of the diverse applications, the state of dispersion of particles is of utmost importance. The Art of Dispersion of nanoparticles has to find solutions in the field of compatibilization as well as functionalization. The key is the correct choice of processing parameters, tailored to the starting material, the formulation, and the application. If it comes to processing nanopowders, the combination of suitable wet phase nano-chemistry and mechanical comminution techniques provides a versatile approach to manufacture ready to use nanoparticle formulations for specific applications in all industries.

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