Dispersion of Functional Nanoparticles – Key to Application

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Abstract

In real-world applications, nanoparticle composite technology should be compatible with existing (downstream-) processes like e.g., mixing, formulating, casting, coating, or molding. These additional requirements from the industrial world make the successful dispersion process for nanoparticles the key element in nanoparticle processing. In contrast to nanoparticle powders, nanoparticles can be easily processed and introduced into product formulations when provided as a nanobatch, a nanoparticle dispersion that is compatible with the requirements of the respective downstream processes. Additional features and constraints given by the requirements of industrial applicability may include, e.g., viscosity, solid content, transparency, or surface roughness.

Introduction

Inorganic nanoparticles as ingredients in composites are interesting because they inherently carry properties of the respective solid. High-surface area powders may be used to provide a highly porous surface, Zr- and Ba-containing solids provide X-ray opacity, $BaTiO_3$ and other perowskites are well-known materials with high dielectric constant, and TiO_2 as well as ZnO provide sustainable UV absorption properties, to name but a few.

The respective raw materials are generally commercially available at nanoscaled particle sizes, and simple mixing of liquid compositions with the powder will generally introduce the respective property into the product formulation.

However, application of nanoparticles in real-world products is more difficult because additional product features are wanted and application-specific constraints must be met. Such requirements comprise e.g., viscosity and rheological properties, transparency and optical appearance, surface roughness and texture. Such additional requirements have to be met in a production environment where downstream formulating and processing impose still further requirements. For radiation-curable composites at least non-interference and ideally supportive properties regarding the curing process are such an additional requirement. Chemically, this translates into a want for radiation-curable functional groups at the particle's surface.

Nanoparticle Masterbatches for Nanocomposites

Nanopowders are specifically challenging to process because of their high specific surface area. The specific surface area is defined as area per unit volume bulk (dense) material and may be given in m^2/ml. This is a reduced figure with respect to the chemical nature and thus density of the material. Dividing the specific surface area by the bulk density ρ in units of g/ml gives the more common surface area in units of m^2/g.

Nanopowders in general have a specific surface area of up to several hundred m2/ml. For homogeneous dispersion results, the surface area must be completely wetted to give smooth particle-matrix interfaces. In order to obtain stable and functional dispersions, the internal interface needs to be chemically controlled.
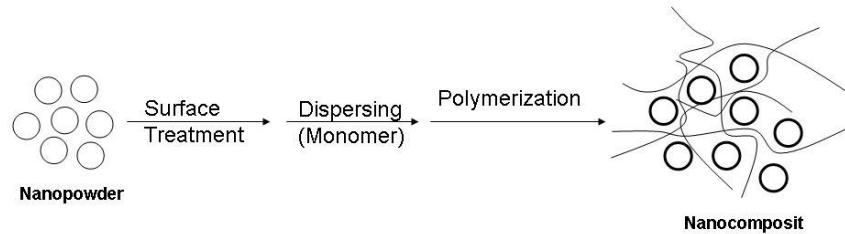
**Figure 1: Basic route from nanopowders to nanocomposites.**

The basic route from nanopowder to radiation-cured nanocomposite encompasses the steps of (i) surface modification of nanoparticles (ii) dispersing (into the monomer formulation) and (iii) photopolymerization of the composition. (Figure 1). Additional steps are possible, such as solvent exchange, drying, or shaping. In some cases, steps (i) and (ii) can be carried out simultaneously, using chemomechanical processing (see below). However, careful design of the surface modified nanoparticle dispersion is always a key component for the successful synthesis of the nanocomposite. The dispersion can be understood as a functional masterbatch of nanoparticles, or a "nanobatch". The nanobatch is made from commercially available starting materials, so it becomes functional by selection of specific process parameters (Figure 2).
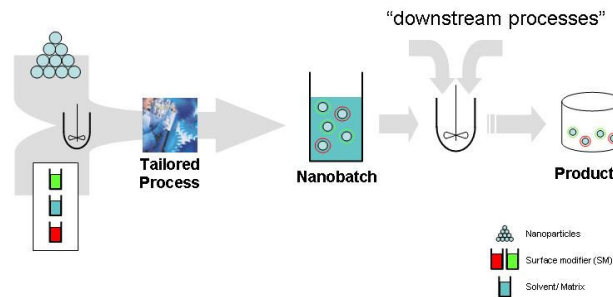
**Figure 2: Central role of nanoparticle dispersions.**

Chemomechanical Processing

In chemomechanical processing chemical surface modification is carried out under well-defined mechanical stress conditions[1]. The use of agitator bead mills is highly effective for delivering the mechanical stress. As many parameters influence the selection of the agitator bead mill, there is no standard equipment which can be used in all cases. Especially viscosity and cooling options for (often temperature sensitive) reactive monomers have to be considered. If the viscosity of the product formulation exceeds device-dependent thresholds of 0.5 – 5 Pas a three-roller mill may be employed to deliver shear forces. For nanoparticle processing, a one-pass operation through the high-energy mill is usually not sufficient. Typically, multi-pass operation or a recirculation mode takes care of the necessary energy input between 1 – 10 kWh/kg (Figure 3).
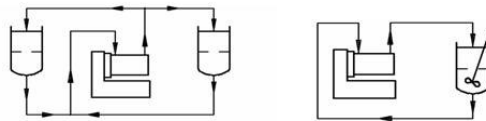
Figure 3: Operational modes for bead mills. left: multi-pass operation; right: recirculation mode.

In chemomechanical processing, the milling chamber is used as reaction compartment for the surface modification reaction. General stabilization mechanisms for dispersions and colloids are well known[2]. The mechanisms are based on changing the surface chemistry of the particles. For stabilizing micron-sized particles in a liquid, a variety of organic polymers is available. The general concept comprises specific groups or segments of a macromolecule to attach at the particles' surface. At the same time, the molecules contain moieties of high compatibility with the solvent.

The surface modification reaction can be carried out using colloidal starting materials, as well. Obviously, in this case no mechanical treatment is necessary. The importance of chemically adjusting the particle surface, however, remains the same. As an example, we have used colloidal silica in organic solvents ("organosols", e.g., iso-propanol) as starting material to produce a nanoparticle masterbatch for an acrylic-based transparent hardcoat.
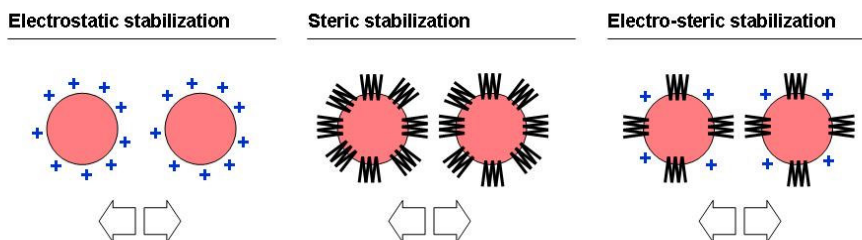
Figure 4: Stabilization mechanisms for colloids.

Colloids in an aqueous medium can be electrostatically stabilized if the pH value is adjusted accordingly. However, many commercial products do not allow this approach as a specific window of pH may be a requirement in itself. As a consequence, steric and electrosteric stabilization mechanisms are used more frequently for product formulations. Figure 4 summarizes the different stabilization mechanisms for colloids. The interparticle distance has a major role in nanoparticle stabilization. The distance between two particles is decreasing with decreasing particle size. Consequently, we have to reflect size considerations when using surface modifier molecules. As a general rule we find that it is helpful to employ smaller surface modifier molecules as the particles get smaller. This concept of 'molecular surface modification' contrasts the classical usage of oligomeric dispersants. The chemistry of nanoparticles can be compared to molecular chemistry rather than to the behavior of micron-size particles[3]. We consequently understand nanoparticles as rather large molecules with functional groups at the surface. For inorganic oxides, the functional groups mostly comprise hydroxyl groups. Using molecular bifunctional additives these groups are accessible to a chemical reaction. Suitable reagents include a wide range of chemicals like e.g. silanes, carboxylic acids, and chelating agents.
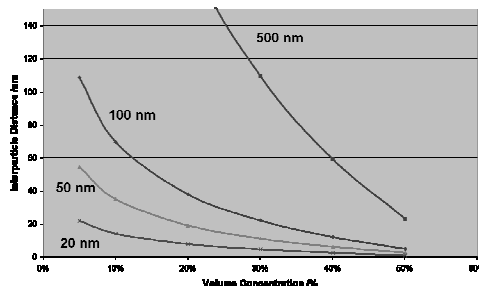
Figure 5: Interparticle distance as function volume concentration for different particle sizes.

Highly filled acrylic resin

As a case study, we have processed pyrogenic silica as filler material for acrylic nanocomposites as used in dental applications. Typical dental materials comprise highly filled complex formulations of light-curable acrylic resins[4]. Filler materials reduce the polymerization shrinkage which is crucial for the repair of dental cavities. In addition, fillers are added to improve mechanical properties like modulus and wear resistance. Generally, the maximum achievable content of fillers is limited by wettability of the filler by the resin formulation. Because of the high specific surface area, this issue is especially pronounced when using small (nano)scaled fillers, which makes the surface treatment even more important. In addition, a molecularly seamless interface between polymeric network and filler particles is necessary to transfer mechanical stress within the composite. Small particles within the composite enable polishable surfaces and low surface roughnesses even after wear. Usually, small-scaled particles are combined with larger scaled particles to accomplish an even higher degree of overall filler density.

Within this context, we thus developed a process to make a highly-concentrated dispersion of functionalized pyrogenic silica in a reactive matrix of acrylic monomers. As an additional downstream-processing requirement, the viscosity of the resulting compound dispersion needed to be sufficiently low to allow mixing with further components of typical dental compositions such as larger filler particles. We used chemomechanical processing to manufacture the silica dispersion. methacrylic functions can be advantageously grafted onto pyrogenic silica surfaces (e.g., Aerosil® 200) using methacrylic-functionalized silanes (e.g., methacryloxypropyltriethoxysilane). The basic underlying chemical reaction is a Sol-Gel type reaction which leads to a strong chemical bond between surface modifier and the particle. The chemomechanical process is carried out directly with the acrylic resin (e.g., Laromer® 8800) using an agitator bead mill in a multi-pass operating mode. A solid concentration of up to 35 wt.-% SiO_2 could be achieved. The resulting dispersion is shear thinning with a dynamic viscosity of less than 3 Pa s (at a shear rate of 150 s-1), which allows for downstream processing into dental composites[5].

Summary

Introduction of nanoparticles by using application-specific masterbatches is a versatile concept. We emphasize the central role that nanoparticle dispersions in general and the respective dispersion processes have in the production of nanocomposites. The requirements of downstream processing need to be taken into account. Using surface modification techniques, many properties such as viscosity, functionality and stability can be controlled. Agglomerated nanopowders can be conveniently processed into masterbatches by chemomechanical processing using agitator bead mills.

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[1] Bühler PARTEC GmbH, patent application WO 2004/69400.
[2] e.g.: H.-D. Dörfler, "Grenzflächen- und Kolloidchemie", VCH, Weinheim (1994).
[3] A.M. Kalsin et al. L. Amer. Chem. Soc. 128, 15046 (2006).
[4] e.g.: www.dentalcomposites.com

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[5] Unpublished patent application, Bühler PARTEC GmbH, Germany.