Liquid nanoparticle masterbatches for the deposition of solid inorganic materials

Steffen Pilotek, Buhler Inc., Minneapolis, MN, U.S.A.
Detlef Burgard and Marc Herold, Bühler PARTEC GmbH, Saarbrücken, Germany.

Abstract

Deposition of materials by digital fabrication methods demands a high degree of homogeneity of the formulation. At the same time, viscosity control is highly important for the processability of the ink. This is especially challenging when it comes to depositing solid high-surface area particles. As well, the particle size and the particle size distribution of the particles in the ink is crucial, especially if ink jet techniques are applied.

We present a process to manufacture liquid nanoparticle-masterbatches from commercially available agglomerated nanopowders. The process thus enables the use of inorganic solids in digital fabrication techniques. Each masterbatch contains specifically surface-modified inorganic nanoparticles dispersed in a low-viscosity solvent, like water, alcohol, acetate, ketone, or hydrocarbon solvents. The powders are deagglomerated using agitator bead mills. The particle-medium interface is chemically tailored with respect to the solvent and to further components of the formulation by use of bifunctional surface modifiers.

Introduction

Building structures from inorganic particles like semiconductors (e.g., TiO_2, ZnO), perowskites (e.g. $BaTiO_3$), or carbon structures (e.g., diamonds or carbon nanotubes, CNTs) may be quite interesting for the use in digital fabrication techniques. However, the homogeneity of the ink is especially critical when it comes to depositing solid particles. Molecules are small enough to statistically ensure a homogeneous distribution in the ink, thus there will be the same concentration of molecules in each droplet. Due to the extended size, however, this may not be true for solid, non-soluble particles. In another aspect, if particles are deposited by ink jet processing, they may lead to clogging of nozzles if they are too large. As a third aspect, digital fabrication techniques are well suited to custom-manufacture miniaturized structures. If it comes to building small and/ or thin film structures, small particles are needed as suitable building blocks.

As a consequence, particles for deposition by digital fabrication techniques are required to be of sub-micron- or even nano-scale and they must be homogeneously dispersed throughout the ink.

Many functional inorganic powders are commercially available in nanoscaled form. However, these particles are usually available only as agglomerated powders. Using these starting materials does not lead to satisfactory results if the particles cannot be de-agglomerated and stabilized in complex ink formulations. We present a process to manufacture liquid nanoparticle-masterbatches from commercially available agglomerated nanopowders which thus enables the use of inorganic solids in digital fabrication techniques.

Chemomechanical Processing

We have proposed the "chemomechanical process" to disperse agglomerated nanopowders into highly homogenous formulations [1, 2]. In chemomechanical processing, a chemical surface modification reaction is carried out under well-defined mechanical stress conditions. The use of agitator bead mills has been found 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 energy density, viscosity, potential contamination and cooling options have to be considered. 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.

In chemomechanical processing, the milling chamber is used as reaction compartment for a surface modification reaction. This is a particular important feature of the process, because it allows us to chemically customize a formulation. Due to their high specific surface area, dispersions of nanoparticles or colloids are known to be very sensitive regarding the ingredients of a complex formulation. The dispersions can be stabilized in a specific formulation, however, by chemically modifying the surface of the particles with respect to the solvent and further ink components.

Aqueous colloids can be electrostatically stabilized if the pH value is adjusted accordingly. However, many commercial products do not allow this approach, e.g. as the ink may require a specific window of pH. As a consequence, steric and electrosteric stabilization mechanisms are used more frequently. We 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.

This concept of 'molecular surface modification' contrasts the classical usage of oligomeric and polymeric dispersants.

Processing Zincoxide Nanopowders

Zincoxide is a versatile material that has been used as UV absorber, functional ceramic, fungicide, and catalyst. For electronic applications, ZnO is broadly used as material for sensors, actuators, varistors and in transparent conductive coatings. As miniaturization continuously goes on in these fields of applications, the need for higher resolution and smaller building blocks grows. Simultaneously, there is a growing demand for more cost effective and flexible production techniques. Under these aspects, high resolution printing techniques in combination with ideally dispersed nano particles become more and more important.

The use of ZnO as UV absorber has increased as it is more efficient in the UV-A region than the classical mineral UV absorber TiO_2. In addition, the lower refractive index of ZnO compared to TiO_2 (n_D 1.9 vs. ca. 2.6, respectively) leads to less hazy films at the same particle size. ZnO provides also denser films leading to higher mechanical and chemical resistance.

UV Absorption properties

ZnO has been used as mineral UV absorber for a long time. The electronic bandgap structure leads to a broad absorption at wavelengths below the cut-off at 368 nm. This contrasts to the more sophisticated spectra of molecular UV stabilizers, which often require the use of several additives that complement each other to provide full UV protection. As a mineral, ZnO does not degrade under irradiation, providing a permanent UV protection. Studies have shown [3] that whereas UV-A absorbers significantly degrade after about 1,500 hrs in QUV testing, no breakdown is seen for ZnO even after 4,000 hrs.

Toughening polymeric films by ZnO

ZnO may be used to toughen water-based clearcoats. Studies have shown [4] that mechanical properties such as dry and wet scrape resistance may be greatly improved by a low percentage of nanoscaled ZnO. At the same time, the chemical resistance of the coatings could be equally improved.

Presumably, ZnO catalyses the curing process and leads to a denser network of the polymer structure. In this case, nanoscaled ZnO is used not only for optical reasons (to reduce haze in clear coatings) but also as it provides a very high surface area for this catalytic effect.

Zincoxide in organic solvents

We have processed an agglomerated ZnO nanopowder into different low-viscosity media to provide dispersions as liquid masterbatches. The primary particle size of the powder (starting materials) is ca. 35 nm, however, the agglomerate size before processing is in the µm-range.

Using chemomechanical processing, we have dispersed ZnO into a variety of organic solvents such as butylacetate, butyl glycole, ethanol, ethyl methyl ketone, xylene, and shellsol (hydrocarbon mixture). The solvents span a wide range of polarities, so a specific surface modification was necessary to stabilize the particles in each solvent. This range of solvents illustrates the freedom that chemomechanical processing provides. A particle size of < 100 nm is generally achieved. The dispersions are processed typically at a concentration of ca. 40 wt.-%. Therefore, they can be used as masterbatch to formulate more complex inks.

Zincoxide in water

ZnO has a non-zero solubility in water. Generally, the solubility of particles is increased by decreasing the particle size. Processing nanoscaled ZnO into water is therefore chemically more challenging than dispersing into organic solvents. At the same time, industry tries to provide more water-based products for environmental and cost reasons.

We have processed the same agglomerated ZnO nanopowder into water. Using a suitable combination of surface modifiers we have been able to provide an aqueous dispersion of nanoscaled ZnO with a particle size of < 50 nm (d_{50}).

Conclusion

Highly concentrated, low-viscous dispersions of inorganic oxides have been prepared as liquid masterbatches. The dispersions may be used as components in fluids for digital fabrication formulations. In some cases, the dispersions may serve as starting point for an optimization with respect to a more complex formulation. The dispersions have been synthesized by chemomechanical processing, which is a versatile technique for processing agglomerated nanopowders into low-viscous dispersions of nanoparticles. The key components “mechanical process parameters” and “chemical formulation” are equally important to produce stable nanoscaled dispersions.

References

[1] Bühler PARTEC GmbH, Patent application WO 2004/69400.

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[3] D. Burgard , C. Hegedus, F. Pepe, D. Lindenmuth, Air Products and Chemical, European Coating Show, Session XXIII, Nuremberg (2007).

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Author Biography

Steffen Pilotek received his Dipl.-Chem. and Dr. rer. nat. from the Universität Bielefeld (Germany, 1999). Following a research position at the Institute for New Materials (INM, Saarbrücken) he joined the nanotechnology group of Bühler AG (Switzerland) in 2002. Since 2007 he works for Buhler Inc. (U.S.A.) as Business Development Director Particle Technology (PARTEC).