Recent Progress in Nanoparticle Dispersion Using Bead Mill†

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Abstract
There is great demand for nanoparticles (NPs) dispersed in liquid phases for practical applications of functional NP materials. However, it is difficult to produce NP dispersions with specific particle sizes, concentrations, viscosities, and purities on an industrial scale (large mass production rate and low energy consumption). In this review, we highlight recent developments in NP dispersion using low-energy bead mill. Such processes enable the use of small beads (7–50 μm). Smaller beads reduce the collision and shear energies of NPs during agitation. This minimizes NP breakage/damage, and retains the shape and crystallinity of the NPs, which determine the inherent NP functions. This review starts with a brief explanation of the theory and current status of NP dispersion and describes the mechanism and experimental results for low-energy bead mill processes, i.e., using uniaxial, dual-axial, and all-separator bead mills, and selection of dispersing agent. Applications of NP dispersions, including nanocomposite materials, and methods for dealing with NP dispersion coloration are also discussed, along with future research directions.

Keywords: nanoparticle, dispersion, bead mill, dispersant, nanocomposite material

1. Introduction
1.1 Importance of NP dispersion
This century, research on the synthesis of nanoparticles (NPs) has attracted much attention because of their advantages compared with bulk materials. When the particle size of a material is reduced to the nanoscale range, quantum size effect and size effect become more important than they are for submicron particles. The former effect shows the specific energy band gap differ from bulk solid one, and the latter effect produces high surface areas, single-domain sizes, and high surface activities. These characteristic properties of NPs are important in industrial applications such as catalysts, magnetic storage, optical devices, and ultrafine wiring.

NPs have large surface areas and excess surface energy, and therefore they tend to agglomerate to minimize the energy, which is larger than the kinetic energy caused by Brownian motion. Cohesion and adhesion forces easily arise between NPs because of intermolecular forces such as van der Walls forces, electric dipole interactions, and chemical bonding (hydrogen bonding), which lead to particle agglomeration and aggregation.

NPs agglomerate and aggregate during synthesis. Agglomerates are loosely attached particles (the so-called primary particles) by van der Waals, capillary, electrostatic or other physical forces. While, primary particles held together by chemical/sinter forces (metallic, ionic or covalent bonds) are termed aggregates. In liquid-phase processes, e.g., precipitation methods, primary particles easily interact each other and agglomerate. Although pH control or surfactant addition is usually used to obtain stable and dispersed NPs (Hwang et al., 2008; Lan et al., 2007), such methods also involve drying at high temperature, which usually causes agglomeration. In gas-phase processes, NP agglomerates and aggregates are easily formed because the high temperature causes sintering. Agglomerations also occurs during condensation and particle collection in NP powder handling.

Control of the repulsive forces between NPs is therefore necessary in NP dispersion. Dispersion control in aqueous or organic solutions is based on the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory or excluded volume effect, respectively.

1.1.1 DLVO theory of dispersion
DLVO theory is based on the van der Waals interaction force \( V_A \) and electrostatic double layer repulsive force \( V_D \), which is generated by the surface charge of the particles. NP agglomeration and dispersion are explained using DLVO theory as follows.

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Fig. 1 shows the potential energy between particles \(V_T\) as a function of particle distance \(H\). When the distance between the particles is small, there is a potential energy minimum in the \(V_T\) curve (primary minimum). This distance is approximately 4 Å and it indicates an agglomerated state, which depends on the strength of the interparticle bonding, e.g., van der Waals interactions, electrostatic hydrogen bonding, and sintering. A secondary minimum potential also occurs when the distance between the particles is large (secondary minimum), indicating stable particle dispersion. When the potential barrier \(V_{\text{max}}\) between these two minimum potentials is 10–20 times larger than the kinetic energy \((kT)\), the dispersed NPs will be stably suspended in the secondary minimum state. When \(V_{\text{max}}\) is lower than the kinetic energy, e.g., the zeta potential of the particles is low, the dispersed particles easily revert to the primary minimum state.

When the particle size is in the nanoscale range, the \(V_A\) and \(V_R\) values become smaller than those of submicron particles. For example, when the particle size is one-tenth that of the submicron range, the potential becomes one-tenth that of the submicron particles. The energy required to disperse agglomerated NPs is lower than that required for submicron particles.

1.1.2 Excluded volume effect for dispersion

The dispersion of particles in an organic solvent is controlled by the dispersant and polymers, and dispersion control is explained based on the excluded volume effect theory. This theory refers to the phenomenon whereby two neighboring particles cannot occupy the same space in the surrounding dispersant because of steric hindrance or an impediment. In the case of spherical NPs, the closest distance to which two NPs can approach each other is equal to the sum of their radii. Dispersion and agglomeration can therefore be controlled by excluding this volume using dispersants. In the case of nanoscale particles, the energy required to approach the dispersed state from the agglomerated one, in which the NPs are surrounded by dispersant, is also lower than that usually observed for submicron particles.

1.2 Current status of NP dispersion

As explained above, agglomeration and aggregation are inevitable in NP synthesis. However, only well-dispersed NPs can be used for further applications as functional materials such as nanostructured particles and nanocomposite polymer materials (Ogi et al., 2014). Innovative techniques for liquid-phase production of well-dispersed NPs with specific concentrations, viscosities, and purities are therefore needed for practical applications.

The energy needed to disperse agglomerated particles to isolated ones consists of physical (mechanical) and chemical (surface modification) energies. The dispersion process also involves complete wetting of particles, and breakup of agglomerated/aggregated particles into primary particles, followed by particle stabilization. In principle, agglomerates can be broken up by applying compression or shear stress forces, and particle stabilization depends on the electrostatic repulsive force between the particles, or the excluded volume effect, influenced by stabilizing additives.

Table 1 shows widely used methods for NP dispersion. Agglomerated NPs are broken up using various machines by applying compression or shear stresses. Each type of

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1.2.1 Three-roller mill

Particles are stressed by a shear gradient arising from the different speeds of the rollers. For high concentrations and large agglomerates, the particles are not only stressed by the shear gradient but also by shear stress in the narrow gap between two rollers. In this condition, the stress force from one roller to the other roller is transferred through the particles. The stress intensity increases with decreasing particle size. (Schilde et al., 2010, 2011).

1.2.2 Media-less dispersion

Particle dispersion is performed using an agitated liquid flow such as sonication, cavitation, or ultrathin high shear dispersion. Such methods are called media-less dispersion. In the case of wet-jet milling, mixing and dispersion are carried out only by mutual collision of particles. Particles flowing in a slurry in an oblique direction at high pressure burst and collide. Dispersion by sonication causes cavitation effects. When a liquid sonicated at high intensities creates vacuum bubbles, which collapse violently, agglomerated particles are separated. Another dispersion technique that involves cavitation force is the use of high-pressure nozzle systems. Collapse of a cavitation bubble can create very high local pressure and release energy, which can break agglomerated particles. Another media-less method is ultrathin-film high-shear dispersion. An ultrathin film is formed along the walls of the vessel, where significant energy from centrifugal force is applied to break up agglomerated NPs.

This media-less dispersion system is appropriate for electronic materials such as battery slurries because it is a contamination-free method. However, in the case of NPs, this method does not give good dispersion because the differences between NP movements in liquid and fluid systems are small because of the low masses of the NPs. In other words, the force applied to the particles will be too small to break up agglomerated NPs. Another dispersion technique such as media dispersion is necessary to provide adequate force to the agglomerated NPs.

1.2.3 Media dispersion

In media dispersion, agglomerated NPs are broken up with the aid of a medium, which is classified as balls or beads, based on sizes of 0.1–40 mm and 0.015–0.5 mm, respectively. A ball mill machine is usually used for crushing large block particles to produce smaller particles for dispersion in a liquid. Bead mill are usually used for dispersion of agglomerated NPs (several micrometers) that are much smaller than the bead size. Collisions and shear stress between the moving beads during agitation cause separation of agglomerated NPs to their primary particles, as explained in detail in the next section.

Among dispersion machines, media dispersion is most widely used and effectively disperses many types of NPs, depending on the agglomerated state. According to the DLVO theory, a low potential energy is usually needed to separate two particles. If the energy is too high, the NPs will be damaged during dispersion. In media dispersion methods, control of the shear stress and collisions is therefore important to provide appropriate energy for dispersion. Bead mill machines usually use a mesh or slit method for separation of dispersed NPs from the beads, and therefore the bead size limit is above 0.1 mm, which is too large with respect to the NP size. This condition results in supply of too much energy to the dispersion system.

Our groups have therefore developed low-energy bead mill methods. Unlike the usual machines, a centri-separator is used for bead separation, and therefore very small beads (7–50 μm) can be used for NP dispersion. The energy that the NPs receive from collisions and shear of beads can be reduced, and therefore particle breakage/damage can be minimized. Only small beads can produce a low dispersion energy. In the following sections, three types of low-energy bead mill processes are explained in detail. The effects of the experimental conditions, i.e., particle shape (spherical, rod, core–shell), rotation speed, and dispersion time, are also discussed, as well as accompanying phenomena such as dispersion coloring.

2. Low-energy bead mill dispersion

Low-energy bead mill dispersion can be understood using the simple model shown in Fig. 2. This model is only applicable when the primary NP size is smaller than 100 nm and the bead size is smaller than 50 μm. Step (i) shows the initial condition of the beads before NP dispersion. The beads move and rotate during agitation. Step (ii) involves collisions between the beads and NPs and application of stress to the agglomerated NPs. After breakup of the aggregated NPs, the surfaces of the isolated NPs become active (formation of activated sites). Step (iii) involves stabilization of the isolated NPs by creating a repulsive force, for example, using a dispersant or zeta potential, to the active sites. The active surface is inhibited by the dispersing agent or zeta potential in the suspension and stable dispersion is achieved. In multicollision phenomena, bead milling affords highly dispersed NPs. This condition can be achieved only when the collision force and shear stress are not too strong. Control of the bead size and rotation speed (very small size and ~3–8 m/s, respectively) is important. Outside these ranges, the energy pro-
vided to the NPs is too high, which results in NP breakage and reagglomeration. Our group has developed three types of bead mill methods, classified based on the provided dispersion energy level, namely, uniaxial, dual-axial, and all-separator bead mills. These are described in the following sections.

2.1 Uniaxial bead mill

The first low-energy bead mill to be developed was a uniaxial bead mill (UAM) (Inkyo et al., 2006). A schematic diagram of a UAM is shown in Fig. 3. The apparatus consists of a 0.15 L vessel, a pump for supplying a slurry, and a slurry tank. The vessel contains a rotor pin and separator, which are set in the lower and upper portions of the vessel, respectively. The vessel is enclosed in a cooling jacket to prevent temperature increases in the system, and is completely sealed from the outside environment. ZrO$_2$ beads of size 7, 15, 30, and 50 $\mu$m are used as the medium (Fig. 4). The ZrO$_2$ beads occupy 65% of the vessel volume. The dispersion process is explained as follows.

A slurry containing agglomerated NPs is pumped into the bead mill vessel and through to the lower part. In this part, agglomerated NPs interact with the agitated beads, and the agglomerated NPs are dispersed by collisions and shear stress between the beads. Gradually, the slurry reaches the upper part of the vessel. In this region, separation is performed using a centri-separator, in which the dispersed NPs are separated from the beads by centrifugal force. The beads remain inside the mill, and the NP slurry is pumped out of the vessel. The product particles are collected in the slurry tank and the dispersion process is repeated.

2.1.1 Dispersion behavior of TiO$_2$ NPs using UAM

This UAM was used for the dispersion of needle-type TiO$_2$ NPs in water (Inkyo et al., 2006). The effects of bead size, dispersion time, and rotation speed on particle breakage and the particle size distribution were investigated; the results are shown in Fig. 5(a). For all the tested beads except those of size 15 $\mu$m, the particle size distribution shifted to smaller sizes, and then gradually shifted back to larger sizes, indicating that the agglomerated NPs were dispersed, followed by reagglomeration of the dispersed NPs. Reagglomeration may be caused by activation of the particle surfaces newly generated by the milling process, followed by interactions among broken particles. Breakup of the agglomerated NPs significantly increases the particle concentration in the slurry, which in
turn significantly reduces the characteristic coagulation time for particles.

When 100 and 50 μm beads were used, no particles were dispersed to primary particles, showing that the collision force from large beads is too high and damages the particles, followed by reagglomeration of broken particles. The particle size distribution shifted from a unimodal distribution to a bimodal distribution for processing times longer than 240 min. This sudden change in the size distribution cannot be explained by any traditional particle agglomeration mechanism. A possible reason for the shift from a unimodal to a bimodal size distribution is that the broken NPs are deposited on the beads and then grow increasingly large as collisions continue to occur. Once the deposits of broken NPs achieve sufficient size, further collisions may cause these NP deposits to break away from the beads, and the broken NPs agglomerate. These results show that the breakup of agglomerated NPs is eventually followed by reagglomeration. There is therefore an optimum milling time for each dispersion with each bead size before reagglomeration occurs, as indicated by the particle size distribution shifting to larger size. In the cases of 30 and 15 μm beads, the agglomerated NPs were completely dispersed and a sharp peak at 15 nm appeared as the minimum particle size distribution.

The changes in particle size as a function of dispersion time for various bead sizes are shown in Fig. 5(b). In this experiment, spherical TiO₂ NPs were also dispersed for comparison. In general, both needle and spherical TiO₂ NPs have the same dispersion behavior.

The particle size gradually decreased as the dispersion time increased, and reached the primary particle size, indicating that the agglomerated NPs were dispersed to primary particles. When excessive energy was provided to the dispersed NPs, the particle size gradually increased, indicating that the primary particles were damaged and broken, resulting in reagglomeration of broken particles. The spherical TiO₂ NPs were easier to disperse than the needle ones. For 8 μm beads only, the agglomerated spherical TiO₂ NPs were dispersed to their primary particles without reagglomeration.
These results are confirmed by transmission electron microscopy (TEM) analysis of the NPs before and after dispersion (Fig. 6). Before dispersion, the TiO$_2$ NP agglomerates were of size 200–300 nm and rod-shaped, like the primary particles. After dispersion with 15 and 30 μm beads, well-dispersed rod-shaped TiO$_2$ NPs were obtained. Beads of size 50 and 100 μm had little effect on the size of the NP agglomerates. Furthermore, the particle morphology changed from rod-shaped to spherical when 100 μm beads were used.

The detailed effects of rotation speed, bead size, and dispersion time on the dispersibility of rod-type TiO$_2$ NPs were reported by Tahara et al. (2014). In this study, two rotation speeds (10 and 8 m/s) and various bead sizes (15–50 μm) were used for TiO$_2$ NP dispersion. At the same rotation speeds, the size of the dispersed particles decreased with increasing dispersion time. The size of the agglomerated NPs decreased rapidly in the initial stage (30 min) and then the particle size changed gradually during dispersion.

At the same rotation speed, larger beads promoted the formation of smaller particles. For the samples dispersed at a rotation speed of 10 m/s and a bead size of 50 μm, the particle size decreased until 330 min and then gradually increased with milling time. This is possibly because of reagglomeration of broken NPs during milling.

The morphologies of the particles after dispersion using various bead sizes and rotation speeds are shown in Fig. 7. Various morphologies are observed, depending on the rotation speed and bead size. At rotation speeds (m/s)/bead sizes (μm) of 8/15 and 8/30, the TiO$_2$ particles retain their rod shape after bead milling. However, under other conditions, the morphology of the TiO$_2$ NPs changed from rod shaped to ellipsoidal, and the particle size decreased. For the conditions 8/15 and 8/30, TEM images showed no change in the crystallinity of the particles after dispersion; this was confirmed by X-ray diffraction (XRD) analysis. These results show that the conditions 8/15 and 8/30 effectively provide low energy for dispersion, producing dispersed agglomerated NPs without changing the particle crystallinity. NP dispersion in an organic solvent has also been reported (Joni et al., 2009). Fig. 8 shows scanning electron microscopy (SEM) images of TiO$_2$ NPs dispersed in diethylene glycol dimethyl ether (diglyme).

Fig. 9 shows a diagram of the morphological and struc-
Fig. 7  TEM images of TiO$_2$ NPs (a) before and (b–g) after bead milling; rotor speed (m/s)/bead size (μm) (b) 8/15, (c) 8/30, (d) 8/50, (e) 10/15, (f) 10/30, and (g) 10/50. Reprinted with permission from Tahara et al., 2014. Copyright: (2014) Elsevier B.V.

Fig. 8  SEM images of TiO$_2$ NPs (a) before and (b–d) after bead milling in organic solvent as a function of milling time: (b) 60, (c) 90, and (d) 120 min. Reprinted with permission from Joni et al., 2009. Copyright: (2009) American Chemical Society.
tural changes in NPs during bead milling depending on supplied energy (high energy or low energy). Low-energy dispersion defines the condition for bead milling that provide the breakup of agglomerated NPs (not grinding/crushing). High-energy dispersion defines the condition that damages the NP structure and changes the inherent properties of the NPs. Although high-energy dispersion enables rapid breakup of agglomerated NPs, the main body (the material itself) is damaged and broken (destruction of crystal). As a result, the dispersed solution contains multi-sized particles. Because of the high energy, this condition cannot be used for fragile materials such as metal, hollow, and core–shell structured particles. The milling time is also important. A milling time that is too long leads to reagglomeration. NPs are typically softly agglomerated, and therefore the optimum conditions that enable breakup of agglomerated NPs at the agglomerating position only are crucial. In low-energy dispersion processes, the slurry contains single-sized NPs with the inherent material properties.

During bead mill dispersion, the physicochemical properties of the particles may change. These changes are caused by decreases in the particle crystallinity during bead mill dispersion. During bead mill dispersion, collisions between beads and agglomerated TiO₂ particles provide energy that can break the main body of the crystal, resulting in production of smaller particles and an amorphous phase on the crystal surface, and this changes the properties of the dispersed particles (bottom image in Fig. 9).

Based on the above results, several operating parameters should be considered for providing low-energy dispersion in bead mill processes, including milling time, temperature, bead and particle sizes, rotation speed, physicochemical properties, and composition of dispersed media and agglomerated particles. Low energy can be obtained when the milling process is conducted at less than 0.50 μW/bead. This condition can be achieved when the process is conducted below a rotational speed and bead size of 10 m/s and 30 μm, respectively. Deviation from these conditions results in reagglomeration, production of broken particles, and impairment of the crystallinity and physicochemical properties of the NPs.

2.1.2 Dispersion of boron nitride NPs using UAM

Hexagonal boron nitride (hBN) NPs are an indispensable material for many industrial applications because of their properties such as high thermal conductivity, low thermal expansion, good thermal shock resistance, high electrical resistance, low dielectric constant and loss tangent, and microwave transparency. When inorganic hBN NPs are used as inclusion particles for reinforcement, dispersion is very important. Poorly dispersed hBN NPs in suspension will not give nanostructured materials with excellent properties.

Our group successfully dispersed hBN NPs of primary particle size 35 nm using a UAM, as shown in Fig. 10. Two silane coupling agents, i.e., (3-acryloxypropyl)trimethoxysilane (A-TES) and (3-acryloxypropyl)triethoxysilane (A-OTES), were used to improve the dispersion. The dispersion was conducted under a vibro-rotating condition to obtain a homogenous slurry. The obtained slurry was used to produce a hot-pressing compact, and the achieved hardness was compared with the hardness of the control sample.

Fig. 9 Diagram of morphological and structural changes in NPs during bead milling depending on supplied energy. Reprinted with permission from Tahara et al., 2014. Copyright: (2014) Elsevier B.V.
thoxysilane (APMS) and trimethoxy(propyl)silane, were used for surface modification to enhance the dispersion stability (Joni et al., 2011). Optimization of the rotation speed, slurry flow rate, and dosage of dispersing agent gave agglomerated hBN NPs that were well dispersed to primary particles. A highly dispersed hBN suspension, with a zeta potential below ~ +40 mV, was prepared using APMS as the dispersing agent. The bead mill process did not significantly change the crystallinity and chemical composition of the hBN NPs, but enhanced the dispersion stability (Joni et al., 2011).

2.2 Dual-axial bead mill

Because of the limited bead sizes available with UAM, dual-axial bead mills (DAM) were developed. A schematic diagram of a DAM is shown in Fig. 11. Unlike the case for a UAM, the separator and rotor pin are separated, and therefore they can run independently. Details of this bead mill were reported by Tahara et al. (2011). Use of a DAM enables the rotation speed to be controlled to be lower than the separator speed, allowing the use of smaller beads to provide a lower dispersion energy.

A DAM was used for the dispersion of rod-shaped TiO$_2$ NPs. Fig. 12 shows the effect of the rotor pin rotation speed in the range from 12 to 3 m/s on dispersion using beads of size 50 μm and separator speed 12 m/s. At a low rotation speed (3 or 6 m/s), the particle size was reduced to 30 nm, indicating that the agglomerated NPs were dispersed to the primary particle size without reagglomeration. At a rotation speed higher than 6 m/s, rod-shaped TiO$_2$ NPs were broken into ellipsoidal shapes and the particle size increased as dispersion continued. Under these conditions, the TiO$_2$ NPs were damaged and then reagglomeration occurred because of the strong interactions among active broken surfaces.
2.3 All-separator bead mill

Even a DAM has limitations in the dispersion of more fragile NPs such as core–shell NPs. In the cases of a UAM and DAM, well-dispersed NPs are crushed in the separator, in which high energy is needed to separate small beads from dispersed NPs.

Another type of low-energy bead mill apparatus was therefore developed, i.e., an all-separator bead mill (ASM). An ASM consists of only a separator, which is aligned from the bottom to the upper part, without a rotor pin, in the vessel. This new apparatus enables lower-energy dispersion at lower rotation speeds with smaller beads.

A schematic diagram of an ASM is shown in Fig. 13. Our group used an ASM to disperse agglomerated core–shell α’-Fe/Al₂O₃ and α”'-Fe₁₆N₂/Al₂O₃ magnetic NPs (Zulhijah et al., 2015). Core–shell α”'-Fe₁₆N₂/Al₂O₃ magnetic NPs, the magnetic material with the highest reported saturation magnetization, have good potential for the construction of high-magnetic-moment rare-earth-free magnetic materials. However, α”'-Fe₁₆N₂ magnetic NPs have strong magnetic lateral interactions between NPs; this enables easy NP agglomeration, and decreases their magnetic performance after structuring. The dispersion process is therefore the key to preparing dispersed single-domain magnetic NPs.

Fig. 14(a) shows TEM images of α”'-Fe₁₆N₂ NPs before and after dispersion using different bead sizes and rotation speeds. When the energy supplied was insufficient to break up the agglomerated particles, the particle size was almost the same as the initial one. When sufficient energy was supplied to the agglomerated NPs, the agglomerates were broken up into primary particles without destroying the core–shell structure. The crystal structure of the core–shell particle after dispersion was the same as that of the original NPs, as shown in Fig. 14(b). When the applied dispersion energy was too high, rapid breakup of the agglomerated particles on either the agglomeration boundary or main body of the particles occurred, resulting in particle destruction.

The magnetic properties of core–shell α”'-Fe₁₆N₂/Al₂O₃ NPs before and after dispersion were also evaluated (Fig. 14c). The saturation magnetization of the particles after
dispersion was similar to that of the particles before dispersion. Different hysteresis was found for the well-dispersed NPs when magnetization relaxation occurred abruptly near zero applied field. This indicates spin coupling of the neighboring magnetic NPs by release of the magnetically decoupled restriction of the high magnetic field, which can be caused by movement of the particles and magnetic moment during measurement (Zulhijah et al., 2015). The morphological changes in the agglomerated core–shell α''-Fe₂₃N₂/Al₂O₃ NPs are shown in Fig. 15.

A summary of the characteristics, i.e., mean particle diameter, concentration, and viscosity, of NP dispersions prepared by bead milling is shown in Fig. 16.

3. Selection of dispersant

As mentioned above, dispersion in organic solvents is also controlled by the excluded volume effect. The presence of a dispersant that interacts with the particle surface controls the excluded volume and prevents interaction between particles. Selection of an appropriate dispersant is therefore crucial for obtaining stable NP dispersions. However, there is a lack of systematic information on dispersant selection, and selection is based on experience and experimental results.

During dispersion, agglomerated NPs are broken up and then the particle surfaces become active sites. An appropriate surfactant will have good attractive forces with the active sites of the particles and solvent. All of the active sites on the particle surface will then bond with the surfactant, resulting in repulsive forces between the particles, and these prevent reagglomeration. Fig. 17 shows a diagram of dispersant selection for NP dispersion.

Dispersants can be divided into two classes according to their chemical structures: polymeric dispersants and surfactants. The primary differences between polymeric dispersants and surfactants are their molecular weights, stabilization mechanisms, and stabilities. Polymeric dispersants stabilize systems sterically. They have a two-component structure, which must meet the following requirements. (1) They can strongly adsorb on particle surfaces and have specific anchoring groups. (2) They contain polymeric chains that sterically stabilize the solvent or solution system.

In contrast, the stabilization mechanism of surfactants is electrostatic: the polar group forms an electrostatic double layer and produces a coating around the particles. Because of the electrostatic stabilization mechanism and chemical structure of surfactants, the final coating tends to be water sensitive.

The effectiveness of a polymeric dispersant is deter-
mined by the anchoring groups on the surface. The anchoring groups can be an amine, carboxylic, sulfonic, or phosphoric acid, or their salts. The crucial requirement is that the chains are successfully anchored to the particle surfaces, and particle surfaces are covered with sufficiently dense chains. The chains must have attractive forces with both the particle surfaces and the solvent, in the presence or absence of a polymer (Takeda et al., 2009).

In general, surfactants are selected based on their polarity and molecular weight, as shown in Fig. 17. The characteristics of a surfactant depend on its polarity and molecular weight. An appropriate surfactant for a system...
can therefore be identified. The various types of surfactant and their applications in NP dispersion are listed in Table 2.

A summary of the use of bead mills and the dispersant types used in dispersion of various NPs is shown in Table 3.

4. Optical properties of NP dispersions

4.1 Coloring of NP dispersion

One of the problems with NP dispersions is that their suspensions are colored (Fig. 18). For example, well-dispersed TiO$_2$ NPs in an organic solvent, i.e., diethylene glycol dimethyl ether, are yellow. This suspension is not suitable as an alternative material to glass, because such materials must be colorless and transparent. NP dispersions may be colored because of their complex physicochemical properties (refractive index, bandgap, chemical functions), the dispersing agent, and the solvent.

Fig. 19 shows possible reasons for coloring of NP dispersions. First, Rayleigh scattering of NPs is strongly related to the color of the NP suspension. Rayleigh scattering involves the predominantly elastic scattering of light or other electromagnetic radiation by particles much smaller than the radiation wavelength. The intensity $I$ of light scattered by a small sphere of diameter $d$ and refractive index $n$ from a beam of unpolarized light of wavelength $\lambda$ and intensity $I_0$ is given by

$$I = I_0 \frac{1 + \cos^2 \theta}{2R^2} \left(\frac{2\pi}{d}\right)^4 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 \left(\frac{d}{2}\right)^6$$  \hspace{1cm} (1)$$

where $R$ is the distance to the particle and $\theta$ is the scattering angle. In the case of a spherical particle, the scattering intensity increases in direct proportion to the sixth power of the particle size and in inverse proportion to the fourth power of the light wavelength. A shorter wavelength (blue) is easier to scatter than a longer wavelength (red). Undispersed TiO$_2$ NPs are white as a result of scattering of all visible wavelengths (sun or room light). In the case of a highly dispersed NP suspension, the transparency is increased because light is not scattered. However, if agglomerated NPs are present in the suspension, only blue light is scattered and yellow light is transmitted as a complementary color. The optical transparency loss of a suspension therefore depends on the average particle size and the presence of aggregates.

The second possible reason is the inherent properties of NP materials. The bandgap of rutile TiO$_2$ is 3.0 eV and it has an absorption edge at around 413 nm (form purple to blue). If the material has lattice defects and impurities in the crystal structure, impurity levels are formed in the bandgap, and the material absorbs light of wavelength longer than 413 nm. This is why blue light is absorbed by TiO$_2$ NPs and yellow light is transmitted as a complementary color (Fig. 19b). High crystallinity and doping of TiO$_2$ NPs effectively changes their bandgap (absorption edge).

The third reason is attributed to the structure and functions of the dispersing agent. In our experiment, KBM 5103(3-Acryloxypropyl-trimethoxysilane) was used for TiO$_2$ NP dispersion. The double bond in KBM 5103 can react with oxygen radicals to form carbon–oxygen radical bonds, as shown in Fig. 19(c). These bonds can cause chemical coloring of the NP dispersion. Selection of an...
appropriate dispersing agent, i.e., without double bonds, is key to avoiding coloration. The use of polymerization inhibitors, which are also considered to cause coloration, should also be avoided.

4.2 Decoloring of NP dispersions via UV irradiation

Joni et al. (2012b) reported a method for decoloring a yellow suspension of rutile needle TiO<sub>2</sub> NPs in an organic solvent (diethylene glycol dimethyl ether). Well-dispersed rod-type TiO<sub>2</sub> NPs of diameter and length 15.5 and 109 nm, respectively, were successfully prepared using a UAM. Although the bead-milled TiO<sub>2</sub> NPs were well dispersed in the organic solvent, the solution was yellow. The color was removed by UV irradiation. After dispersion, the suspension was illuminated under UV irradiation (λ = 254 nm) for 5 h. Fig. 20(a) shows the transmittance properties of the dispersed TiO<sub>2</sub> NPs before and after UV irradiation. UV irradiation changed the surfaces of the

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Nanoparticles</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic surfactant</td>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(Du L. et al., 2013; Hait S. and Chen Y., 2014)</td>
</tr>
<tr>
<td>Carbonate (Na stearate)</td>
<td>FeO, Ag, Cu,</td>
<td>(Saterlie M.S. et al., 2012; Wang W. et al., 2014; Zong B.-Y. et al., 2014)</td>
</tr>
<tr>
<td>Phosphate salt</td>
<td>CNC, CoFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, γ-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(Kovalenko A. et al., 2014; Salajková M. et al., 2012; Tang B.Z. et al., 1999)</td>
</tr>
<tr>
<td>Sulfonate salt (SD)</td>
<td>Ag</td>
<td>(Sondi I. et al., 2003)</td>
</tr>
<tr>
<td>Cationic surfactant</td>
<td>Laponite,</td>
<td>(Li W. et al., 2012)</td>
</tr>
<tr>
<td>Aromatic Quaternary amine salt</td>
<td>Ag</td>
<td>(Sondi I. et al., 2003)</td>
</tr>
<tr>
<td>Nonionic surfactants</td>
<td>ZnS</td>
<td>(Naskar M.K. et al., 2006)</td>
</tr>
<tr>
<td>Ester type (span)</td>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, acrylamide</td>
<td>(Guha S. and Mandal B.M., 2004; Guskos N. et al., 2005)</td>
</tr>
<tr>
<td>Ether type (PEG dodecyether)</td>
<td>Pt, Ag</td>
<td>(Ingelsten H.H. et al., 2001; Sondi I. et al., 2003)</td>
</tr>
<tr>
<td>Polymer (brushing polymer)</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;, Ag, Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, BaTiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>(Hajdú A. et al., 2012; Pu Z. et al., 1997; Shen Z.-G. et al., 2004; Zhang Z. et al., 2000)</td>
</tr>
<tr>
<td>Polyurethane, polyester type</td>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>(Ashjari M. et al., 2010)</td>
</tr>
<tr>
<td>Poly(N-isopropyl acrylamide)</td>
<td>Ag</td>
<td>(Dong Y. et al., 2007)</td>
</tr>
<tr>
<td>Fluoride surfactant</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(Yang J. et al., 2011)</td>
</tr>
<tr>
<td>Perfluoroocanoic acid</td>
<td>Ag, polyampholyte</td>
<td>(Fan X. et al., 2006; Thünemann A.F. et al., 2002)</td>
</tr>
<tr>
<td>Silicone (silylating agent)</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>(Ouyang G. et al., 2012)</td>
</tr>
<tr>
<td>Propyltrimethoxysilane (TMS)</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;, SiO&lt;sub&gt;2&lt;/sub&gt;, BTO</td>
<td>(Luo K. et al., 2008; Nomoto H. et al., 2014; Yang X. and Liu Z.-H., 2010)</td>
</tr>
<tr>
<td>Coupling agent</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;, Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, ZnS</td>
<td>(Warad H. et al., 2005; Zhang Y. et al., 2008)</td>
</tr>
</tbody>
</table>
dispersed TiO$_2$ NPs (1 wt%), indicated by a change in the solution color from yellow to colorless and transparent (Joni et al., 2012b).

Optical scattering loss is avoided if the particle mean diameter is less than one-tenth the length of the visible-light wavelength (200–800 nm), typically < 25 nm. In these experiments, the particle size in the dispersed suspension was 25 nm, and therefore the contribution of the particle size to optical transparency loss can be neglected. The main factors responsible for the strong light scattering loss of the suspension are therefore the refractive indices of the particles and the matrix. Surfactant desorption

<table>
<thead>
<tr>
<th>Material</th>
<th>Solvent</th>
<th>Dispersant</th>
<th>Conc. (wt%)</th>
<th>Particle size (before bead mill)</th>
<th>Particle size (after bead mill)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Water</td>
<td>—</td>
<td>10</td>
<td>140</td>
<td>25</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Diglyme</td>
<td>Trimethoxypropyl silane</td>
<td>1.0–10</td>
<td>1000</td>
<td>15</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>MMA/Toluene</td>
<td>3-Acryloxypropyl trimethoxysilane</td>
<td>1.0–15</td>
<td>&gt; 100000</td>
<td>90–150</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Neo pentyl glycol dimethacrylate</td>
<td>Butyl acetate</td>
<td>10</td>
<td>85</td>
<td>50</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>Neo pentyl glycol dimethacrylate</td>
<td>Polymeric dispersant solperse</td>
<td>10–20</td>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>BN</td>
<td>Water</td>
<td>3-Acryloxypropyl trimethoxysilane</td>
<td>0.5</td>
<td>1000–3000</td>
<td>46</td>
</tr>
<tr>
<td>Al(OH)$_3$</td>
<td>MMA</td>
<td>3-Acryloxypropyl trimethoxysilane</td>
<td>1.0–10</td>
<td>750</td>
<td>210</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Methanol</td>
<td>3-Acryloxypropyl trimethoxysilane</td>
<td>4</td>
<td>1000–10000</td>
<td>12</td>
</tr>
<tr>
<td>ZnO</td>
<td>Toluene</td>
<td>—</td>
<td>1.0</td>
<td>1000–10000</td>
<td>10</td>
</tr>
<tr>
<td>ITO</td>
<td>Toluene</td>
<td>—</td>
<td>1.0</td>
<td>1000–10000</td>
<td>20</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Toluene</td>
<td>—</td>
<td>1.0</td>
<td>1000–10000</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 18 Coloring of highly dispersed NP slurries: (a) TiO$_2$ (15 nm); (b) ZrO$_2$ (20 nm); (c) indium-tin oxide (ITO) (20 nm); and (d) BaTiO$_3$ (20 nm).
was suggested to be the main cause of changes in the refractive index of the matrix, caused by excess surfactant in the organic solvent. UV irradiation of the suspension resulted in matching of the refractive indices of the particles and the organic solvent. Optical scattering loss was therefore avoided, and the prepared suspension was colorless and transparent.

4.3 Decoloring of NP dispersions via nitrogen doping

Another method for preparing colorless suspensions of TiO$_2$ NPs in organic solvents is nitrogen doping. Joni et al. reported a study of the synthesis of nitrogen-doped TiO$_2$ NPs and their dispersion in an organic solvent (diethylene glycol dimethyl ether), with 3-(acryloyloxy)propyltrimethoxysilane as the dispersing agent, using bead milling (Joni et al., 2012a). Yellow nitrogen-doped TiO$_2$ NP powders were prepared by combustion of a mixture of rutile TiO$_2$ NPs and urea at 800 °C, and then dispersing the NPs using a UAM.

Fig. 20(b) shows photographs and the UV-vis transmissions of dispersed solutions of nitrogen-doped and bare rutile TiO$_2$ NPs. The bare rutile TiO$_2$ NP suspensions were yellow. When the materials were doped with nitrogen, the resulting TiO$_2$ suspensions were colorless (Joni et al., 2012a). This change in color and transparency as a result of nitrogen doping of TiO$_2$ NPs can be explained by Rayleigh scattering, as follows. According to the Rayleigh law, if the volume fractions are assumed to be the same, the particle sizes and refractive indices of the particles...
and monomer (solvent) can be used to reduce the scattering loss and improve the transparency. The refractive indices can be controlled by choosing appropriate fillers and solvents, and through design of the interface. The particle size has to be considerably less than the wavelength of the visible light. As explained above, optical scattering loss can be avoided if the particle domain size (typically < 25 nm) is less than one-tenth of the visible-light wavelength. Ideally, TiO₂ should therefore have a diameter < 10 nm to avoid coloring issues.

The suspension of bare TiO₂ particles in diethylene glycol dimethyl ether was not transparent, and was yellow because of the presence of some large aggregates of TiO₂ NPs (> 100 nm). These aggregates led to strong light scattering in the visible region. In contrast, in the case of a nitrogen-doped TiO₂ NP dispersion, the particles were smaller and monodispersed, which considerably improved the transparency, and reduced the color, of the suspension.
However, a small percentage of nitrogen-doped TiO$_2$ was present as aggregates (>100 nm), indicating that the transparency was not only dependent on the particle size but was also affected by the interfacial properties. These results suggest that nitrogen atoms on the TiO$_2$ surface also contributed to the lack of color and transparency of the suspension.

5. Applications of NP dispersions

Many reports have shown that composite formation with NPs can alter the thermomechanical properties of polymers, such as the elastic modulus, viscosity, and glass-transition temperature, and the optical properties. NP–polymer composites can be synthesized by dispersing NPs in the monomer and polymerizing in the presence of the NPs.

5.1 Poly(methyl methacrylate)-TiO$_2$ nanocomposites

Inkyo et al. (2008) studied the synthesis of poly(methyl methacrylate) (PMMA)–TiO$_2$ NP composites. TiO$_2$ NPs were dispersed in MMA monomer using a bead mill, followed by polymerization to form PMMA–TiO$_2$ nanocomposites, as shown in Fig. 21(a). The TiO$_2$ NPs were well dispersed in the MMA monomer, and therefore transparent composites were formed. In contrast, PMMA–TiO$_2$ nanocomposites synthesized from undispersed TiO$_2$ NP suspensions were opaque.

SEM confirmed that the TiO$_2$ NPs were evenly distributed in the composite, as shown in Fig. 21(b), unlike the case for a composite comprising undispersed TiO$_2$ NPs. Well-dispersed TiO$_2$ NPs enhanced the UV-absorbing properties of MMA and increased its thermal stability. Because these PMMA–TiO$_2$ nanocomposites are transparent and have high refractive indices, they have good potential optical applications.

Our group has also developed TiO$_2$-dispersed nanocomposite polymer films with a high concentration of TiO$_2$ (65 wt%), as shown in Fig. 21(c) (Takeda et al., 2009). bead mill dispersion was used to prepare finely dispersed TiO$_2$ NPs in the polymer; two monomers (neopentyl glycol dimethacrylate or divinylbenzene) and an organic solvent (butyl acetate) were used as the dispersing medium. The prepared films (thickness: 5 μm) were transparent (81.5%) and had a high refractive index (1.85). These films had smoother surfaces than films prepared by direct dispersion without bead milling.

Takeda et al. successfully prepared TiO$_2$ nanocomposite microspheres of high concentration (40 wt%) with acrylic monomer, as shown in Fig. 21(d). These TiO$_2$ NPs were dispersed in butyl acetate by bead milling. The TiO$_2$ nanocomposites were prepared by replacement of butyl acetate with the monomer used as the medium. The TiO$_2$ NPs were close packed and well distributed, without any vacancies in the microspheres (Takeda et al., 2008).

5.2 PMMA–aluminum trihydroxide nanocomposites

Aluminum trihydroxide (ATH) is an attractive alternative to halogen-based flame retardants, which give off heavy smoke and hazardous gases during combustion. The use of these NPs as a filler in polymers such as PMMA, which is widely used as a shatterproof replacement for glass and in surface coatings, improves the thermal stability and mechanical properties of the polymer. The size and dispersibility of the filler (NPs) in the polymer are important in obtaining high-performance materials.

Our group used bead mill dispersion to control the size distribution of an ATH NP filler in MMA. A dispersed solution was obtained by surface modification of ATH NPs using a silane-based dispersing agent, (3-acryloxypropyl) trimethoxysilane (APTMS). In the final product, the ATH NPs were well dispersed in the PMMA, as confirmed by TEM and digital photographs (Fig. 22a, b). The mechanical properties and thermal stability of the PMMA–ATH nanocomposite were also investigated (Fig. 22c). The storage modulus of the PMMA–ATH nanocomposite in the glassy state was larger than that of pure PMMA. In the composite reported by Joni et al. (2010), the storage modulus increased with increasing amount of ATH NP filler.

6. Conclusion

NP dispersion is an important technique in the synthesis of functional NP materials for practical applications. NP dispersion is also essential for NP assembly and structuring. In this paper, recent progress in the development of bead mill processes for NP dispersion was reviewed. The bead mill machines described here enable the use of smaller beads (5–50 μm) than those normally used. These small beads have a lower dispersion energy and minimize damage to the shape and crystal structure of the NPs. This is a significant advantage and enables NPs to show their inherent superior material properties. Because of their capacity of large-scale operating capacities (10–30 L), these low-energy dispersion machines are now used in many industries. However, the following problems have become apparent: 1) how to find appropriate dispersants efficiently; 2) how to control coloring phenomena of NP dispersions; and 3) how to disperse fragile NPs (metal NPs and hollow NPs) without breaking their structures. NP dispersion using lower dispersion energies should help
To overcome these problems; this would broaden the range of industrial applications of NPs.

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