Mixing Nanomaterials

➤ **Various mixing technologies are available for the efficient processing of products containing nanoceramics and other nanomaterials.**

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Nanomaterials are finding their way into an increasing number of modern products. Manufacturers benefit from introducing small amounts of nanomaterials into their products to enhance existing properties or provide new functionalities. This trend does come with a new set of unique processing challenges, however, including the efficient mixing and dispersion of nanoparticles into a formulation.

Nanomaterials Defined

By loose definition, nanomaterials are structures of 100 nanometers or smaller in at least one dimension. To put that scale into context, consider that a human hair is approximately 80,000 nanometers in diameter.

Nanomaterials possess novel quantum mechanical properties because of their size. For instance, an increase in the ratio of surface area to volume translates to an exponential increase in the portion of constituent atoms at or near the surface, which then creates more sites for bonding or reaction with surrounding materials. This results in improved properties such as increased strength and greater chemical or heat resistance.

In the production of coatings, nanopigments increase transparency, gloss, and smoothness, as well as resistance to scratching, corrosion, and ultraviolet radiation. Innovations in nanomaterials are also driving advances in battery technology by increasing capacity, improving cyclability, and enhancing rate capability and mechanical toughness. The technical breakthroughs of nanomaterials apply to many additional markets as well. In reality, "nanotechnology" is more a set of technologies than an industry itself, because it impacts virtually all process industries.

Ceramics comprise a significant group of nanomaterials; these are split into metal oxide ceramics (such as titanium, zinc, aluminum and iron oxides) and silicate nanoparticles (nanoclays). Various mixing technologies are available to manufacturers for the efficient processing of products containing nanoceramics and other nanomaterials.

Low-Viscosity Nanodispersions

The dispersion of nanomaterials into a low-viscosity formulation typically involves a pre-mix stage to combine the raw materials. This is done with the use of low-speed propellers, turbines, or simple agitators. Due to attractive forces between the individual nanoparticles, "wetting out" (i.e., combining the particles with the liquid vehicle) only disperses agglomerates of the nanoparticles. High shear forces are necessary to break up groups of these agglomerates.

How aggressive those shear forces need to be can vary from one formulation to another. The premix can be fed into a high-pressure homogenizer, a colloid mill, or an ultra-high-shear mixer (UHSM) for creating the final dispersion. Of the three devices, UHSMs are the newest solution in nanoprocessing. (The UHSMs' interchangeable mixing heads are detailed in the sidebar on p. 11.)

In certain applications, UHSMs effectively replace high-pressure homogenizers and colloid mills. Manufacturers often welcome the change because high-pressure homogenizers and colloid mills are high-maintenance machines that require a labor-intensive cleanup procedure during crossovers of different batches. In addition, UHSMs cost less up front, and throughput rates of a similarly powered UHSM are far greater than a high-pressure homogenizer or colloid mill.

Figure 1. The ported rotor generates an intense vacuum that draws hard-to-disperse powders such as fumed nanosilica into the mix chamber. The powders are injected directly into the high shear zone and dispersed into the liquid stream.

One application that has proven to be successfully processed in an UHSM is polyol filled with carbon nanotubes. In their dry form, nanotubes appear pearl-like and not very dusty. The "pearls" are actually bundles of nanotubes, and the mixing objective is to detangle the strands and disperse them in the liquid vehicle. The exposure of as much of the nanotubes' surface as possible gives rise to enhanced electrical and thermal conductivity, as well as excellent mechanical load-bearing capacity.

Carbon nanotubes are improving a variety of end products from aircraft components and computer chips to batteries and sports equipment. Compared to traditional fillers, which can be relatively spherical particles, carbon nanotubes have a higher aspect ratio (the ratio of its longer dimension to its shorter dimension) and can provide the same conductivity in much lower loadings. High filler loadings in a polymer tend to result in brittleness, an issue that can be averted by using carbon nanotubes.

In one lab test, the resin-nanotube premix was recirculated through the MegaShear. The mixture progressively became more viscous and glossier in appearance, and a rise in temperature further indicated the intense shear imparted to the product. A look at the sample under the microscope showed significant debundling of the nanotube strands.

Not all nanoparticles require extreme shear to go into dispersion. Some materials need only mild stirring but may require elevated temperatures or several hours of gentle agitation. One example is nanoclay in caprolactam, a raw material used in the production of synthetic fibers. At relatively low levels (less than 5%), nanoclay is reported to improve mechanical, thermal and gas barrier properties of the final polymer product.

Caprolactam monomer (a solid in room temperature) is melted, and nanoclay is dispersed into the liquid phase prior to the polymerization step. The nanoclay particles "swell" as the monomer enters into the spaces between silicate layers. Monomer intrusion is time-dependent and aided by temperature. As the distance between silicate layers increases, their mutual attraction decreases and the level of shear required to disperse the nanoclay drops accordingly.

A mixing trial was performed to find a fast and efficient way of introducing nanoclays into caprolactam. Melted caprolactam (150 lbs) was recirculated through an inline high-shear mixer with a powder injection SLIM system (a modified rotor/stator style mixer designed to generate its own vacuum for drawing powders right into the mix chamber). Nanoclay (13½ lbs) was charged through the SLIM funnel in 15 seconds, and the mixture was continuously heated through the jacketed recirculation vessel and through the shear imparted by the mixer.

As the swelling of the nanoclay progresses, the nanocomposite mixture gains viscosity; due to the application of shear, however, it is easily recirculated by the high-shear mixer and can be just as easily "pumped" downstream to the reactor at a later point. Overall processing is streamlined with the use of a powder injection system. Compared to traditional slow-speed agitation systems, the SLIM enables the easier handling of raw materials, quicker dispersion, shorter cycle time, reduced dusting, and improved operator safety.

For applications involving hard-to-disperse powders, the SLIM system can be an appropriate solution. Even with a strong vortex generated by a top-mounted mixer in an open vessel, some powders—such as fumed nanosilica—resist wetting out and could float on the surface for hours. Using the SLIM, solids are combined with the liquid stream and instantly subjected to intense shear (see Figure 1). In other words, solids and liquid meet at precisely the point where high shear is generated and where flow is most turbulent. When solids and liquids are combined and mixed simultaneously, agglomerates are prevented from forming because dispersion is virtually instantaneous.

Medium-Viscosity Nanodispersions

Higher loadings of nanoparticles result in a premix of substantial viscosity, rendering single-shaft devices inadequate. In addition, when the starting liquid vehicle is already viscous, it is useful to prepare the premix in a multi-agitator mixing system.

This type of mixing system comprises two or more independently driven agitators working in tandem. A low-speed anchor complements one or two stationary high-speed devices, such as an open disc-style disperser blade or a rotor/stator assembly. On its own, a disperser blade produces acceptable flow patterns in batches up to around 50,000 centipoise (cP); the rotor/stator can be effective up to around 10,000 cP. For higher viscosities, a supplemental agitator is therefore needed to improve bulk flow, deliver material to the high-speed devices and constantly remove product from the vessel walls for better heat transfer.

Interchangeable Mixing Heads for Ultra-High Shear Mixers

The X-Series head (U.S. patent number 5,632,596) consists of concentric rows of intermeshing teeth. The product enters at the center of the stator and moves outward through radial channels in the rotor/stator teeth. Tolerances are extremely close and the rotor runs at very high tip speeds (typically up to 11,300 fpm). This combination subjects the product to intense shear in every pass through the rotor/stator. The gap between adjacent surfaces of the rotor and stator are adjustable from 0.010-0.180 in. for fine-tuning shear levels and flow rates.

The QuadSlot mixing head is a multi-stage rotor/stator with a fixed clearance. It is used for applications where very high shear levels are required. The QuadSlot generator produces higher pumping rates and requires higher horsepower than a similar size X-Series rotor/stator set.

The MegaShear head (U.S. patent number 6,241,472) operates at the same tip speed as the X-Series and QuadSlot heads, but it is more aggressive in terms of shear and throughput levels. It consists of parallel semi-cylindrical grooves in the rotor and stator, toward which product is forced by high-velocity pumping vanes. Different streams are induced within the grooves and collide at high frequency before exiting the mix chamber.

The most common low-speed agitator designs are the two-wing and three-wing anchor. For added efficiency, especially in terms of axial flow, a three-wing anchor can be modified to feature helical flights in between wings (see photo on p. 9). In combination, stationary high-shear devices and an anchor will process formulations that are several hundred thousand centipoise.

One advantage to processing in a multi-shaft mixer (or any closed system) is the ability to pull vacuum, which results in improved shearing and contact of the different components in the batch. A sample procedure is to load the liquid phase into the mix vessel, pull vacuum to release any entrapped air, then load the nanopowders and establish full vacuum again before any agitators are turned on. This prevents the micronization of air bubbles. The vacuum environment can also cause powder agglomerates to explode. After the batch is mixed and returned to atmospheric pressure, liquids then fill the interstitial spaces between solid particles.

The premix can later be recirculated through an ultra-high shear mixer for the final dispersion step. For example, such a mixing setup was successfully applied for a sunscreen product containing nano-sized zinc oxide, a mineral that provides UVA/UVB protection and has anti-inflammatory properties. Nano-sized zinc oxide becomes translucent once properly dispersed, and—unlike regular zinc oxide—does not leave a white residue on the skin.

The specialty vehicle (a combination of two solvents and a dispersant gel) was heated in a multi-shaft mixer under full vacuum. Once the proper temperature was reached, the nano-sized zinc oxide was added in increments. For each powder charging, full vacuum was pulled prior to starting the agitators. The premix was then passed through an X-Series UHSM. The true single pass achieved a median particle size of 0.29 microns, which was below the target of 0.39 microns.

Having the ability to fine-tune shear levels by adjusting the gap setting and flow rate in an X-Series is important for nanomaterials that may actually degrade from too much shear at some level. Paste- or gel-like nanodispersions may also be "polished" in a three-roll mill, which comprises three horizontally positioned rolls rotating at opposite directions and different speeds. The material to be milled is placed between the feed and center rolls and gets transferred from the center roll to the apron roll by adhesion. Dispersion is achieved by the shear forces generated between the adjacent rolls.

Milled material is removed from the apron roll by a knife that runs against the roll. The cycle can be repeated to improve dispersion until equilibrium is reached. The three-roll mill is an old technology with inherently low throughput and requires a skilled operator, but it remains one of the best methods for preparing very fine dispersions. Gaps are set relatively tight (often less than 0.001 in.).

High-Viscosity Nanodispersions

As product viscosity continues to build up, a multi-agitator mixing system will eventually fail to produce adequate flow. This can be characterized by an anchor that simply carves a path through the batch (instead of pushing product away from the walls and into the center) or by high-temperature zones right near the disperser and rotor/stator assemblies. At this point, stationary agitators no longer suffice and a move to a planetary mixer is recommended. The agitators of a planetary mixer rotate and travel through the mix vessel by passing through every point within the batch—not just along the periphery.

Many R&D labs use commercially available kitchen mixers and blenders, such as single planetary mixers. However, when processing viscous applications, single planetary mixers impose serious limitations if products become too sticky, thick or heavy, or if they start to climb up the stirrer. In these cases, the double planetary mixer, which has two blades that rotate on their own axes while revolving around the mix vessel, is a more practical choice. The degree of mixing is enhanced by blade-to-blade interaction that is not present in a single planetary mixer.

A double planetary mixer can be equipped with rectangular stirrer blades, finger blades, or high-viscosity (HV) blades. The latter is a patented blade design that generates a down-thrust action owing to its precisely angled helical contour.* This sweeping curve firmly pushes the batch material forward and downward—a mixing action that solves the "climbing" problem that is commonly experienced when processing highly filled materials. In addition, the HV blades do not have a lower crossbar so they can be cleanly lifted from a very viscous batch without pulling it out of the vessel.

A manufacturer of high-quality electronic pastes explored the suitability of using a vacuum-rated double planetary mixer with high-viscosity blades to make its premix, along with a three-roll mill for preparing the final product. The company was previously hand-mixing a silver conductive paste prior to milling it. The paste was packaged into syringes, and the manufacturer was experiencing issues with voids, inconsistency in conductivity levels, and agglomerates in the dispensed lines of silver.

The test batch began with the loading of solvents and silver powders (micro- and nano-sized) in a 1-quart mix vessel. Vacuum was established prior to starting the HV blades. Continued additions of silver raised the viscosity to over 1 million cP. The premix was then transferred to the three-roll mill, and, in one pass, became more silvery and glossy (a visual indication that the dispersion of silver particles was better than that achieved with the hand-mixed batches).

A Ross discharge system was used to empty the premix after its processing in the double planetary mixer; the discharge system was also used to fill syringes with the final milled product. In a discharge system, a stainless steel platen is hydraulically lowered into an internally machined vessel. An O-ring on the platen rides against the vessel walls, wiping them clean. Product is forced out through a bottom valve or an adaptor for connecting a syringe or cartridge tube. The very small amount of remaining undischarged product, mostly on the vessel bottom, is easily cleaned by a quick wipe down.

Nevertheless, not all viscous dispersions can be produced successfully in a double planetary mixer. For these applications, high-torque kneader extruders (sigma blade mixers) can muscle through blocks of rubbery or semi-solid materials. They are the most powerful tools for manufacturing extremely viscous formulations.

Several factors still make planetary mixers a better choice for certain applications. One of those considerations is that kneader extruders rely on the product being highly viscous at all times in order to mix properly; liquid components must be added very slowly, portion by portion, or they can act like a lubricant and reduce shearing efficiency. While this issue is also present in a vertical double planetary mixer, its blades run at higher tip speeds than sigma blades, which makes it less sensitive to liquid additions or shifts in viscosity. Additional comparisons are explained in Table 1.

Table 1. Planetary mixer benefits.

Easy Cleaning	A vertical mixer design has no shaft seals, bearings, packing glands or stuffing boxes submerged in the product zone. In addition, the agitators are raised and lowered in/out of the mix vessel by a hydraulic lift, which enables easy access for cleaning between batches. Mix vessels are interchangeable and can be dedicated to a particular formulation and/or color, so concern for batch-to-batch cross-contamination is reduced.
Small Footprint	The footprint of the double planetary mixer is considerably less than that of a double-arm/sigma blade mixer.
Energy Savings	Since the double planetary mixer uses less motor horsepower to operate, everyday energy/operating costs will be less and can become significant over time.
Semi-Continuous Operation	With the use of extra mix vessels, the double planetary mixer can produce material in a semi-continuous basis: one vessel can be charged while other vessels in the loop are under the mixer, being discharged, and/or cleaned.
Lower Cost	Depending on the specifications, a double planetary mixer is generally one-half to one-third the cost of a comparably sized new sigma blade mixer.

Conclusion

A huge part of any successful discovery in the laboratory rides on our capability to mass-produce the final product in a cost-effective manner. A seemingly minor change in formulation, like the addition of a nano-sized component, can present a processing challenge that calls for careful reevaluation of mixing methods and equipment.

Many of today's mixing technologies overlap in use and function in such a way that certain applications can actually be successfully produced by two or more types of mixing systems. In these situations, the economics rule out the more costly initial investments, but difference in efficiencies must also be taken into account. In a highly competitive market, one can easily miss out on a business opportunity by deciding to simply stick to what works rather than exploring what may work better.

A visit to a mixer manufacturer's test center could be very helpful in your selection process. Be sure to test a variety of equipment and techniques using your own raw materials, simulating conditions as close to your actual process as possible. Renting equipment to run trials on your process floor before making a purchase commitment is another option. In either case, quantitative test results will provide the best assurance that you have chosen the best mixing system for your particular nanocomposite product. 🌐

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*The high-viscosity blade design has been patented by Charles Ross & Son Co.