**Nanoparticle Safety and Value in Thermoplastics**

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**Introduction**

Nanoparticle technology was first developed as separate field of material science in the late 1980’s, with the bulk of detailed studies beginning in the 1990’s. It was enabled due to technology advancements in new types of electron microscopy developments. While the technology became more available, few were able to actually administer and apply nano materials into commercial applications. This obstruction to the successful evolution and commercialization of nano particle uses, was hindered by the inability to provide a continuous, even disbursement and exfoliation of nanoparticles. There are few scientists able to successfully navigate adding nano particles in a continuous process vs. batch process.

“Nanoscale” simply means 10-9 meters. This means it takes a billion nanometers to make one meter. A nanoparticle of a given material has very high surface to volume ratios. Bentonite clay for example, has 1600Ft2 of surface area per gram of material.

In the case where the material is prone to chemical reactions at the surface, these reactions are greatly accelerated. Iron (Fe), a common macro-scale material, will rust over a period of hours when left in moist oxidizing conditions. If reduced to millimeter sized filings, this oxidation occurs faster, often within minutes in the same conditions of high moisture and ambient oxygen. The same iron undergoes explosive oxidation in the same conditions if the particles are nanoscale making nanoscale iron, a high explosive. This change from slow rusting to immediate explosion based on particle size illustrates the effects of high surface area when a material is reactive.

Nanoparticles can be anything chemically stable enough to persist in the nanoparticle size range. These range from metals, to metal oxides, to nonmetals and nonmetal oxides, to organic and organ metallic compounds. Their applications range from metallurgy to catalysts to reinforced materials. Biochemicals can also be converted to nanoscale particles for a variety of new uses.

**Nanoparticles in Food Contact Thermoplastics**

By the early 2000’s concerns about safety and nanoparticles begin to emerge in the public debate. Due to cost and technical constraints inherent to thermoplastics and their use, we will limit the scope of this white paper to commercially available nanoparticles that are economically viable within acceptable plastics industry pricing ranges.

This focus will be around organoclays, CNT’s( carbon nanotubes), and metal oxides, which form the majority of nanoscale thermoplastic additives which are market available today.

We will also examine safety issues as they relate to FDA standards.

Today a few Nano particle materials are approved FDA GRAS( Food and Drug Administration, Generally Recognized as Safe) nanotechnology for packaging applications. The EU has a size-only approach to nanoparticle safety, but this falls short in assessment methods. We will use the FDA for this review.

FDA guidelines have varying degrees of allowed migration test results for different compounds. Based upon the risk to human health, nanoparticles should be considered individually, based on inherent chemistry and physical properties. Studies have been carried out with mice which indicate that airborne exposure to nanoparticles can lead to

pulmonary and other organ damage over time. However, effects vary greatly depending upon particle configuration, size and chemistry. These should be considered on a case by case basis, and in context (loose powder vs encapsulated plastic additive). FDA

tests are based upon particle migration out of the plastic using standardized tests, and allowable levels of the *nano* materials, based on a variety of safety factors considered for a given chemistry and configuration of the nanoparticles.

The first group of widely used nanoparticles for packaging research are organoclays. Their geological origin is usually eruptive volcanoes whose silicate emissions are carried high into the atmosphere. Molecule sized clay particles are purified into bands by air transport and then deposited locally in large geological deposits at the end of their transport.

Organoclays are montmorrilonite (platelets) and certain minerals (Kaolinite) can be (nanotubular) clays (silicate-based minerals) which have been artificially coated with an oily layer of quaternary amine salts. They are the size of red blood cells across the surface, and a hundred or so plus Angstroms (10-10 Meters) in profile thickness on the edge. Chemically polar before treatment, they are silicates (SiO4-) with a free negatively charged oxygen ion group on the surface. This negatively charged group (Si-O-) acts as an ionic anchor point for positively charged quaternary amine salts, (R)3NH+. The aliphatic or “oily” portion of the molecule faces outwards and allows the normally polar clay to be non-polar, due to its oily salt coating, and thus to wet plastics and be more easily dispersed inside non-polar polymers.

The processing of quaternary amine salts during plastics compounding does pose some risks, if for example, the plastic feed runs out before the nano clay feeds into an extruder. This results in the decoupling of quaternary amines from the clay surface inside the extruder barrel and a blast of pure salt vapors, which emits from the extruder

barrel. In their pure form, quaternary amine salts are highly toxic, however in ionic bond with the clay they are not bioavailable. Once inside a plastic matrix, nano clays are relatively immobile.

The main risks to nano clay uses are during handling and compounding. Silica content of the clays is very important to long term exposure risks. The FDA requires low silica content for any organoclay used in food contact material. With low silica content, nano clays can even be used directly as cosmetic ingredients. This type of organoclay is available for commercial food contact.

Another class of plastics additives, which are not as widely used as nano clays but are growing in use, are carbon nanotubes and graphene. The basic hexagonal subunit is the graphene molecule, an allotrope of carbon, along with diamonds and graphite.

Originally discovered in outer space,”buckyballs“

(Buckministerfullerenes) were the object of a Nobel Prize in chemistry. This opened the door to graphene and carbon nanotube research. In their pure form, carbon atoms in graphene form sheets with characteristic hexagonal carbon-based subunits. When these are arranged in a “soccer ball” configuration, you get “Bucky Balls”. When the same graphene is arranged in a sheet, it is referred to as “graphene sheets”. If the sheet is rolled up into a tube, it’s referred to as a single wall nanotube SWNTs. If the tube contains multiple wall layers, it’s referred *to as a* multi-walled nanotubes (MWNTs). The subunit of all is the graphene molecule, which is a completely reduced hexagon of carbon like multiple benzene rings stacked on top of each other.

SWNT’s in particular have been shown to have a variety of deleterious effects on living tissues. MWNT’s less so, but handling precautions are recommended, nonetheless.

Effects similar to asbestos have been observed in lung tissue along with an increase in lung cancer and a variety of cell damage mechanisms for SWCNT’s and MWCNT’s which are more pronounced with particle size.

Graphene and graphene oxide seem to be mild irritants thus far and accumulate only in low levels in the lungs and liver, unlike MWCNT’s and SWCNT’s which show much greater potential risks, and show up in all tissue samples.

One of the most common plastics additives now available in nanoparticle size range is titanium dioxide. Titanium dioxide plays a number of roles as an additive into plastics including UV inhibition and whitening. In its normally occurring pure powdered form, there are already concerns about long term increases in lung cancer. Studies with zebra fish have shown lethal effects of titanium nanoparticles on embryos, and a variety of targeted organ damage in various tissue samples. Bioaccumulation is accelerated in nanoparticles like titanium dioxide. This means that more intimate contact at the intercellular level now can modify biomolecules at the macromolecular scale, like DNA and proteins. While mice studies show short term inflammation which some authors have suggested makes TiO2 particles safe, zebra fish studies, which carry more embryological and environmental data, suggest greater health and environmental risks.

**Conclusion**

For thermoplastics, and thermosets with food contact roles, two factors should be considered when using nanoparticles. The first is inherent toxicity and chemical stability. This favors silicate, graphene and graphene oxide as additives, over other types of compounds. Secondly is migration from the plastic. If the nanoparticle wets the polymer well, then even if it is protruding slightly, it will be mostly retained inside the plastic by surface affinity, and encapsulation, especially if well dispersed.

Finally, migration should be measured according to standardized testing methods, and the results should be compatible with acceptable food storage contact levels of migration allowed by the test method for a given nanoparticle.

The benefits to adding nanoparticles, as an FDA food grade approved additive, to polymers are many, however, the most notable rely on providing barrier properties. In this case, Nano particles act as a physical tortuous path against oxygen, moisture and to some extent UV degradation. Additionally, certain Nano particles prevents leaching, which sustains greater longevity and value to plastics, as well as preventing leaching from other plastics when recycled.

Third party test results on Polypropylene (PP), show a 100% increase in oxygen barrier with a 5% loading rate of nano particles, 200% with a 10% loading rate. In Polylactic Acid (PLA) results showed a 40% increase in oxygen barrier properties with a 5% loading rate, 80% increase in barrier properties with a 10% loading rate of Nano particles.

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Multifunctional Nano clays for food contact applications

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