

The Next Innovative Wave:  
Nanotechnology in Packaging

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## **Introduction**

Technology keeps society moving forward; and the next wave is here: nanotechnology. The term nanotechnology refers to ‘the control or manipulation of matter at the atomic, molecular, or macromolecular level, in which one of the components affects functional behavior.’ (Brody) Nanotechnology involves manipulated particles no more than 100 nanometers in any dimension. (Brody, Nanocomposite Technology) To keep that size in perspective, a human hair is 80,000 nanometers thick. (Crowley)

Material development efforts focus primarily on enhancing thermal, mechanical, and barrier properties; although different industries have different hopes and goals for nanoparticle applications. Industries from packaging to automotive parts to electronic components can benefit from nanotechnology. All stand to gain from the availability of lighter, more durable materials created with nanoparticles.

Nanocomposites made their debut in the automotive industry. In the late 1980’s, Toyota used a nylon-6 nanocomposite for timing belt covers. (Nanocompositech) As it is their original market sector, the automotive industry employs more nanocomposite materials than any other industry; 80% of the nano market belongs to automotives. (Markarian) However, the packaging market is expanding. Now a \$7 billion market, nano-packaging is expected to grow as large as \$20 billion by 2020 (Halliday), gobbling up 25% of the market. (Think Big, Think Nano)

In the packaging world, developers are out to enhance material properties including mechanical strength, moisture retention, barrier (to gas and light), clarity, and thermal properties. Glass outperforms plastic in all of these areas; so the main goal of embedding nanoparticles into the polymer matrix is to mimic the properties of glass—or metal. (Plastic Fantastic) Plastic weighs less than glass or metal—even when they are lightweighted. Using plastic for packaging could afford manufacturers and distributors significant savings.

### **Divisions of Nanotechnology**

While nanotechnology can be lumped together for general purposes, there are four distinct divisions: nanoclay; carbon nanoparticles/nanotubes; nanoscale metals and oxides; and biobased

nanocomposites. The largest applications in packaging come from nanoclay—or polymer-clay nanocomposites (PCN). (Chen) Packaging professionals can foresee uses for nanoscale metals and oxides, but those applications are in the very early stages. Carbon nanoparticles/nanotubes are practically nonexistent in the packaging world.

Nanoclay enhances many desirable qualities in packaging, including stiffness, toughness, and barrier properties. One to five percent (by weight) of nanoclay particles can replace fifteen to twenty percent of standard fillers like calcium carbonate to both reduce cost and improve mechanical properties. (Markarian) Also, the addition of ten percent (by weight) of clay can cut the permeation rate by as much as 75%--in some materials—due to the high surface area of the clay platelets. (DeGaspari) Clay nanoparticles are typically approximately one nanometer thick, but up to 100nanometers in length and width.

Available in natural and synthetic varieties, nanoclay is gaining popularity in plastic packaging. Montmorillonite (MMT), a natural clay, is the most common nanoclay used in packaging applications today because it is the most available (Brody) and least expensive—at \$2.25 to \$3.25 per pound. (Sherman) Synthetic clay is more expensive at \$10 to \$20 per pound; and nanostructured silicons are more expensive still at \$200 per pound. While price does not disqualify the material, the process by which MMT is embedded in the polymer matrix is more expensive than commercially viable at this time. (Brody, Nano and Food...) Discovering more uses and creating demand will help drive cost down in the future. Some expanding applications include automobile parts, construction, aerospace, electronics and electrical, coatings, and pigments. (Chen)

Because MMT is a relatively inexpensive, but highly effective material, it could potentially open a larger sector of the market to lower quality and lower cost plastics. The quality of these nano-materials could be improved to match or exceed that of 'pure' materials used in applications such as retort pouches, paperboard coatings, and aseptic packages. (Hotchkiss) Many materials have been studied in combination with MMT clay nanoparticles including polyethylene (PE and LDPE), nylon, PVC, and biopolymers. Among the compatible materials are PP, PET, PE, PS, and nylon. (Sherman) Nylon-6 has

the greatest return: for every one percent (by weight) of nanoclay particles added, property output increases ten percent. (Cho)

Nanoscale metals and oxides, though not as common as nanoclay, have their place in packaging, too. A 40-50 nanometer thick layer of aluminum nanoparticles applied directly to plastic film can replace the need for foil laminations. The nanoparticles are commonly applied by method of vapor deposition. Using the same technique, silicon oxide nanoparticles (40-60 nanometers thick) can be applied to glass, strengthening it. In theory, these ideas sound like time and money saving ideas; however scientists are not sure that these inorganic particles do not migrate, so the technology remains a work in progress for now. (Nanotechnology—Applications, Trends, and Risks)

Still part of the nanotechnology family, carbon nanoparticles and nanotubes do not really have a place in packaging. Applications for these particles include automotive applications—such as fuel system components—and electronic components. “The primary benefits of carbon nanotubes and nanofibres are excellent electrical conductivity and use at very low loadings that do not negatively affect polymer properties such as durometer barrier or mechanical strength.” (Markarian) Since these benefits do not apply to packaging, they will probably never nudge their way into packaging technology.

### **Enhanced Properties**

Nanotechnology provides many benefits to the packaging industry; and as applications grow, so do advantages. One benefit of using nanocomposites is the ability to use less material to achieve more performance. For example, some nanocomposites require only one gram of nanoparticles to satisfy the needs of 750 square meters of material. (Brody) Maximum benefit is achieved when the nanoparticles are properly arranged. As they are only one nanometer thick, if the particles end up with their large surface perpendicular to the material surface, they become obsolete; so the manufacturing is important.

Among the properties affected by nanoparticles are mechanical properties. Application of nanoparticles can increase tensile strength up to forty percent (Nanocompositech), allowing packaging engineers to decrease the gauge of film used for pouches. When the price of the nano-enhanced films

decreases, lightweighting plastic film could allow multi-million dollar savings to some companies—especially those in the cereal and snack food business.

Nanoparticles provide multiple benefits, not just mechanical properties. Thermal properties also improve. Adding just five percent (by weight) of MMT can increase thermal stability up to 350 percent. (Brody) Consumers appreciate the flexibility to cook or reheat food in its original packaging—steam fresh pouches for steaming vegetables, single serve frozen meals, etc. With the employment of nanoparticles, this is a possibility. Enhanced thermal properties are not just a convenience to consumers, but also manufacturers. Now, more plastics can withstand the temperatures of the hot fill process.

Nanocomposites improve barrier properties by leaps and bounds. Barriers against “oxygen, carbon dioxide, ultraviolet light, moisture, and volatiles are perhaps the most important properties that nanocomposite food packaging can offer.” (Chen) All of these elements can affect the quality and freshness of food, thus shortening the shelf life. Improved barrier properties—by way of nanoparticles--increase shelf life, and less waste occurs. Also, because the materials can be custom created for specific applications and tailored for desired results, it may be possible in the future to create a material that is impermeable to one type of particle (moisture, gas, etc.) and highly permeable to another. (Brody)

When the nanoparticles are properly exfoliated (dispersed) and aligned—with their large surface area parallel to the surface of the film—they create a ‘tortuous path’ for gas and moisture particles to navigate. (Chen) These particles cannot make their way around and in between the large, flat faces of the nanoparticle wall in front of them. Combine this tortuous path with oxygen or moisture scavengers, and the material achieves an impenetrable barrier.

A tortuous path through the film does not only prevent outside particulates from getting *in*, it also prevents particulates from getting *out*. Packaging can affect many variables in foods. Occurring by the basic principle of permeation, agents from the packaging can scalp the flavor or odor, and can change the color or consistency of the product. Hence, packaging can actually lower the quality of foods, which is opposite from its purpose. Nanotechnology improves this dilemma in two ways. Difficult for moisture and gas particles to navigate, the tortuous path also proves challenging for flavor, odor, and color

molecules to enter; thus keeping those elements in the food, not the package. Also, some common fillers act as scalping agents. To compensate for the anticipated scalping, food technologists need to modify the product. The characteristics provided by these fillers—be they mechanical, thermal, or other—are necessary, so they cannot be removed; but they can be replaced. Nanoparticles can be added to films without concern of scalping. Because nanoparticles are multi-benefit achievers, the material could be improved beyond expectations. ([www.flavorscalping.com/more.htm](http://www.flavorscalping.com/more.htm))

Barrier improvements are not without limitations. Factors including relative humidity (RH), temperature, and duration of intended preservation must be accounted for when designing a nanocomposite for a specific purpose. Nanocomposites have the ability to out-perform unaltered (or pure) polymeric resins, but not under all conditions. Researchers performed a barrier test on pure LDPE and a nanocomposite of LDPE and montmorillonite-layered silicates to test the barrier properties. The test included two-millimeter and six-millimeter pure and nanocomposite LDPE for 19 days in three different conditions: conditioned air at 39°C, 90% RH; 39°C, 50% RH; 23°C, 50% RH. At the end of the test, researchers determined that the conditions at which the water vapor barrier properties of the nanocomposite outperformed those of the pure LDPE were as follows: 2-mm nanocomposite at 23°C, 50% RH; 6-mm nanocomposite at 23°C, 50% RH; and 6-mm nanocomposite at 39°C, 50% RH. At all other conditions, the pure LDPE outperformed the nanocomposite. (Emerging Food R&D Report, 01-OCT-07). It is possible that additional technology, such as moisture scavengers could be added to the nanocomposite to further enhance properties. It is important for packaging engineers to understand plausible applications for nanocomposites. In some cases, it is beneficial to use nanocomposites, and in others, it would not be worth the cost.

Increased gas barrier properties are not only of interest in the food market, but also in the beverage market. More specifically, nanocomposites could capture a large portion of the carbonated beverage (soft drinks, seltzer water, beer, etc.) industry. The addition of nanoparticles by just five percent weight can reduce oxygen and carbon dioxide permeation up to 80-90 percent. (Hotchkiss) Also, because nanoclays do not differentiate between oxygen and carbon dioxide (as scavengers do), they are more

universally applicable. (Brody, Case Studies...) Beer is an expensive product to ship due to the large volume and weight of the glass bottles. For years, plastics could not be considered to replace glass because the barrier properties are not strong enough to protect the beer from losing carbon dioxide. However, nanotechnology can reinforce plastics to have nearly equivalent barriers. Currently, nanoclay plastic bottles grant beer a six-month self life, and is only expected to improve. (“Food Packaging Using Nanotechnology Methods...”)

Despite nanoparticles creating a tortuous path for gas and moisture molecules (among others), their size does not allow them to scatter light. Because the light does not scatter, the material does not appear cloudy. Hence the small particles do not affect material clarity (Brody), allowing engineers to design packages around showing off the product inside.

### **Limitations**

All of the advantages do not come without some drawbacks. One factor that has stifled the nanocomposite use in packaging is the difficult process of even dispersion of particles. Of the four most common manufacturing processes, none offer the guarantee of evenly distributed material. (Science Daily) “Barrier properties require the greatest degree of dispersion and exfoliation, in which the clay platelets must be both separated and aligned to create a tortuous path that is a barrier to gases and chemicals.” (Markarian) One possible solution to the even distribution *within* the polymer matrix dilemma is to coat the surface of the material—as is done with silicon and aluminum oxides. Vapor deposition can apply a nanometer-thick layer of nanoparticles to a material’s surface. Fortunately, this method still does not affect material clarity. (Brody, Nano, Nano...)

One rising concern involves human and environmental health. As this technology is still in its infancy, its effects on the human body are unknown. “The high surface-to-volume ratio [ $750 \text{ m}^2/\text{g}$ ] of nanomaterials makes them more reactive and potentially more toxic.” This reactivity means that nanoparticles may react with pure materials during recycling and disposal. Effects include possible allergens and new toxic strains. (Brody)

Nanocomposites undoubtedly have a place in the packaging market, but scientists and consumers express concern regarding implementation. Most fear adverse affects on health and the environment. In a study, researchers found that nanoparticles “accumulate in the nasal cavities, lungs and brains of rats, and that carbon nanomaterials known as 'buckyballs' induce brain damage in fish.” (Brahic) The fish were exposed to 0.5 parts per million nanocomposites. After 48 hours, tests revealed that their brain cell membranes were disturbed. This type of disruptions linked to illnesses like Alzheimer ’s disease. (Leahy) Long-term effects of build-up are unknown.

The effects of carbon nanotubes have been tested on animals. The results sparked great concern in the science community. Just like their benefits, the dangers of nanoparticles result from their nano-size. When animals inhaled carbon nanotubes, they experienced lung damage. Even more concerning is that the nanoparticles are small enough to exit the lung wall and find their way to the animals’ DNA. Scientists fear nano-embedded DNA could cause diseases, allergens, or mutations. (Leahy)

Development of new and uncertain technology involves the cooperation of “scientists, governments, civil society organizations and the general public.” (Brahic) When all of these groups do not work together, nano-development is bound to spark more than environmental problems. Countries could engage in an ‘unstable arms race’ over the newest and greatest nano developments. Disagreements could fuel a nano-black-market. The economy could experience disruption from a flood of cheap products. (“Dangers of Molecular Manufacturing”) Although the problems are ‘unknown,’ they are not unanticipated.

Nanomaterials are a double-edged sword. Because they use less material and resources they are viewed as ‘cleaner’ than current alternatives. It is not certain how these new, tiny particles will interact with the environment. Because of their small size, they can travel great distances—carried by air. Researchers argue that nanoparticles could accumulate in the environment and trigger unknown reactions. Nanoparticles could also accumulate in the food chain. No material tested to date can be used as a precedent to predict the affects of nanoparticles. Nonmaterial research is true uncharted ground. The U.S. government and independent agencies are spending money and man-hours trying to answer the

questions about nanotechnology to lay concerns to rest. In 1997, the US National Nanotechnology Initiative's budget was \$116 million. In 2004, they requested \$849 million. (Brahic)

Concern is not limited to scientists; as the nano-wave moves forward with some uncertainty—as does each new technological phase—consumers grow skeptical. (ElAmin) Only seven percent of consumers volunteered that they would purchase food products enhanced by nanotechnology; while twelve percent said they would buy products packaging using nanotechnology. (Eyre) A survey conducted by German risk assessor BfR concluded that 84 percent of consumers are against “the idea of making foods look appealing for longer through the use of nanoparticles.” For the most part, consumers only expressed concern in the area of food—be it product or packaging. Many supported the use of nanotechnology in other areas such as automotive and medicinal. (Halliday) More fuel to the fire of suspicion is the lack of regulations on terminology. Right now, the nano world is a gray area. With no regulations, the door is open to misuse the “nano-buzzword” for products with negative side-effects, while not even being nano; thus creating a negative stigma for the up-and-coming technology. (Think Big, Think Nano)

### **Applications**

Nanocomposite technology can be applied to flexible or rigid packages. Nanoparticles can be applied to the surface or embedded in the polymer matrix in either application; and they can be used in multilayer structures. It is the hope of packaging and material engineers that the incorporation of nanoparticles into the polymer matrix will allow enough control over material properties that the need for multilayer material will disappear. By converting bottles from a multilayer container to a single layer container (coated or incorporated), manufacturers save money and less material enters the waste stream. (Markarian) This flexibility makes nanotechnology appealing in the food *and* beverage markets. Plastic beer bottles are becoming increasingly popular—especially at professional sporting events and outdoor picnics. Nano-bottles are practically tailored to the beer market; nano-enhanced nylon-6 has three times the oxygen barrier of pure nylon-6. First available in China in late 2007 (Leaversuch), the early nano beer bottles give the product a shelf life of six months. (Advantage Magazine, 2004)

In the early stages of nano-materials, scientists experienced difficulties creating films with both strong and stretchy properties. Searching for answers, scientists turned to a natural phenomenon: spider silk. Spider silk is five times stronger than steel by weight (Knight), and is both strong and flexible. The questions about its strength can be answered by examining its nano-crystalline structure, which forms during production. Hence, the nano world received new direction; and this new path leads to military Meals Ready-to-Eat or MREs. The military is looking for lighter material with improved properties to protect the troops' meals. Conditions can be unpredictable, so it is that the material be able to withstand a wide range of rigors. (Trafton)

Nanocomposites can improve the shelf life of many varieties of foods. Because of their ability to slow the 'respiratory exchange' process, nanocomposites can significantly improve the shelf life of fresh produce and fresh, frozen, and processed meat, poultry, and seafood products. Capacity to retard permeation of moisture protects the product from discoloration and oxidation, preserving product appearance. (Akbari) The current market for "active, controlled, and smart" packaging materials for the food and beverage market is \$54 billion—ballooning from just \$38 million in 2004. ("Food Packaging Using Nanotechnology Methods...") Nanotechnology is not limited to the food packaging industry; it is also used in the food industry. Some spices use nanotechnology to prevent clumping. (Halliday) Titanium dioxide nanoparticles are also available in the form of stain resistant material, sunscreen, and some cosmetics. (Leahy)

### **Future Possibilities**

Nanotechnology opens the doors to many possible innovations in 'smart' packaging and 'active' packaging. Three new functions being considered are: the "enhancement of plastic materials' barrier; incorporation of active components that can deliver functional attributes beyond those of conventional active packaging; and sensing and signaling of relevant information." (Brody, Case Studies) Barrier properties in nanotechnology-enhanced packaging material, as discussed earlier, help ensure protection against the migration (in *and* out) of oxygen, carbon dioxide, aroma, and water vapor molecules, keeping food better preserved. (Brody, Case Studies)

Conventional active packaging includes susceptor film and laminates, and any material with an improved barrier to separate the food from the environment. (Hotchkiss) Active packaging enhanced with nanotechnology could have antimicrobial benefits, which would not allow certain bacteria or microbes to grow, thus preserving food products for a longer time. These antimicrobial packaging materials could prevent pathogens from growing even after consumers open the packaging—a feature of particular interest in the dairy, meats, and fresh produce markets. (Brody, Case Studies)

Intelligent packaging could be used to alert manufacturers, customers, or consumers of dangerous or contaminated foods. Packaging materials could use detection nanoparticles that are capable of alerting people (by changing color, emitting odor, etc.) when unwelcome pathogens are present—a feature useful from point of manufacture to point of consumption. (Brody, Case Studies)

Scientists and food technologists are dreaming up all kinds of applications for new smart or intelligent packaging. One such example is a milk carton. It is possible to alter the composition of milk to initiate a change in color when certain harmful bacteria begin to grow. Altered packaging could alert grocery store stock persons and consumers of declining product. Some alterations go beyond color change; researchers are examining the possibility of packaging that alters its properties in response to environment. Material scientists are considering the ice cream market as one potential buyer—if they can design a material whose molecules tighten so that outside heat does not melt the product. (Advantage Magazine, 2004)

## **Conclusion**

Nanotechnology encompasses ideas, concerns, and lots of research. Somewhere therein lies a balance. The FDA announced in 2007 its preparedness to get involved. Since, they have been working on developing a task force to oversee and regulate the development of nanotechnology in foods and food packaging, as well as medical devices and their packaging.

The key to overcoming existing and rising concerns over nanomaterials is answering questions. As is shown by the increase in nanotechnology budget, many agencies are expanding their research. Some answers will only lead to more questions, so the road to end use and market appearance is long; but

the uncertainty of the final destination/application is what keeps consumers and scientists alike interested in the prospects. Right now, the possibilities are endless.

The main concern for consumers is the unknown long-term health effects. The general public is not satisfied just with being informed, they want to be involved; and they should be. Studies showing the number of consumers willing to use nanomaterials reflect apprehension. Consumers are not involved in debates or discussions at this time; that power belongs to scientists and researchers.

Before heading to market health questions will need to be addressed, as well as societal questions. It is the intention of the FDA and other government agencies to control the economic, societal, and health issues by way of regulations. After the questions are answered and the regulations are enforced, no one knows for sure what theoretical applications will materialize. Products are largely dependent upon consumers' reactions.

With all the products on the market today, it is hard to say which ones nanotechnology will permeate; but as the experts say, "Think big...think nano."

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