Alexia Karpilov

Nanomaterials In Food Packaging: Promise and Potential Peril

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INTRODUCTION

Nanotechnology (derived from the Greek word nano, for "dwarf") centers around particles and devices so small that they need to be measured in nanometers (nm), or one-billionth of a millimeter. Richard Feynman is an important figure for initiating interest in nanotechnology; in 1959, he gave a presentation to the American Physical Society meeting at Cal. Tech. outlining the potential of having greater control of things at smaller dimensions. Once materials are reduced to less than 100 nanometers, they begin to be influenced by quantum physics, and assume completely new properties. When properly dispersed and manipulated, the use of these composites can result in a tremendous increase in a material's strength, decrease in weight, as well as changes in optical, conductive, and magnetic properties (Ewels). The word "nanotechnology" applies to the entire field of research; nanomaterials are the raw, fabricated particles created to achieve the results; and nanocomposites are comprised of nanomaterials bound to other materials, in order to make the technology usable.

Though most often used when talking about the newest computer technology or automotive manufacturing, nanotechnology is also becoming a major driver in packaging technology development. Because of their tremendous versatility, researchers are trying to coax nanomaterials into providing extended

shelf-life, higher barrier properties, temperature control, fighting microbes, and helping in inventory control. However, there are many safety concerns about nanomaterials, as their tiny size may allow them to penetrate into the human body, and may remain in the system. Researchers are exploring nanomaterials for use in a variety of packaging applications; however, the current usage has been focused overwhelmingly on the food-packaging industry, as its potential applications could solve a myriad of challenges when packing these fragile substances. At the same time, many are concerned about the safety of packaging materials interacting with the products they contain. In this paper, we will explore the promise, and the potential drawbacks, of nanotechnology in the food-packaging industry.

THE FOOD PACKAGING INDUSTRY

"Food is the ultimate complex mixture," says David Weitz of Harvard University. Because of the complex, and often fragile nature of the products, food packaging has been one of the most concentrated areas of nanotechnology development. One study has predicted that in 2006, beer packaging will use the highest weight of nanocomposites (3 million lbs) followed by meats and carbonated soft drinks (PIRA). Dr. Manuel Marquez, a senior scientist at Kraft Foods, states, "nanotechnology is going to have broad, sweeping applications that have the potential to significantly improve the quality and safety of food... to how we will display in-store signage, clean freezers and floors, and track inventory" (Ewels). Many major food companies, from Kraft to Kellogg's, have

hired "nanotechnology gurus," to help them develop safer, more attractive products, with longer shelf-life, and (hopefully) lower costs. Some of the potential uses of this technology include modifying permeation properties, increasing barrier properties, improving mechanical and heat-resistance, developing active antimicrobic and antifungal surfaces, and sensing and signaling microbiological and biochemical changes (Food Production Daily).

BARRIER PROPERTIES

Barrier properties are perhaps one of the most important and challenging components of food packaging. The penetration of light, moisture, or gases can alter the sensory characteristics of food products, as well as foment spoilage. Whereas many applications of nanotechnology are far in the future, nanocomposites that enhance barrier properties are already commercially available. Nanoclay and carbon nanotube fillers both demonstrate improvements in the structural, thermal, barrier, and flame-retardant properties of plastics, and carbon nanotubes also enhance electrical conductivity. Nylon 6 nanocomposites are being developed by a number of companies, including Honeywell, Bayer, Ube America, and Mitsubishi Gas Chemical, for high-barrier packaging.

As nanoclays enhance the oxygen-barrier and stiffness of nylon 6 films, they allow for significant lightweighting possibilities for a variety of oxygensensitive products, ranging from pet food, boil-in bags, vacuum packs, and standup pouches. "Nano-clays significantly boost the barrier performance of nylon 6,

while retaining most of its favorable characteristics – toughness, clarity, hot-fill heat resistance, and oil/grease resistance," states Lance Altizer of Honeywell. No modification of cast-film equipment is needed to run these materials (Leaversuch).

The beer industry is one of the largest business areas exploring the use of polymers enhanced with nanomaterials, in an effort to complement and/or replace costly and fragile glass. Not only are these materials considerably lighter and more durable than glass, their properties have allowed manufacturers to dramatically extend shelf-life. Honeywell's Aegis nylon 6 nanocomposites were developed with PET beer bottles in mind. A version introduced in 2003 containing an oxygen scavenger was used, with great success, for a 1.6-liter Hite Pitcher beer bottle from South Korea. The nylon 6 is the barrier layer in a threeply structure, which is said to provide a 26 week shelf-life. Mitsubishi Gas Chemical has developed a similar, three-layer PET bottle, with an Imperm core. Imperm is said to have a 100-fold lower OTR than that of straight PET, and ensures a 28.5 week shelf life (Leaversuch). Honeywell is also working on other nanocomposite grades, to be used as replacements for EVOH in films and pouches. These grades would be lower in cost than EVOH, provide a better barrier, better puncture resistance, and good clarity (Sherman).

SPOILAGE

Spoilage is probably the largest concern for food companies, as it can have tremendous negative effects on both image and the bottom line. Hence, nano developments in identifying – and in some cases, reversing – spoilage are tremendously important. A team from Purdue and Clemson Universities is creating nanoparticles that fluoresce or are magnetic, and will attach themselves to any number of food pathogens. Employees using handheld sensors could then note the presence of even miniscule amounts of pathogens, such as e-coli bacteria. Researchers hope to use the changing molecular composition of milk that is beginning to spoil to bring about a reaction with nanoparticles embedded in the packaging, causing the color of the packaging to change. The advantage of such a technology is that store owners and consumers alike could easily tell if the product's quality has declined" (Ewels).

There are several other projects underway addressing the next generation of anti-spoilage packaging. Researchers in Holland are developing a preservative-releasing packaging material, from which the preservative is released only when the presence of a microorganism is detected. Known as "release-on-command" preservatives, they offer the advantages of only targeting areas of spoilage (thereby reducing the total amount of preservatives in the food), as well as adding a selective matrix to items such as pharmaceuticals or fermented products. Researchers are also investigating the ability of synthesized adhesion-specific nanoparticles to irreversibly bind to targeted types of bacteria, inhibiting them from binding to and infecting their host (PIRA).

ACTIVE PACKAGING

Active packaging reacts to outside influences, such as temperature and contamination. An example of an active package is a programmable barrier that controls the atmosphere inside of a package. Also currently in development now are self-cleaning surfaces that destroy bacteria, isolate pathogens, or fluouresce under certain conditions (Ragauskas).

The largest force driving active packaging is consumer demand for fresher foods and more convenience features. Packages that can tell the consumer if the product has been defrosted in transport, or preserve freshness for twice as long, currently have the most defined markets. The most common active packaging in use today is that of oxygen scavengers, the use of which grew 15 times in the 1990s (Active Packaging).

To address cleanliness issues, Asahi Glass and Pilkington Glass are manufacturing a self-cleaning glass. The glass is embedded with titanium dioxide nanoparticles, which in the presence of light, react with dirt and grease and break down the smudges into a pool that will literally roll off the glass (Ewels).

Researchers are also experimenting with materials that change their properties to address outside environmental factors, such as temperature or humidity. An example would be an ice-cream carton that tightens its existing molecular structure to prevent heat from affecting the content, should it be left in the sun on a hot summer day (Ewels).

Other areas of development include separation technologies such as those which can locate and eliminate heavy metals, thinner metallic films, edible and biodegradable films, and detection of internal stress and strain on various materials (Nano Materials).

INVENTORY CONTROL

Because food packaging is a high-turnover, low-margin business, inventory control is paramount to maintaining profitability. Nanotechnology offers an alternative to RFID that is cost-effective and far more versatile. Nanobarcode particles are encodable, machine-readable, sub-micron-sized taggants which can be produced in an infinite number of combinations. They are produced by electroplating strips 250 – 500 nM wide, and are far more cost-effective (PIRA). Current RFID technology requires the purchase of tags (at a cost of \$.06 - \$.75 / tag), as well as an antenna, which must be either printed or inserted. Furthermore, RFID waves do not travel through liquids consistently, thereby making readings somewhat unreliable on everything packaged in paper-based materials, to Windex. Nanobarcodes allow accurate readings regardless of the

product, or the material it is packaged in (PIRA). These same particles serve a dual purpose, as they could also be used to fight counterfeiting. Nanoparticles are virtually impossible to duplicate; hence, brandowners could identify knock-offs by simply scanning their barcodes.

SAFETY CONCERNS

Nanoparticles do indeed hold great promise. The miniscule size of these particles, however, might be a double-edged sword. There is growing concern, both in the US and abroad, about the environmental and health impacts of this technology. Whereas their diminutive size may allow nanoparticles to create super-strong materials and deliver drugs with great accuracy, the same properties might also allow them to penetrate deeper into the lungs, pass more readily through the skin, or linger longer in the environment as pollutants (Amato). "New nanomaterials could be the next cure for – or cause of – cancer," said Chad Mirkin, or Northwestern University's nanotech center. "It's clear that the potential for this field is enormous. We must push ahead with the proper respect for new nanomaterials" (Van).

The explosive growth in new materials and nanotech-based production is alarming to some; it is estimated that global production of these materials will exceed \$ 1 trillion within 15 years (Amato). Because the technology has evolved very quickly, and is often the product of smaller companies, governance and industry regulation have not kept pace. Many are calling for increased oversight

and, in some cases, a moratorium on research altogether, until the impacts are known.

The situation is further complicated by the fact that there is very little data available illustrating environmental and/or health impact. "The lack of technical data on the topic provides fertile ground for both nanotechnology proponents and skeptics alike to make contradictory and sweeping conclusions about the safety of engineered nanoparticles, " says Vicki L. Colvin of the Center for Biological and Environmental nanotechnology at Rice University. She continues by stating that the next few years should yield significantly more data, which could in turn be used for regulation (Hibbert).

In terms of environmental impact, the largest concerns have been focused on "buckyballs" – soccer-ball shaped carbon molecules - and carbon nanotubes, which are common nanoparticles. Buckyballs are extremely stable and robust, and can absorb toxic materials. By binding with the buckyballs, toxins themselves could potentially become more chemically stable, thereby traveling further through the air or in water (Amato). This issue is particularly pertinent regarding disposal of nanomaterials, as landfills often contain a "toxic soup" that buckyballs may help perpetuate.

The situation becomes murkier regarding human and animal health. "There is very little evidence of people getting sick from exposure to

nanomaterials," said Andrew Maynard, chief scientist with the Woodrow Wilson International Center, a government think-tank focused on nanotechnology. Nanoparticles are far smaller than red blood cells; hence, it is assumed that they could circulate freely within the body, perhaps even moving to the brain, which larger particles cannot do. What harm these tiny fragments could cause is purely speculation, as nanoparticles tend to have different properties than larger particles of the same material (Van).

The major health concerns are for those who will be working directly with nanoparticles in the fabrication stages, and not consumers. Almost all studies have focused on subjecting animals to concentrated amounts of nanoparticles, unbound and unadulterated by other materials. In these conditions, recent published scientific studies have not been particularly reassuring:

- Researchers at the New Jersey Institute of Technology found that nanoparticles of aluminum oxide stunt root growth of several crops, including soybeans and corn – mainstays of US agriculture (Weiss).
- Japanese researchers found that a type of nanosphere used to deliver drugs or vaccines into the body is a potent stimulator of immune-reaction genes, perhaps explaining fatal inflammatory responses seen in animals exposed to nanomaterials (Weiss).
- Lab animal studies have shown that some carbon nanospheres and nanotubes behave differently than other ultrafine particles, causing fatal inflammation in the lungs of rodents, organ damage in fish and death of

ecologically important aquatic organisms and soil-dwelling bacteria (Weiss).

 When inhaling nanoparticles, carbon nanotubes from the particles ended up deep in the air sacs of rats' lungs, where they caused lesions indicative of toxicity. In 15 % of the rats, the nanotubes aggregated into lethal, suffocating clumps (Amato).

David Warheit, a DuPont toxicologist, responsible for the rat-nanotube test, indicated that size does matter; nanoparticles generally are more toxic when inhaled than larger particles of the same material. However, he goes on to state that his methods were relatively crude, in that he essentially squirted nanoparticles into the rats' tracheas with a syringe. He is working on developing more realistic exposure methods, which will simulate situations those who work with nanoparticles might face. Unfortunately, it will take several years before results are realized (Amato).

The US government has begun to take note of these concerns, but results are mixed. The EPA has begun research studies, but is unsure as to where this technology falls in its regulatory scheme. It is relying on existing protocols, but does not have a particular nanotechnology division. The Toxic Substance Control Act, which regulates new chemical substances, seems to be where the materials are falling; however, it does not distinguish by the size of the particles, and the chemical composition of many nanocomposites would allow them to be regulated by other arms of the EPA. Clarence Davies of the Woodrow Wilson

Foundation, has stated that, since nanoparticles behave differently than traditional materials, they pose a regulatory dilemma that would best be solved through new federal legislation. This legislation would have to affect both the EPA and the FDA, as both environmental and consumption issues need to be addressed (Van). The EU is also working on its own legislation, and several countries are taking their own initiatives. In the UK, the Royal Society and the Royal Academy of Engineering have been commissioned to complete preliminary studies of the risks and benefits of nanoparticles, and to specify the research that is needed to enable informed regulatory decisions (Amato).

Regarding safety, many researchers in the food industry have been extremely careful about selecting their products and materials, and stress that they have not been working with materials that have raised concerns. Manuel Marquez of Kraft Foods states, "We work with materials that are already in nature... materials that reasearchers are using to develop flavor-encapsulating nanoparticles derived from natural ingredients that break down in the body. Using degradeable and biocompatible polymers to fabricate biosensors for food packaging could also address potential health and safety issues" (Goho).

CONCLUSION

Nanocomposites are one of the most exciting and far-reaching developments in the history of materials science. If successful and financially viable, the use of these materials could result in stronger, lighter cars, flame-

retardant airplanes, and highly efficient drug-delivery systems. In packaging, it can provide materials that protect and communicate with the consumer in ways previously unimagined, providing safer products with longer life spans. However, the scientific community must assess the risks associated with any new technology, lest it damage those it was created to protect. Because the development of nanotechnology has been so rapid and—until recently—virtually unregulated, its risks are unknown. The stakes are high. Research and development is extremely costly, and companies understandably would like to see a return on their investment as quickly as possible. The market for nanocomposites is growing rapidly, with an annual predicted growth rate of 18.4% per year from 2003 – 2008 (Sherman). Unlike the developments of the composites themselves, research into the possible effects of nanomaterials on the environment and population can take years, creating quite the conundrum for all.

Nanotechnology's explosive growth must be tempered with a concern for its impacts, fomented by sound, scientific research. Unfortunately, over the years we have seen many products—from drugs to pesticides—that were released into our fragile ecosystem before their risks were known. The potential benefits of nanotechnology could indeed be life-changing. We must hope that these changes are for the better, and not at the expense of our environment and health.

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