Nanocomposites Improve Package Properties

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Abstract: *Nanocomposite technology has been described by some as the next great frontier of material science in packaging. This technology was developed to improve barrier performance pertaining to gases such as oxygen and carbon dioxide. It also enhances the barrier performance to ultraviolet rays, as well as adding strength, stiffness, dimensional stability, and heat resistance. New plastics created with this technology demonstrate an increased shelf life and are less likely to shatter. Once perfected, these plastics will offer these improved characteristics at competitive prices. It will also make them attractive for use in food and beverage packaging and pharmaceutical packaging applications.*

Introduction

In 2001, nearly 100,000 pounds of nanocomposite materials were used in the packaging industry; by 2011, the market in the United States is expected to be around 100 million pounds for rigid and flexible packaging ("Nanocomposites for packaging," 2002). "Polymer nanocomposites consist of resins [either thermoset or thermoplastics] that have fillers added with a least one dimension measured in nanometers. These fillers fall into three categories: nanotubes, nanoscale oxides and metals, and nanoclays" (Brauer, 2003, ¶ 2).

Nanotube-based nanocomposites are used for electrostatic dissipation applications; nanoscale oxides and metals are used for abrasion-resistant films; and nanoclay-based nanocomposites are used for barrier packaging applications (Scott & Wood, 2003). "Nanocomposites have received considerable attention over the past decade because of their potential to achieve property enhancements significantly greater than that attainable using conventional fillers or polymer blends" (Dean, Abadalla, & Ganguli, 2003, p. 12). The use of nanoclay-based nanocomposites in food and beverage packaging applications, and the properties that make them superior to conventional plastics, will be focused on.

Background

Nanocomposites were first referenced in the 1950s and polyamide nanocomposites were reported around 1976. In the early 1980s Toyota's ® Central Research and Development Labs began working with polymer-layered silicate-clay mineral composites and this is when the technology began to be studied more widely (Acquarulo & O'Neil, 2002). The clay mineral that is generating the most interest for use in nanocomposites is montmorillonite, generically referred to as nanoclay, and sometimes referred to as bentonite. "It is natural clay that is most commonly formed by the in situ alteration of volcanic ash or by the hydrothermal alteration of volcanic rocks" (Briell, 2004, ¶ 3). This clay is widely available and relatively inexpensive, thus becoming the most widely used clay in nanocomposite applications.

The first step in the preparation of the nanoclay involves purifying approximately 99 percent of the montmorillonite. The second step involves surface treatment of the clay. Montmorillonite is hydrophilic and relatively incompatible with most hydrophobic polymers, so it must be chemically modified to make its surface more receptive to dispersion (Capanescu & Capanescu, 2002). After the clays are chemically treated, they are dispersed in the polymer. The clays are incorporated into the polymer matrix by one of two approaches: during polymerization or by melt compounding (DeGaspari, 2001). This is the difficult part of the technology and may limit the use of nanocomposites (DeGaspari, 2001). The dispersion process requires a custom solution for each polymer used, so developing polymer nanocomposites becomes a capitol intensive research and development project. Very few compounding firms have this kind of capability, and this leaves resin producers or well-funded startup companies to develop these materials ("Nanoparticle News," 2003).

Nanoclay Composites Create a Torturous Path

A nanocomposite behavior is entirely dependent on the size of the clay fibers added. The smaller and thinner the fiber, the more surface area is available to interact with the polymer matrix and an improved plastic. The size of the clay fibers has grown smaller, which means that even tiny amounts of filler (two percent of total volume) can be added to achieve the same effects (Buchholz, 2003). The nanoclays used in plastic composites are extremely small, irregular platelets. They are approximately one nanometer thick and 100 nanometers in diameter. A single human hair is 80,000 nanometers thick, so one can understand how a little goes a long way (Dambeck & Latzel, 2003). Once these tiny flat platelets are dispersed into the plastic, they create a path that gases must follow to move through the material, greatly slowing their transmission (Demetrakakes, 2002).

Nanocomposites Deliver

"Today's nanocomposites typically demonstrate unique improvements in materials properties, including rigidity, strength, and barrier characteristics, while maintaining a level of transparency and offering the potential for recyclability" (Acquarulo and O'Neil, 2002, ¶ 25).

> Polymer-clay promise a veritable explosion of thermoplastic polymer applications because they are lightweight materials that rival metals in stiffness and strength while providing enhanced gas-barrier characteristics, superior dimensional stability, and high heat distortion temperatures – all with low mineral loading and virtually no loss in impact resistance (Chaiki, Leyva & Niyogi, 2003, p. 44).

Making this technology even more impressive is the fact that the properties improve with few penalties (such as higher density, brittleness, or loss of clarity) than with conventional reinforcements such as talc or glass (Leaversuch, 2001).

Nanocomposites Find a Niche in Food and Beverage Packaging

"Nylon is often touted as one of the most promising resins for nanocomposite additives" (Demetrakakes, 2002, ¶ 8). In packaging, the major application focus for nylon 6 nanocomposites is in high-barrier packaging. "Much of the attention is on PET bottles, where nanocomposites demonstrate an improved oxygen and carbon dioxide barrier" (Leaversuch, 2001, p. 66).

Honeywell's ® Aegis Role

Honeywell offers three grades of nanoclay nylon 6 resins; Aegis OX, HFX, and CSD. Aegis OX resin is an oxygen-scavenging nylon formulated for the high oxygen barrier demands of plastic beer bottles. "Honeywell has turned its attention to creating nano-nylon materials that can beat the cost of higher-barrier plastics or even glass" (Leaversuch, 2001, p. 67). The nanoclays act as the passive barrier and the nylon specific oxygen scavenger acts as the active agent ("There's No Barrier," 2004).

"Honeywell claims this one-two punch brings a 100 fold reduction in OTR versus nylon 6, taking oxygen ingress to near-zero levels" (Leaversuch, 2001, p. 67). Aegis OX demonstrates excellent resistance to delamination, it can be processed easily, has excellent clarity, is recyclable, and cost competitive ("There's No Barrier," 2004). Aegis OX is currently used in a three-layer PET bottle where it is the core layer for a 12-ounce premium beer bottle for Anchor Brewing of San Francisco (Leaversuch, 2003).

Honeywell's Aegis HFX Role
Aegis HFX is specifically formulated to address the growing requirement for improved delamination resistance in hot-fill bottle applications. It is a passive-active system that adds more oxygen resistance for foods. Customer trials have demonstrated that Aegis HFX meets shelf life requirements for hot-fill applications including juice, tea, and condiments (Leaversuch, 2003)

Honeywell's AEGIS CSD Role
For carbonated soft drinks, Aegis CSD provides delamination resistance during production. It also provides a high level of a passive carbon dioxide barrier compared with monolayer PET. "At 3.5 percent of bottle weight, Aegis CSD extends the shelf life of 0.5 liter bottles from 9 to 14 weeks. New data extends the shelf life to 16 weeks" (Leaversuch, 2003, p.53).

Honeywell's Specialty Film Roles
Films produced from Honeywell Specialty Polymers' provide excellent barrier properties to oxygen, flavors, and aromas. Each resin provides the extra performance needed for suitable films for a wide range of flexible packaging applications. They also provide toughness, strength, tear, and puncture resistance, and resistance to grease and gas penetration. Applications for this film include processed meat, fresh red meat, poultry, fish, cheese, dried food, and chilled fruit juices (Honeywell International, Inc., 2004).

Nanocor®-Mitsubishi's Gas Chemical Company, Incorporated® M9 Role
Nanocor has a different high barrier option. Through an alliance with the Mitsubishi Gas Chemical Company, Inc., Nanocor has rights to melt-compound its nanoclay additives with Mitsubishi's MXD6 nylon for use in barrier PET bottles and films under the trade name of "M9" (Leaversuch, 2003, p. 51).

Mitsubishi Gas Chemical Company, Inc. has supplied MXD6 plastics to the packaging market for 15 years. MXD6 features an excellent barrier for foods and beverages against harmful gases. It is preferred over competitive barrier plastics because it is easy to process and yields packages with high transparency. According to Peter Maul, President of Nanocor, said "M9 boosts the CO_2 and O_2 barrier of standard MXD6 respectively by 50 percent and 75 percent. The material also retains high clarity and delamination resistance equal to standard MXD6" (Leaversuch, 2003, p. 51). It is currently being used as the core of a three-layer 16-ounce non-pasteurized PET beer bottle and is said to have 100-fold lower OTR than that of straight PET. It also adheres to PET without tie layers and retains sufficient clarity to meet requirements for the amber bottle (Leaversuch, 2001).

M9's superior gas barrier provides flexibility in bottle design with a range of layer thickness to meet specific shelf life needs. Layer adhesion is virtually the same as standard N-MXD6, so it can be separated from PET by normal recycling methods. Because M9 is miscible with PET at layer thickness of five percent or lower, recyclers have the option of reprocessing thin-layer bottles in total, eliminating the separation step.

Rancor-Mitsubishi is able to extend the shelf life of a 28 gram weight PET bottle from 14 weeks to 21 weeks. They use the standard N-MXD6 with a five percent barrier layer of M9 due to its high carbon dioxide barrier (see Figure 1). The cut-off is at 90 percent CO_2 retention (Mitsubishi Gas Chemical CO., Inc., 2004).

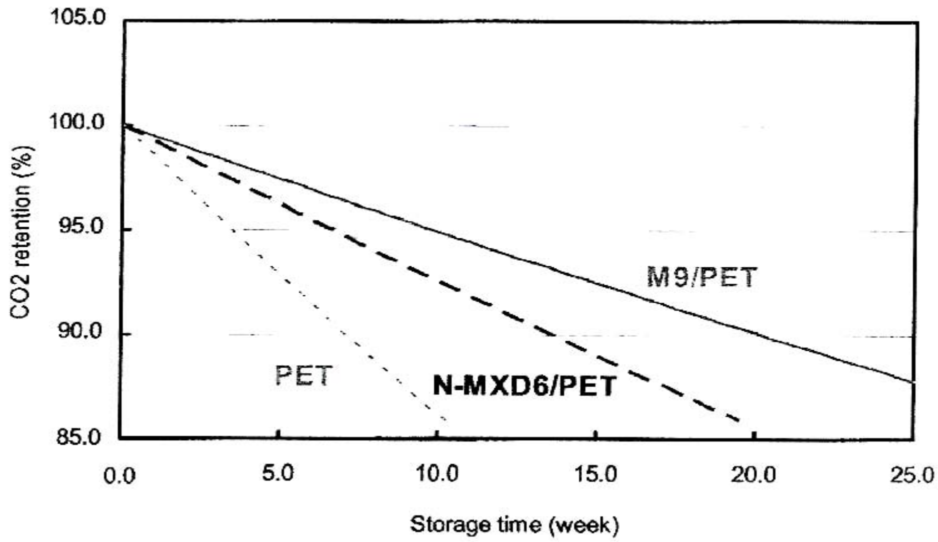

Figure 1. CO_2 Retention of Multilayer Bottle

Bayer's® Durethan Role

Bayer's research team is aiming nylon 6 nanocomposites at cast film. It is referred to as a hybrid system that uses Nanocor's clay to reduce OTR by around 50 percent versus nucleated nylon. "Stiffness of the nanocomposite is doubled, and its gloss and clarity rival those of a costly high-clarity polyamide film. Anti-blocking properties are also improved" (Leaversuch, 2001, p. 67). The new film material with nanoparticles unites the advantages of EVOH and polyamide 6. The embedded particles prevent gases from penetrating the film and moisture from escaping. Durethan KU 2-2601 is suitable for applications where conventional polyamides are too permeable and EVOH is too expensive. Bayer's Durethan KU 2-2601 makes an ideal candidate as a plastic coating for paperboard juice containers. It can protect highly oxygen-sensitive package contents, such as orange juice, at a much lower cost (Bayer, Inc., 2003).

Triton Systems, Incorporated® ORMLAS Role

Triton Systems, Inc. also has a class of commodity polymers that have been enhanced with organically modified nanoclays. These materials are sold under the trade name, ORMLAS, and have demonstrated improved barrier performance, impact resistance, as well as flame resistance (Triton Systems, Inc., 2004).

ORMLAS have been incorporated into a long-life food tray that offers high barrier performance and impact resistance. They also include high clarity, ease of manufacture, and recyclability (2004).

Nanoclay Resin Solution

In addition to its alliance with Mitsubishi, Nanocor offers its nanoclay resins to other converters for use in various consumer applications (see Figure 2). The dominant property improvement seen is a higher quality shelf life. This improvement can lead to lower weight packages because less material is needed to obtain the same, and if not better, barrier properties. This, in turn, can lead to reduced package cost. Improved shelf life and lower package cost are the reasons why nanotechnology is being pursued in consumer packaging (Nanocor, 2004).

	IMPROVED SHELF LIFE	COST REDUCTION	HOT STRENGTH	ODOR CONTROL	VITAMIN PRESERVATION	FLAVOR SCALPING	IMPROVED PRINTABILITY	CHEMICAL RESISTANCE
BOTTLES								
JUICE	X				X	X		
SOFT DRINKS	X							
CATSUP	X	X						
BEER	X					X		
VEGETABLE OIL	X							
BAGS & PACKS								
FATTY SNACKS	X							
SMOKED MEAT	X			X				
CHEESE	X	X		X				
BOIL-IN-BAG		X	X					
DOG FOOD	X			X	X			
ELECTRONICS		X						X
FILMS								
FRESH MEATS	X	X						
VACUUM-PACK CHEESE	X	X		X				
CARTONS								
JUICE	X	X			X	X		
MISC.								
SOUP LIDS			X				X	
STAND-UP-POUCHES		X					X	
MICROWAVE TRAYS	X		X					
SAUSAGE CASINGS		X						
AEROSOL CAN LINERS		X						
BUBBLE WRAP		X						X
ANTI-FREEZE CONTAINERS		X						
CIGARETTE WRAPPERS	X		X					

Figure 2. Nanocomposite Consumer Packaging Applications versus Property Improvements (Nanocor, 2004)

Challenges

Real world applications for nanocomposites are coming slowly. There appears to be a reluctance to embrace this new technology due to cost and variability in the quality of some of the products ("Nanocomposites Prove," 2002).

John Jones, a market development specialist at Honeywell, believes that manufacturers of these materials have to prove to the market that these new materials can meet their performance expectations ("Nanocomposites Prove,"2002).

Another challenge nanocomposite producers face is the production of the nanocomposite itself. Both methods, pre-polymerization and post polymerization, for preparing nanocomposites have drawbacks. "Pre-polymerization production can disrupt the polymerization process, which is often critical and requires much developmental time and expense to achieve good yields and controllability, and post polymerization often requires a lot of time to achieve a good dispersion of the nanoparticles in the composite" ("Nanoparticle News," 2003, ¶ 4). This then becomes an expensive and low cost-competitive initiative.

Another concern deals with equipment conversion that accepts new material through recalibration; this is a big investment for converters to make (Demetrakakes, 2002).

> It's a complicated process to go from plastic pellets to a blown bottle. It requires heating and blowing that form to the shape of the bottle. This is expensive equipment, very high-speed equipment, designed for the material that you're going to run. You can't just take another material with different flow characteristics, crystallization rate, and those kinds of things, throw that in there and make it run (Demetrakakes, 2002, ¶ 23).

Conclusion: Nanocomposites Advance into the 21ST Century

Today, nanocomposite research is widespread and is conducted by companies and universities across the globe. Plastic suppliers who have already commercialized nanocomposite materials include Basell USA, Bayer, Dow Chemical, Eastman Chemical, Mitsubishi Gas Chemical, Nanocor, Triton Systems, Honeywell, and RTP Co. ("Cutting Edge," 2001). Most of these efforts are currently focused on either polyolefins or nylons, but, in theory, the clay nanoparticles could be used in any resin family.

> Optimism surrounding these novel materials has increased since they burst into industry consciousness two or three years ago, and exploratory effort has intensified as a growing body of data substantiates the potential established by nylon/clay nanocomposites, emerging polyolefin versions, and a range of other resin matrixes and nano-fillers….the promise of nanocomposites is undiminished (Leaversuch, 2001, p. 64).

It appears that the momentum is building. The success of Honeywell, Mitsubishi Gas and Chemical, Bayer, Triton Systems and Nanocor will lead to other successes. As production reaches a sufficient scale, incorporating the clay into polymers will become more cost-effective as well. Equipment recalibration used for conventional plastic resins will also show success.

The popularity of nanocomposites comes from the fact that a little goes a long way. It provides a marked increase in oxygen, carbon dioxide, moisture and odor barrier properties, increased stiffness, strength and heat resistance, and maintains film clarity and impact strength. For the packaging industry, these new materials and their commercial applications are coming into focus.

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