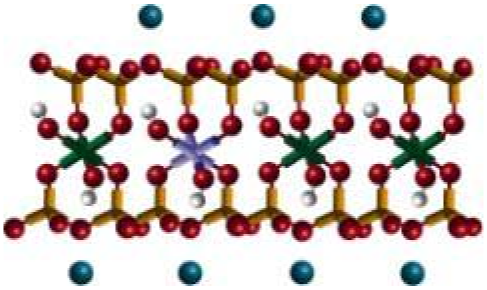
POLYMER NANOCOMPOSITES ARE THE FUTURE



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Introduction

Flexible packaging consumption's rapid growth represents a $38 billion market in the global community (Thibeault, 2004). As the demand in the industry continues to rise at an average of 3.5% each year, flexible materials need to meet and exceed the high expectations of consumers and the stressors of the supply chain (Butschli, 2005). Increased competition between suppliers along with government regulations translates into innovations in films that enhance product and package performance as well as address worldwide concerns with packaging waste.

One such innovation is polymer nanocomposite technology which holds the key to future advances in flexible packaging. According to Aaron Brody in a December, 2003 Food Technology article, "…nanocomposites appear capable of approaching the elusive goal of converting plastic into a superbarrier—the equivalent of glass or metal—without upsetting regulators" (Brody, 2003). This paper will discuss how nanocomposites are made and the growth of nanocomposite materials as a function of their numerous advantages in the packaging industry today and in the future.

Nanotechnology growth predicted

Nanocomposites, defined as polymers bonded with nanoparticles to produce materials with enhanced properties, have been in existence for years but are recently gaining momentum in mainstream commercial packaging use (Butschli, 2004). The United States is leading in nanotechnology research with over 400 research centers and companies involved with over $3.4 billion in funding. Europe has over 175 companies and organizations involved in nanoscience research with $1.7 billion in funding. Japan is also very involved in research with over 100 companies working with nanotechnologies (Anyadike, 2004). Globally, the market for nanocomposites is expected to grow to $250 million by 2008, with annual growth rates projected to be 18-25% per year (Principia, 2004).

How nanocomposites work

Polymer nanocomposites are constructed by dispersing a filler material into nanoparticles that form flat platelets. These platelets are then distributed into a polymer matrix creating multiple parallel layers which force gases to flow through the polymer in a "torturous path", forming complex barriers to gases and water vapor, as seen in Figure 1 (Demetrakakes, 2002). As more tortuosity is present in a polymer structure, higher barrier properties will result. The permeability coefficient of polymer films is determined using two factors: diffusion and solubility coefficients:

$$P = D \times S.$$

Effectively, more diffusion of nanoparticles throughout a polymer significantly reduces its permeability. According the Natick Soldier Center of the United States Army, "the degree of dispersion of the nanoparticles within the polymer relates to improvement in mechanical and barrier properties in the resulting nanocomposite films over those of pure polymer films".

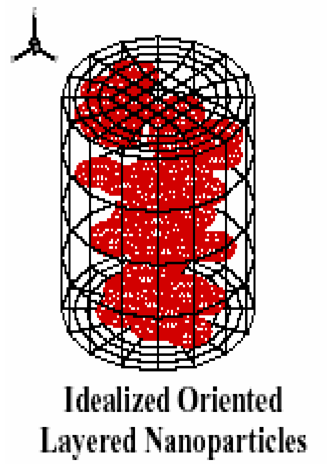


Figure 1 (Source: University of South Carolina, 2004)

Nanoparticles allow for much lower loading levels than traditional fillers to achieve optimum performance. Usually addition levels of nanofillers are less than 5%, which significantly impact weight reduction of nanocomposite films. This dispersion process results in high aspect ratio and surface area causing higher performance plastics than with conventional fillers (Brody, 2003).

Different types of fillers are utilized, the most common is a nanoclay material called montmorillonite—a layered smectite clay. Clays, in a natural state, are hydrophilic while polymers are hydrophobic. To make the two compatible, the clay's polarity must be modified to be more "organic" to interact successfully with polymers (Hay, 2000; Ryan, 2003). One way to modify clay is by exchanging organic ammonium cations for inorganic cations from the clay's surface (Sherman, 1999).

Additional nanofillers include carbon nanotubes, graphite platelets, carbon nanofibers, as well as other fillers being investigated such as synthetic clays, natural fibers (hemp or flax), and POSS (polyhedral oligomeric silsesquioxane). Carbon nanotubes, a more expensive material than nanoclay fillers which are more readily available, offer superb electrical and thermal conductivity properties. The major suppliers for nanoclays are Nanocor and Southern Clay.

There are three common methods used to enhance polymers with nanofillers to produce nanocomposites: melt compounding, in-situ polymerization and the solvent method. Melt compounding – or processing – of the nanofillers into a polymer is done simultaneously when the polymer is being processed through an extruder, injection molder, or other processing machine. The polymer pellets and filler (clay) are pressed together using shear forces to help with exfoliation and dispersion (Chen, 2004; Brody, 2003). With in-situ polymerization, the filler is added directly to the liquid monomer during the polymerization stage. Using the solution method, fillers are added to a polymer solution using solvents such as toluene, chloroform and acetonitrile to integrate the polymer and filler molecules (Chen, 2004). Since the use of solvents is not environmentally-friendly, melt processing and in-situ polymerization are the most widely used methods of nanocomposite production.

Packaging industry uses of nanocomposites

Advantages of nanocomposite films are numerous and the possibilities for application in the packaging industry are endless. Because of the nanocomposite process's dispersion patterns, the platelets result in largely improved performance in the following properties (Anyadike, 2004):

- Gas, oxygen, water, etc. barrier properties
- High mechanical strength
- Thermal stability
- Chemical Stability
- Recyclability
- Dimensional stability
- Heat resistance
- Good optical clarity (since particles are nano-size).

A majority of consumer products that use nanocomposite packaging are in the beverage industry. Many different types of commercial plastics, flexible and rigid, are utilized for nanocomposite structures including polypropolyene (PP), nylon, polyethylene terephthalate (PET), and polyethylene (PE).

Gas Barrier

Studies show that “Nylon-6 nanocomposites can achieve an OTR (oxygen transmission rate) almost four times lower than unfilled nylon-6” (Brody, 2003, p53). In the case of Honeywell Aegis™ OX, the nanoclay layers act as a trap to retain the active oxygen scavengers in the polymer while reducing OTR 100-fold (Leaversuch, 2001). Imperm®, produced by Mitsubishi Gas Chemical Company, has similar results when added to a multilayer PET structure. Imperm’s® oxygen barrier is two times the standard Nylon MXD6 and it’s carbon dioxide barrier is four times that of the standard (Imperm, 2004). It also requires no adhesion tie layers to PET and is very recyclable.

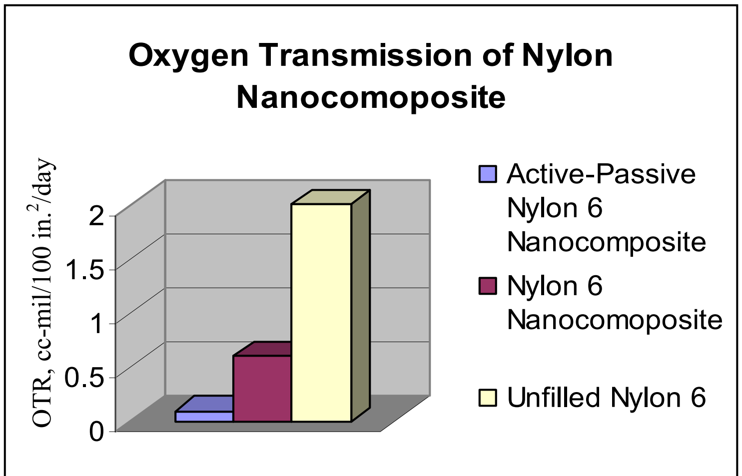


Figure 2 (Source: Plastics Technology, 2001)

Nylon nanocomposites, used as barrier layers for multilayer PET containers prove to perform better -- as much as two to three times better -- than the traditional EVOH barrier layer since nylon has a 50°F higher melt temperature (Demetrakakes, 2002). When used in a 16 oz. beer bottle, Imperm® nanocomposite guarantees almost seven months of shelf life.

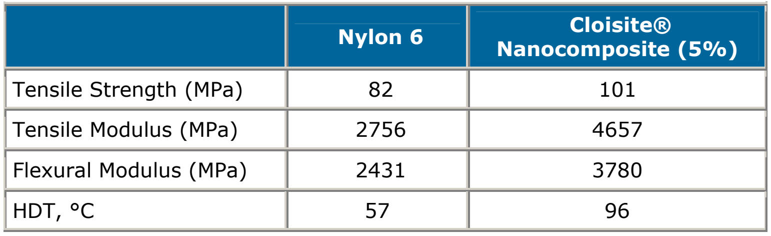
Honeywell produces three versions of their nylon-6 nanocomposite Aegis™: OX, HFX and CDSE. Aegis™ OX contains an oxygen scavenging component

Figure 3 (Source: Butschli)

intended for use in beer bottles that provides a shelf life of 6-12 months – comparable to glass bottles. In 2003, Aegis™ was used in a three layer 1.6 liter structure for a South Korean brewery.

Mechanical Strength

Tensile strength, tensile modulus and heat distortion temperature (HDT) characteristics are improved with the use of nanotechnology. Cloisite®, a nylon nanocomposite produced by Southern Clay Products with a clay loading of 5%, exemplifies these increased mechanical properties. Nanoclays in nylon increase tensile strength in this example by 23% (see Figure 4). The tensile modulus is increased by 69% and the flexural modulus is increased by 56%. In addition, HDT is raised by 68%. The amount of change in mechanical properties is directly related to the quantity of nanofiller used in the particular nanocomposite. For example, by adding 2% nanoclay to a nylon 6 nanocomposite increases tensile strength by 49%. However, adding 6% nanoclay dramatically increases the tensile strength by 98% (Ling, et. all, 2004). This pattern also applies to the HDT and flexural modulus characteristics. Other nylon nanocomposite polymers have increased mechanical properties similar to Cloisite®.



	Nylon 6	Cloisite® Nanocomposite (5%)
Tensile Strength (MPa)	82	101
Tensile Modulus (MPa)	2756	4657
Flexural Modulus (MPa)	2431	3780
HDT, °C	57	96

Figure 4 (Source: Southern Clay Products, 2005)

Environmental Aspects

As the global flexible packaging market increases, we will see more and more specialized products utilizing films. Nanocomposites would ease the transition between current packaging with metal layers and glass containers to flexible pouches or rigid plastic structures. Many current structures require multiple layers which render the packaging un-recyclable, but in the face of global recycling issues, nanocomposite polymers would help to reduce packaging waste and would allow recycling efforts. Waste reduction is a very pressing issue in the world and the U.S. military is a good example of how nanocomposite polymers can positively impact the environment.

Waste Reduction Applied in Military Packaging

Since 2002, the U.S. Army Natick Soldier Center has been conducting extensive research into the use of no-foil polymer nanocomposite structures for military food rations -- Meals Ready-to-Eat (MRE's). The goal of the research is to reduce the amount of solid waste associated with the current packaging as well as reducing costs through material savings. Each year, 14,177 tons of MRE packaging waste is generated because the foil layer, which is susceptible to pinholing, does not allow the pouch to be recycled. One Army ration creates 1.04 pounds of waste, while a Navy ration creates 3.8 pounds of solid waste (SERDP, 2003).

Figure 5 (Source: U.S. Army, 2005)

The current MRE packages, which are three to four-layer retortable pouches with a foil layer, do not meet the rigorous standards of the military (U.S. Army, 2004). MRE packaging needs to withstand the following conditions: air-droppable, a minimum three year shelf life at 80°F and six months at 100°F (Culhane, 2005). Using nanocomposite polymers, which offer higher barrier properties, will extend shelf life and greater product protection for military rations.

Nanocomposite ration pouches are not in production at the moment but according to Natick they are in advanced stages of development for future use. Natick researchers are working with a variety of different materials including LDPE, Nylon, EVOH, PHA's, PLA, and PCL to find the right blend of polymers and nanofillers when delivered through various extrusion processes such as: cast film, multilayer film, blown film, single screw and twin screw (Culhane, 2005). It is possible that the technologies developed by Natick would be accessible to commercial food packagers to increase processed food shelf life since the military standards are more rigid.

According to U.S. Army research, costs of the future nanocomposite structures are estimated to be 10-30% less than the current pouches. Expected savings come from less material cost, improved manufacturability with more automation, and less waste handling costs. Overall cost savings are estimated at $1-3 million (U.S. Army, 2004).

Challenges

Despite the prosperous future of nanocomposites, there are a few issues that warrant concern about the mass commercialization of these polymers. According to University of South Carolina researchers, there are four main issues dealing with the production and use of nanocomposites:

- Exfoliation
- Orientation
- Compatibility
- Reaggregation.

Exfoliation and Orientation

When using clay fillers, it is necessary to separate the particles into the right shape and layer structure called “exfoliation”. They need to be very thin – one nanometer — and very wide — 500 nanometers — to be able to achieve optimal gas permeability without effecting optical quality. Particle orientation also has an effect on the success of a nanocomposite. Nanoparticles need to be dispersed throughout polymer so they are parallel to the material’s surface. This position ensures a maximum “torturous path” for the gases when migrating through the polymer. For converters, proper particle orientation is an ongoing problem (Dematrakakes, 2002).

Compatibility and Reaggregation

Compatibility between the nanofillers and the polymer substrate may cause issues as well, depending on how they interact with each other. Certain nanofillers need to be prepared so they can perform well with the substrate. Another concern is during the processing stage. There is a possibility of reaggregation where the particles clump together. If this happens, the creation of the nanocomposite is unsuccessful.

Future of Nanocomposites

By 2009, it is estimated that the flexible and rigid packaging industry will use five million pounds of nanocomposites materials in the beverage and food industry. By 2011, consumption is estimated to be 100 million pounds. Beer is expected to be the biggest consumer by 2006 with 3 million pounds of nanocomposites until carbonated soft drinks bottles are projected to surpass that to use 50 million pounds of nanocomposites by 2011 (Butschli, 2004).

Polymer nanocomposites are the future for the global packaging industry. Once production and materials cost are less, companies will be using this technology to increase their product's stability and survivability through the supply chain to deliver higher quality to their customers while saving money. The advantages that nanocomposites offer far outweigh the costs and concerns and with time the technology will be further refined and processes more developed. Research continues into other types of nanofillers (i.e., carbon nanotubes), allowing new nanocomposite structures with different improved properties that will further advance nanocomposite use in many diverse packaging applications.

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