by Claire Koelsch Sand

Promised Land Dairy's Midnight Chocolate Milk *is packaged in polyethylene terephthalate packaging by CKS Packaging.*
Photo courtesy of Promised Land Dairy

Superior Barriers

Packaging with superior barriers provides extended shelf life for many packaged foods. Determination of a required barrier is a function of the deteriorative mechanisms in the food, desired shelf life, and distribution conditions. In general, for adequate shelf life, food packaging needs to provide appropriate barriers to oxygen, water, carbon dioxide, and a host of flavors and aromas. Polymer selection and polymer modifications with micro- and nano-additives and advanced coating technology allows for a wide selection of cost-effective superior barrier polymers for foods.

Barrier Polymer Selection

Barrier polymers are characterized by their interaction with the permeant and their restriction of permeant transfer. Permeation is a function of both solubility and diffusion. The polymer structure is altered when it has high solubility to a permeant. For example, limonene, a flavor component of orange juice, readily absorbs into low-density polyethylene (LDPE) and alters the polymer's structure; this decreases the juice's orange flavor, package seal strength, and integrity. Replacing LDPE with a polymer that has lower solubility allows retention of orange flavor and package characteristics. LDPE is not suitable for packaging juice, but for many bread products, LDPE is adequate. After permeant absorbs into the polymer, diffusion through the polymer becomes relevant. Diffusion in polymers is dictated by many factors, including polymer crystallinity, orientation, free volume, and cohesive energy density. The main barrier polymers in use for food packaging are polyethylene terephthalate (PET), ethylene vinyl alcohol (EVOH), polyvinylidene chloride (PVDC), and nylon.

PET is on the low end of the superior barrier spectrum and is the most common barrier polymer used in food packaging because of its clarity, variations, and sustainability. While low oxygen, water, and carbon-dioxide permeability is the primary reason for PET selection, the clarity of PET is a major factor in the adoption of PET. For example, Promised Land Dairy, Dallas, Texas (promisedlanddairy.com), uses blow-molded PET bottles by CKS Packaging, Atlanta, Ga. (ckspackaging.com), which extends the shelf life of milk. In the 1980s and 1990s, conversion from glass to PET for packaging of peanut butter, beverages, salad dressings, vegetable oils, and mayonnaise was driven by the energy cost of transport, production, and recycling as the glass industry consolidated. Since then, PET has been formulated to meet specific needs, such as readily formable amorphous PET (APET), oven-safe/microwaveable crystallized PET (CPET), microwaveable clear PET, and freezer-grade PET. As a superior barrier polymer, PET is well positioned environmentally: Recycling rates are high (with Switzerland's PET recycling rate above 85%), thin-walled containers are viable, and PET derived from sugarcane byproducts is projected to create 45 billion bottles worldwide by 2020.

EVOH, a copolymer made of ethylene and vinyl alcohol, offers an oxygen barrier with significant improvement upon PET. EVOH is hydrophilic and usually contains 50%–75% vinyl alcohol. Specific grades of EVOH offer enhanced barriers, clarity, and flavor retention. Since moisture is often within products and distribution environments, EVOH requires moisture protection within a package structure. For this reason, EVOH is sandwiched between high-moisture barrier polymers and engaged with desiccants to absorb excess moisture. Because the cost of EVOH is high, its optimal use is as a thin layer within extrusions or laminations with lower cost packaging materials. In many cases, EVOH has replaced aluminum foil due to the propensity of foil to form pinholes and stress fractures, the expense of lamination that foil requires, and its lack of transparency. For example, fresh pasta is packaged in a polypropylene (PP)/EVOH/PP thermoform container that can withstand distribution at a lower cost than foil lamination, which allows consumers to see the product. Other applications include components within condiment bottles, modified atmosphere packaging (MAP), and coffee lidding and bags.

EVOH is used to package products requiring conventional retort processing, but during elevated processing temperatures, EVOH gains moisture. This affects EVOH's ability to maintain its superior oxygen barrier. For example, after retort processing, oxygen permeability increases 100% through structure of PET/EVOH/crystallized PP. Solutions to inhibit moisture gain are complex and relate to the use of micro- and nano-particles to boost the functionality of PP or PET and the use of moisture and oxygen scavengers. Processing alternatives such as microwave-assisted thermal sterilization (MATS) and high pressure processing (HPP), which require shorter processing time and lower temperatures, are also solutions. In particular, MATS requires less processing time than conventional retorting, and this results in less water absorption and a lower impact on the oxygen permeability of EVOH. Interestingly, since HPP decreases the free volume and can increase the crystallinity of polymers, processing can result in superior barrier properties after processing.

Other barrier polymers in use include PVDC and nylon. Until EVOH was discovered, PVDC and nylon were the only commercial high oxygen barrier polymers. Yellowing, environmental issues due to chlorine, processing issues, and temperature sensitivity have resulted in decreased use of PVDC. However, PVDC is used to achieve high barriers in the *CHB Bronze* pouch by Glenroy, Menomonee Falls, Wis. (glenroy.com), and offers a superior oxygen barrier with fewer moisture concerns than EVOH. Nylon is a moisture-sensitive oxygen barrier similar to EVOH but has improved puncture resistance and is used as a layer within cheese and meat packaging. Nylons such as *Ultramid* by BASF, Ludwigshafen, Germany (basf.com), are used in vacuum food packaging. Nylon-MXD-6 and amorphous nylons, introduced in the 1980s and 1990s, offer superior barrier properties compared to traditional nylons.

Polymer Modification

The chemical structure of a plastic package can be altered to restrict solubility and diffusion and achieve a superior barrier. Modifying high- and low-barrier polymers to achieve the desired barrier is often a cost-effective alternative to laminations, extrusions, or thick polymer packaging. Altering crystallinity, orientation, plasma treatments, and fluorine assists with increasing polymer barrier properties. *ACTIS* by Sidel, Hünenberg, Switzerland (sidel.com), creates a nanoshield by using an amorphous hydrogen-rich carbon treatment inside PET bottles to enhance barrier properties. However, some modifications can affect package seal and mechanical strength. For example, CPET has a superior oxygen barrier, but it becomes more opaque and hard to seal. Usually, CPET containers requiring sealing have a top layer of APET to achieve adequate seal characteristics. In many polymers, nucleation technology is employed to reduce crystal size, resulting in a more tortuous path and an improved barrier.

Micro- and Nano-Additives

Impermeable micro- and nano-additives within polymers create a tortuous path for diffusion, resulting in improved barriers. Their addition to polymers such as PP, PE, and PET achieves superior barriers in a cost-effective manner. Polymers containing 2%–25% micro- and nano-composites have been in use since the 1980s, but their use is being refined. With such additives, barriers to oxygen, water, and carbon dioxide can be improved with little effect on adhesion and mechanical properties of the package, and issues with lamination or extrusion compatibility with multiple layers within a package are eliminated. Ceramics, carbon nanofiber, and multi-walled carbon nanotubes are in common use and more functional dual purpose fillers are under development to meet needs in the food value chain.

Micro-and nano-particles with a high aspect ratio that readily disperse within a polymer are required to achieve effective superior barriers. There is rapid development in this area. Exfoliation processes use compatibilizers to weaken van der Waals forces and enable nano-particle dispersion within a polymer. This dispersion allows maximization of the surface area of the particle and lengthening of the path for permeant diffusion through a polymer. This improves barrier properties. Tightly controlled processes are needed, and recent research shows that proper exfoliation of modified graphene oxide allows for barrier properties to improve by 65%. Use of micro- and nano-particles are need specific. For example, *REVOH* technology by Winpak, Winnipeg, Canada (winpak.com), employs micro-particles within the PP layers surrounding EVOH to reduce moisture gain due to retort processing. This allows for higher retort temperature processing with an improved oxygen barrier and less plastic packaging. The micro- and nano-technology is often coupled with moisture and oxygen scavengers such as in *OxyRx* by Mullinix Packaging, Fort Wayne, Ind. (mullinixpackages.com), which has selenium nanoparticles between PET and LDPE layers. These scavengers absorb excess moisture and oxygen throughout product shelf life.

While micro-and nano-particles have focused on decreasing the flow of oxygen, water, and carbon dioxide through polymers, rationale for their use is expanding due to the potential for increased functionality. Particles within polymers can serve as multiple function fillers by aiding in fraud and spoilage detection, transferring flavors and aromas, imparting mechanical functionality, and improving sustainability. For example, fluorescent-based technology allows detection of polymer counterfeiting. And the addition of biosensitive micro- and nano-particles can detect product expiration as well as provide a superior barrier. Micro-and nano-clays enable pouches containing juice, milk, and other beverages to remain upright during retail and consumer use. And glass and mineral-filled PP materials such as *Echo* by Ravagorg, Pasadena, Texas (ravagorg.com), can be readily adapted for the food packaging industry to enhance permeability as well as mechanical properties. Other functional particles such as hardwood-derived non-sulfonated lignin by Sweetwater Energy, Rochester, N.Y. (sweetwater.us), have the potential to offer enhanced polymer properties while reducing the need for synthetic polymers. However, superior barrier properties cannot be readily achieved by adding particles with extremely poor barriers. Therefore, matching synthetic polymers with edible polymers containing micro- and nano-particle barrier properties cannot be realized because plasticizers within edible films are needed to establish sufficient mechanical and package-forming properties. The use of polymer functional fillers is becoming widespread in the packaging industry due to the need for cost-effective barriers and their potential for multiple functions.

Coatings and Layers

Coatings and surface treatments continue to provide superior barriers needed in food

Superior Barriers continued...

Sidel's* ACTIS *barrier solution *is available on its modular* Matrix Combi *equipment, which can be integrated in bottling lines or converter lines.*
Photo courtesy of Sidel

packaging. In use are coatings of silicon dioxide, silicon nitride, and 40-nanometer metalized coatings. Coating PET bottles with silicon dioxide increases the shelf life of orange juice by two months. Thin multilayer films formed by layer-by-layer (LbL) assembly offer new possibilities as well. For example, with LbL assembly, polyelectrolyte multilayer nano-coatings improve PP barrier properties by 300%. Tera-Barrier Films, Singapore (tera-barrier.com), uses reactive and nonreactive nanoparticles within an encapsulated layer to flex and fill polymer inconsistencies and pinholes that reduce barrier properties.

Nanolayers of vanadium oxide in electrochromic layers improve barrier properties and enable color changes with temperature. Besides barriers for oxygen, water, and carbon dioxide, there is a growing need for other barrier protection and multifunctional coatings for food packaging. Barriers to control specific migrants and extend shelf life are a focus of coating technologies. For example, migration of mineral oil toxins from recycled content paperboard can be controlled by polymer-based paper coatings.

Gordon Robertson will provide a glimpse of plastic packaging and shelf life complexities in the IFT short course "Plastics Packaging and Shelf Life," April 27–28, 2017. "Development of food packaging that provides just enough protection to ensure that food maintains its acceptability until the end of shelf life requires detailed understanding of both food and packaging and how they combine to deliver the desired shelf life," he explains. **FT**

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