Treading lightly

The pressure is on for designers to pick materials that will leave little to no environmental footprint at the end of a product's useful life.

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Senior Editor

Films such as NatureFlex NVS from Innovia Films in the U.K. are said to provide improved dimensional stability under chill conditions and enhanced transparency in packaging applications. The high-gloss film also has good antistatic properties, is semipermeable to moisture, and will completely biodegrade in a compost heap.

Product designers have historically focused on performance and how much it will cost to mold parts when spec'ing engineering resins. With FEA and CAE software, it's easy to narrow the field of options based on mechanical, thermal, and physical performance. But these tools won't tell designers about the environmental footprint the various resins (including fillers, additives, and reinforcements) leave at the end of a widget's useful life.

"Environmental responsibility requires that designers look at the entire product cycle from basic feedstock to ultimate disposal from a holistic point of view," says Ramani Narayan, professor chemical & biochemical engineering at Michigan State University. Biodegradability is a big part of biobased polymers' appeal. These renewable resource-derived plastics (as opposed to petroleum-based plastics) can be disposed of through composting, soil application, and biological wastewater treatment. This makes them prime candidates for use in short-life and disposable consumer goods and packaging. "To use them, however, designers must engineer products so they retain the material's biodegradability," says Narayan. "For durable products, biobased materials are also an option, but need to be engineered for performance and long life which may impact how well the material will biodegrade."

BIODEGRADABLE MATERIALS

"Biodegradation of natural materials (including biodegradable plastics) produce valuable compost as the major product, along with water and CO_2," says Narayan. "But the CO_2 produced doesn't contribute to an increase in greenhouse gases because it is already part of the biological carbon cycle."

But polymers have historically been designed to resist degradation as happens in a compost heap. "The challenge," says Narayan, "is to design polymers that have the necessary performance during use, but destruct under the stimulus of an environmental trigger when discarded. The trigger could be microbial (anaerobic digestion). They could also have hydrolytically or oxidatively susceptible linkages built into their polymer backbones or additives that catalyze polymer-chain breakdown in specific environments (marine/ocean and soil)."

NatureFlex NM is a cellulose-based film made from renewable wood pulp. It has passed EN13432 and ASTM D6400 protocols and can be used in home composting.

"Ideally, polymers should break down in one or two growing seasons and not leave any toxic breakdown products. Most petroleum-based polymers don't pass this test. Polyethylene (PE) or PE-wax-coated paper products, for example, are problematic in composting. The paper fully biodegrades but the PE or wax coatings don't. "Paper products coated with fully biodegradeable films can provide water resistance and tear strength comparable to PE coatings," says Narayan. "And will be completely biodegradeable and noninterfering in recycling operations.

DEGRADABLE VERSUS BIODEGRADABLE

"Making or calling a product biodegradable or recyclable has no meaning whatsoever if it doesn't end up in a disposal infrastructure that uses biodegradability or recyclability features," says Narayan. Recycling makes sense if the recyclable product can be converted into something useful. "Likewise, biodegradable products make sense only if they go into a disposal system that uses biodegradation," says Narayan. Disposal systems in this category include composting, wastewater/sewage-treatment facilities, and managed, biologically active landfills (where methane landfill gas gets harvested for energy).

There is an important distinction between products that degrade and those that biodegrade. The problem is that products designed to degrade may break up into small fragments which may not biodegrade. "These degraded, hydrophobic, high-surface-area plastic residues migrate into the water table and other compartments of the ecosystem to harm the environment," says Narayan.

It has been reported that plastic debris can degrade into microscopic granular or fiberlike fragments. These fragments have been steadily accumulating in the oceans. Research has shown that marine animals consume microscopic bits of plastic. "The Algalita Marine Research Foundation reports that degraded plastic residues can attract and hold hydrophobic elements like PCB and DDT up to 1 million times background levels," says Narayan. "The PCBs and DDTs are at background levels in soil, and diluted out so as to not pose significant risk. But degradable plastic residues with high surface area concentrate these highly toxic chemicals, resulting in a toxic time bomb, a poison pill floating in the environment posing serious risks." Fish, for example, are not only exposed to background PCBs in the water through skin and breathing, they consume smaller fish and insects also contaminated with PCBs. This food chain "bioaccumulation" reportedly can magnify PCBs up to a million times that of background levels. Adverse health effects from PCBs may in-

BIOBASED POLYMERS

There are two basic ways of making polymers out of agricultural feedstocks. The first is to directly extract natural polymer materials (cellulose, starch, proteins), fibers, and vegetable oils that can form the platform on which polymer materials and products can be developed. The second biomass feedstocks can be converted to biomonomers by fermentation or hydrolysis. The biomonomers can be further modified by biological or chemical means. The biomonomers can be fermented to give succinic acid, adipic acid, 1,3-propane diol — precursor chemicals for the manufacture of polyesters. Sorona polyestyer from **DuPont**, Wilmington, Del., for example, is made from a bio 1,3-propane diol.

Biomonomers can be fermented to lactic acid, which is then converted into poly (lactic acid) — currently commercialized by **NatureWorks LLC**, Minnetonka, Minn. Biomonomers can also be microbially transformed to biopolymers including polyhydroxyalkanoates (PHAs).

Instead of microbial fermentative processes, chemical conversion of biomonomers yields intermediate chemicals including ethylene, and propylene glycols. Vegetable oils offer a platform to make a portfolio of polyols, lubricants, polyesters, and polyamides. Likewise, an ozone mediated transformation of vegetable oils can also produce polyols, urethane foams, polyesters, and polyamides. Surfactants, detergents, adhesives, and water-soluble polymers

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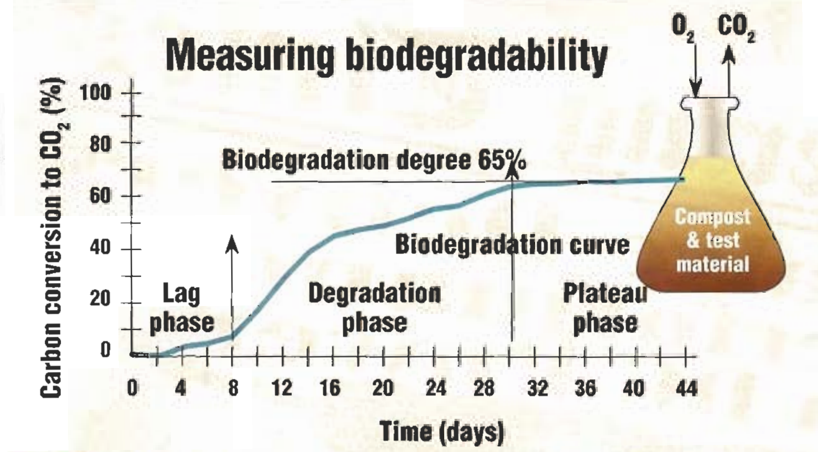

Test method to measure the rate and extent of microbial utilization (biodegradation) of biodegradable plastics.

clude disruption of reproductive function, neurobehavioral and developmental deficits in children, and increased cancer risks.

Recently, continues Narayan, Japanese researchers reported finding high concentrations of PCBs, DDE (major metabolite of DDT), and nonylphenols (NP) in degraded polypropylene (PP) resin pellets collected from Japanese coasts.

"Designing hydrophobic polyolefin plastics like PE to be degradable, without ensuring that microbial populations completely assimilate the degraded fragments, poses more harm to the environment than if it was not made degradable at all," says Narayan. "Heat, moisture, sunlight, and/or

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can be engineered from biomass feedstocks.

Starch is a polymer of anhydroglucose and is one of the most abundant renewable polymers found in nature. Cereal grains, primarily corn, are the major sources of starch. Plastic starch can be synthesized by the use of appropriate plasticizers that break the hydrogen bonds, and let the starch flow like a thermoplastic. Through reactive compounding plastic starches with biodegradable polyesters films with excellent performance properties can be made.

Modification of the starch-OH groups by esterification chemistry is another method of making starch esters with thermoplasticity and water resistance. Unmodified starch shows no thermal transitions except the onset of thermal degradation at around 2,600°C. Starch acetate materials have shown a sharp glass transition (T_g) at 1,550°C and starch propionate has a T_g of 1,280°C.

Starch esters have much more water resistance than unmodified starch. The starch-ester resin reinforced with biofibers has properties comparable to general-purpose polystyrene. Appropriately formulated starch esters with plasticizers and other additives provide resin compositions that can be used to make injection-molded products and for direct lamination onto Kraft paper. Starch acetates can undergo complete and rapid biodegradation. In the case of starch triacetates, 70% of the carbon is reportedly converted to CO_2 at 580°C in 45 days.

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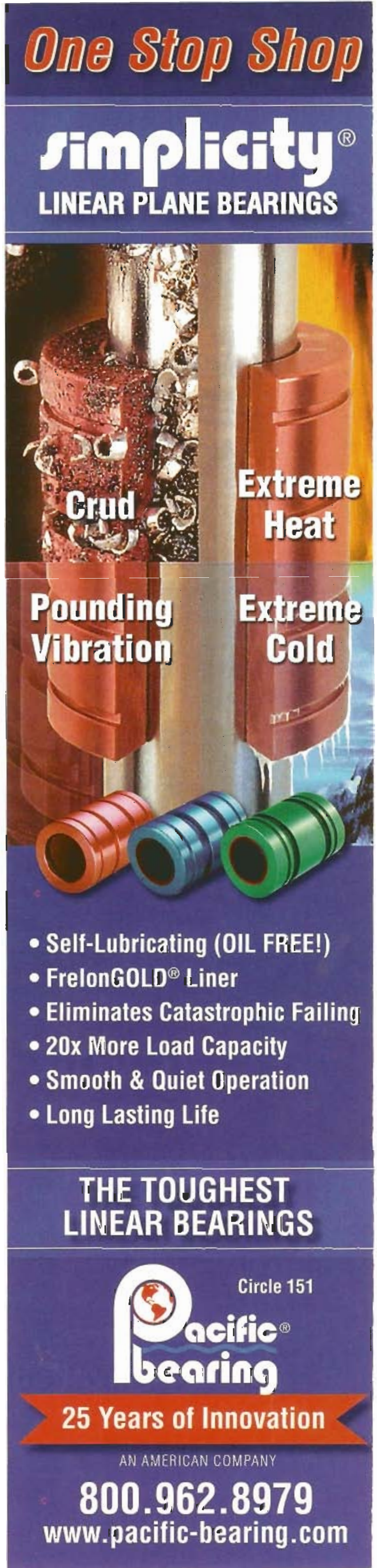
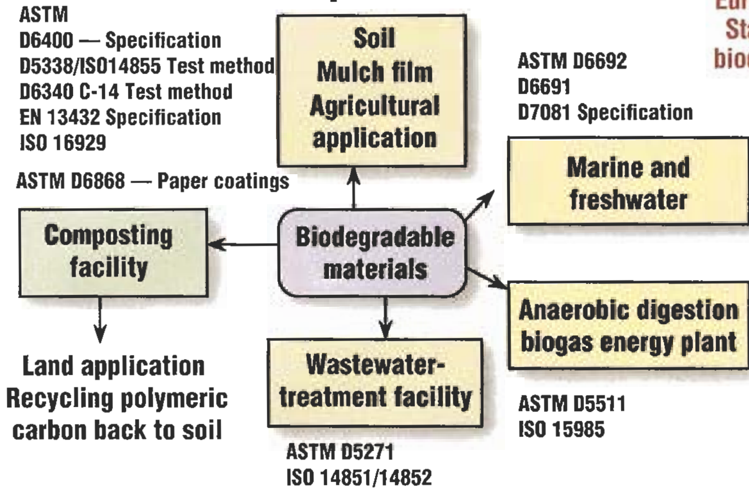


U.S. and European standards



ASTM and European (EN) Standards for biodegradable plastics in different disposal systems.

enzymes shorten and weaken polymer chains," continues Narayan. "This fragments the plastic and causes more cross linking which, in turn, creates more intractable persistent residues."

ASTM TESTS

A formal life-cycle assessment (LCA) of a product can give insights into disposal options. And a new ASTM standard (D7075) has recently been published on evaluating environmental performance of biobased products using LCA methodology. ASTM and other standards gauge biodegradability by measuring the amount of CO_2 given off during composting. The CO_2 is a direct measure of the amount and rate of microbial utilization (biodegradation) of the biopolymer. "The biopolymer serves as the

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Michigan State University (MSU) has developed a one step, environmentally friendly extrusion process to manufacture foam sheets and blocks for packaging. The foam is biobased, nontoxic, and biodegradable. And is said to have comparable performance as polyethylene-based foam in targeted applications and complies with ISO 1401. After use, it can be composted in soil.

The MSU process uses water as the plasticizer and blowing agent. Water and the shear imparted in the extrusion process helps break the hydrogen bonds holding the starch molecules in the granule state. This releases the polymer chains without significantly reducing the molecular weight of the amylose/amylopectin chains. Nucleating agents and process aids control cell structure and maintain foam flexibility. Screws in the extruder control the foaming process. MSU's focus is to develop process parameters for making a portfolio of foam products with varying cell structures, resiliences, and barrier properties.

Green Cell foam sheets made by **KTM Industries,** Lansing, Mich., are used in cushion packaging and insulation. Based on successful trials, they have been used for over 12 months by Toyota to ship automotive video entertainment systems, windshields, and end caps without failing.

Ramani Narayan, Dept. of Chemical Engineering and Materials Science, MSU

sole carbon source in a test system containing a microbially rich compost in the presence of air and under optimal temperature conditions (preferably at 580°C the temperature best suited for thermophile organisms)," says Narayan. "As carbon converts to CO_2, there is first a lag phase during which the microbial population adapts to the biopolymer. Next, biodegradation begins as the adapted microbial population starts using the carbon for its cellular life processes and converts carbon in the test material to CO_2. Finally, the output reaches a plateau when all of the substrate is completely used."

MEASURING BIODEGRADABILITY

The ASTM has developed the ASTM D6400 standard to cover products claiming to be biodegradable via composting. It is intended to establish the requirements for labeling of materials and products, including packaging made from plastics, as "compostable in municipal and industrial composting facilities." It determines if plastics and products made from plastics compost satisfactorily, including biodegrading at a rate comparable to known compostable materials (i.e., food stuffs, lawn wastes, and paper). The standard identifies three criteria: complete biodegradation, disintegration, and safety.

Using the ASTM D5338-93 test method will determine aerobic biodegradation of plastic materials under controlled composting conditions. The plastic must completely mineralize — convert to CO_2, water, and biomass via microbial assimilation. The plastic is mixed with stabilized and mature compost derived from the organic fraction of municipal solid waste. The net production of CO_2 is recorded relative to a control containing only mature compost. After determining the carbon content of the test substance, the percentage biodegradation is calculated as the percentage of solid carbon of the test substance converted to CO_2. In addition to carbon conversion, disintegration and weight loss can be evaluated.

Sixty percent of single polymer materials must mineralize in six months. Polymer blends, copolymers, and plastics with low-molecular weight additives or plasticizers must show 90% biodegradability in the same time frame.

Materials in product form must show intense microbial activity. They must disintegrate into fragments with less than 10% of the material being caught on 2-mm sieves. Finally, after land application, remaining materials must not be toxic nor deter plant growth. Regulated (heavy) metals content in the polymer should be less than 50% of EPA (U.S., Canada) prescribed threshold.

U.S. AND EUROPEAN STANDARDS

ASTM D6400 is in harmony with standards in Europe, Japan, Korea, China, and Taiwan. This includes the European standard EN13432 "*Requirements for Packaging Recoverable through Composting and Biodegradation – Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging.*" The International Standards Organization (ISO) is also developing a similar standard ISO 17088, *Specification for Compostable Plastics.* **MD**

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