Innovations

Spinning Corncobs into Socks Farming Plastics with "Green" Chemistry

Since the 1950s, cheap, durable plastics derived from fossil fuels have become ubiquitous in every part of our lives. Yet as plastics have proliferated, the very qualities we appreciate about them-their low cost, durability, and long life-have made them an environmental problem. They degrade slowly and accumulate in the environment. The toxins that plastics release as they decompose can be ingested by birds, animals, and marine life, or the plastics themselves can clog the creatures' digestive systems if swallowed.

For decades, companies have been pursuing routes to plastics derived from bacteria and plants rather than from fossil fuels. Only now do advances in genetic engineering and process technologies promise to make bioplastics commercially viable. Besides the environmental issues associated with petroleumbased plastics, the recent surge in oil prices is making bioplastics more attractive. These developments could be the next wave of a new kind of industrialized biotechnology or "Green chemistry." The green chemistry movement started with the 1990 Pollution Prevention Act and was spurred both by government grants and private initiatives. The movement advocates chemistry that has minimal impact on the environment by making processes less toxic and more energy efficient while reducing waste products.

Not Your Mom's Polyester

Polymers are macromolecules constructed from smaller molecules called monomers. Most of the biomass that surrounds us exists as polymers. Materials such as DNA and RNA (deoxy- and ribonucleic acid), proteins (polypeptides), wood and pulp (cellulose), and starch (amylose) are all chain polymers. The challenge is to convert the biomass into usable form. One approach is to convert biomass into monomers such as succinic acid or adipic acid and either polymerize or copolymerize them with petroleum-derived monomers, yielding polymers such as DuPont's (http://www.dupont.com/) Sorona polytrimethylene terephthalate (PTT) made from 1,3-propanediol, generated from corn and terephthalic acid.

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Corn is also fermented to lactic acid, a precursor for polylactic acid (PLA) developed by Cargill Dow Chemical (http://www.cargill.com/) in the late nineties. Cargill Dow's subsidiary NatureWorks, LLC, (http:// www.natureworksllc.com/) processes PLA into textile fibers under its Ingeo brand, that end up in consumer goods such as socks. Under the slogan "We milk the cows and grow the bottles," Naturally Iowa, LLC, is using PLA for milk containers. Walmart announced that starting late 2005, it is using PLA containers to package fresh fruit and vegetables.

Another green strategy is to harvest natural polymers such as polyhydroxyalkanoates (PHA) directly from genetically engineered bacteria or plants. The polymer itself is produced in vivo with this approach. PHAs are currently made by Cambridge-based Metabolix (http:// www.metabolix.com/).

Magic Carpet

Dr. Jeff Lievense's wife chose their Mohawk "SmartStrand" stain-resistant pale yellow carpet to remind her of the Tampa beach while in the Midwest winter. The carpet is spun from DuPont's Sorona PTT fiber. To Lievense, now vice president of Engineering and Biochemicals R&D at Tate & Lyle (http://www.tateandlyle. com/), a British food and industrial ingredients producer, the carpet is a souvenir of his five years as a member of the Tate & Lyle-DuPont research team that developed the fermentation process to make the 1,3-propanediol (PDO) for Sorona commercially viable. DuPont decided to take an alternate synthesis route to brew the PDO monomer out of corn sugar. The reason for Du-Pont to take the bio road? PDO used to be scarce and expensive.

In the early 1990s, DuPont scientists engineered microbes that could ferment sugar to PDO in a single step. To make a commercially competitive product, DuPont collaborated over a 10 year period with Genencor International to optimize the microbes, and with Tate & Lyle to develop and optimize the fermentation process for large-scale commercial production. DuPont Staley Bio Products Co., LLC, was formed with Tate & Lyle to produce PDO. "We invested between the two partners approximately \$100 million dollars to build a large scale fermentation plant, which will start up later this year. Let there be no doubt we are doing that because we believe we will make money selling Bio-PDO," Lievense says.

"We are part of the green revolution, if you will," says Dr. Karl Sanford, vice president of Technology Development at Genencor International. According to Sanford, biologically produced polyester has almost the same functional properties as the petroleum-based material. The economics of producing it, however, have just gotten more attractive. "When we undertook the program, oil was at \$15 a barrel, now it is at \$60 a barrel," Sanford says.

At Genencor, new product ventures are evaluated by a complete lifecycle assessment, including sustainability. "It is a new way to think," says Sanford. "A number of leading companies are reporting an audit of environmental sustainability as a way of appeasing their stockholders and institutions that invest in them. It is good business. It gets very, very expensive to keep cleaning up stuff."

Growing AstroTurf on Erie Street

On Erie Street near MIT, Metabolix is growing plastics in grass, the ultimate in AstroTurf. Metabolix was cofounded in 1992 by professors Oliver Peoples and Anthony Sinskey based on their metabolic engineering work at MIT. The 38 person company has been genetically engineering bacteria to produce PHA more efficiently. In 2001, Metabolix bought Monsanto's PHA, Biopol, and integrated it into its research program.

Metabolix plastics are "functionally equivalent to a range of petrochemically based plastics," Peoples says. "We were driven by the idea of degradable materials from day one." According to Peoples, Metabolix's plastics do not hydrolyze in water and have good UV stability but will degrade in active microbial environments.

Now, Metabolix is focusing on harvesting PHA directly from genetically engineered switch grass. "Switch grass is the holy grail of the field," Peoples says. Switch grass, high in cellulose that can be converted to sugar, is easy and cheap to grow and is a promising feedstock for both ethanol and plastics. "The genetic engineering tools for switch grass are in the early stages of development. We can introduce multiple genes and have pathways working. We see switch grass as an advanced production platform for bioplastics," Peoples says.

The question facing Metabolix and its collaborator, agribusiness giant Archer Daniels Midland (http://www. admworld.com/), is what should the PHA yield be to make it a viable commercial product? Although biotechnology firms like Genencor and Metabolix talk about sustainability, the giant agroprocessors to whom they sell look at profit and developing new markets.

Green, as in Cash

Dr. Jim Stoppert, senior director of Minneapolis-based Cargill's Indus-Bioproducts development trial group, was the first CEO of Nature-Works. Stoppert is interested in translating green chemistry into green cash. "At Cargill, we are building whole families of products based on renewable feedstocks," Stoppert says. "In the past, a lot of effort in this area was driven by environmental issues. Taking ethanol out of it, the bio-based industry was 'nothing,' compared to the \$1.5 trillion chemical industry," Stoppert says. "The misperception was thinking people would pay a premium for environmentally friendly solutions." People will pay a premium for functionality, Stoppert suggests, but continued that if you base your business on people paying a premium for environmental friendliness, "you will lose your shirt."

Environmental concerns are growing, however. "People are becoming more aware of CO₂ emissions," Stoppert says. According to Stoppert, biotechnology-based plastics take less energy to manufacture than hydrocarbon-based products. Another advantage is the smaller factory size that lowers capital costs. "I guarantee that the chemical industry is taking this seriously," Stoppert says. "Almost every chemical company has a program."

As with Metabolix, it boils down to what kind of yield can be expected. Everybody has their own parameters in calculating the overall cost of making bioplastics. "You can buy PLA that is cost competitive with PET [polyethylene terephthalate, the plastic used in soft drink bottles]," Stoppert says. NatureWorks analyses are done from seed corn through polymer pellets, which the company sells. The company says that PLA is cost competitive with PET at \$30/barrel of oil. According to NatureWork's lifecycle analysis, the company can produce PLA at 25% to 55% below the cost of PET, depending on volume.

DuPont's PDO has petrochemical competition. In 1998, Shell Chemical introduced a petroleum-derived

PDO marketed in a PTT polymer dubbed Corterra for, among other things, carpet. Because both Shell's petrochemically derived and Du-Pont's bio-derived PTT require less terephthalic acid per pound, they could be potentially cheaper to produce than rival polyester PET, depending on volatile raw material prices. PTT requires less terephthalic acid to produce than PET because the percentage of terephthalic acid carbons in the repeat units of PTT is lower than in PET. To large-scale industrial producers, a few cents in materials adds up fast.

Hidden Fees

An underlying issue is how green exactly are these biomass-derived approaches? Corn production in the U.S. is subsidized and produced by intensive farming. As a consequence, it is inconclusive whether producing plastic from biomass really consumes less energy than making it conventionally. Moreover, the U.S. Department of Agriculture 10 year forecast (http://www.ers.usda. gov/briefing/corn/2005baseline.htm) projects that corn prices will rise because of increasing demand, and increased yield is to come from genetic engineering, gated by available water. If new markets for biopolymers emerge, we may be looking at a totally different demand and price structure.

Dr. Tillman Gerngross, assistant professor of engineering at Dartmouth College, is not optimistic. Gerngross worked at Metabolix for several years and believes green chemistry is energy inefficient and will not result in notable cost savings. According to Gerngross, making a biopolymer still requires consumption of fossil fuels, so overall, not only the fossil fuels required to make the monomers but the farming and processing costs must be considered as well. "It is necessary to look at total energy consumption in the process," Gerngross says. "What the previous work has shown rather convincingly is that the energy required to make these polymers far exceeds the energy required to make conventional polymers." According to Gerngross, as oil prices increase, energy and processing costs go up as well. "In fact, they are very correlated, and that is because of the heavy dependence

[on fossil fuels] of the corn wet-milling industry as well as the farming activity," Gerngross says. "That is the case for PLAs. The economics for PHAs are even worse." According to Gerngross, the more energy used, the more CO_2 emissions. "In my view, these processes are not green at all," Gerngross says.

The greening of plastics involves more than just the production side. "Carbon is the basic building block of polymers," says Dr. Ramini Nayaran, professor of chemical engineering, Department of Chemical Engineering and Material Science at Michigan State University. Narayan argues for plastics based on organic sources that use carbon sustainably. He cautions that before compostable biopolymers will have a real environmental impact, we must improve our waste-collection and disposal systems.

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