



Renewable plastic

Firms use ethanol and bacteria as the raw materials to make substitutes for oil products

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The consumer market boom and pressure on the costs of petroleum-derived raw materials have led the plastics industry to look for renewable sources to replace their raw materials. Sugar cane ethanol plastics, which can be recycled, as well as biodegradable polymers produced by bacteria that feed on saccharine and other substances, are at the forefront of the research and investments announced by petrochemical giants Dow Química, Braskem and Oxiteno, which make plastic resins from naphtha and other oil-based raw materials. Braskem, Latin America's leading resins producer, invested US\$ 5 million in R & D in the discovery of a certified polyethylene made from sugar cane alcohol, called a "green polymer".

The research that resulted in the new product started back in 2005, though since 1998 the company has been evaluating the properties of other polymers made from renewable raw materials available in the market. Since at that time there was no real market interest in this type of product, the matter did not progress. "When we reopened discussions we assessed the existing options and began to work with green polyethylene from cane alcohol", said Antônio Morschbacker, Technology Manager for Green Polymers from the Triunfo Petrochemical Center in Rio Grande do Sul and the man in charge of the project.

The available information indicates that the company may arrive at a competitive product. "Throughout 2005, after cost estimates, we saw it would be feasible to manufacture it and, in 2006, we decided to build a pilot plant, while also carrying out a more in-depth study of the global market", says Morschbacker. "The process, which is fairly efficient, transforms 99% of the carbon in the alcohol into ethylene, the raw material for polyethylene. "The main sub-product is water, which can be purified and reused.

Dehydrating ethanol - At the pilot plant, which began operating in June 2007, the ethanol (obtained using a biochemical fermentation of the wash, centrifuging and distillation) is transformed into ethylene. The conversion occurs through a dehydration process, during which catalysts (compounds that speed up chemical reactions) are added to the heated ethanol, transforming it into an ethylene gas. From this point to get to polyethylene, the most widely-used plastic in the world, the manufacturing process is the same as that used for raw materials from fossil sources, i.e. polymerized ethylene results in polyethylene. Polymerization is a reaction in which the smaller molecules (monomers) combine chemically to form long ramified molecules.

With the ethylene produced by this technology one can produce any type of polyethylene. Initially, Braskem plans



Biodegradable polymer produced by bacteria



Rigid plastics made from PHB from sugar

to produce high and low density resins, for hard and flexible applications in the automotive, food packaging, and cosmetics and personal hygiene products packaging sectors. Some customers in Brazil and abroad are already receiving samples of the green polymer produced on a pilot scale. The start of production on an industrial scale, which should reach 200,000 tons per year, is forecast for the end of 2009. The company is yet to define where the new polymer plant will be built, but it is likely to require some US\$ 150 million in investments.

The product, which will probably cost between 15% and 20% more than traditional polymers, will be initially

sent to Asian, European and North American markets. Before it has even been launched on a commercial scale the green polyethylene is already a success story. At the International Trade Fair for Plastics and Rubber (K 2007), the world's biggest petro-chemical event, held in late October in Düsseldorf, in Germany, Morschbacher gave ten highly heavily attended product presentations in eight days and talked to many people interested in the product and the project.

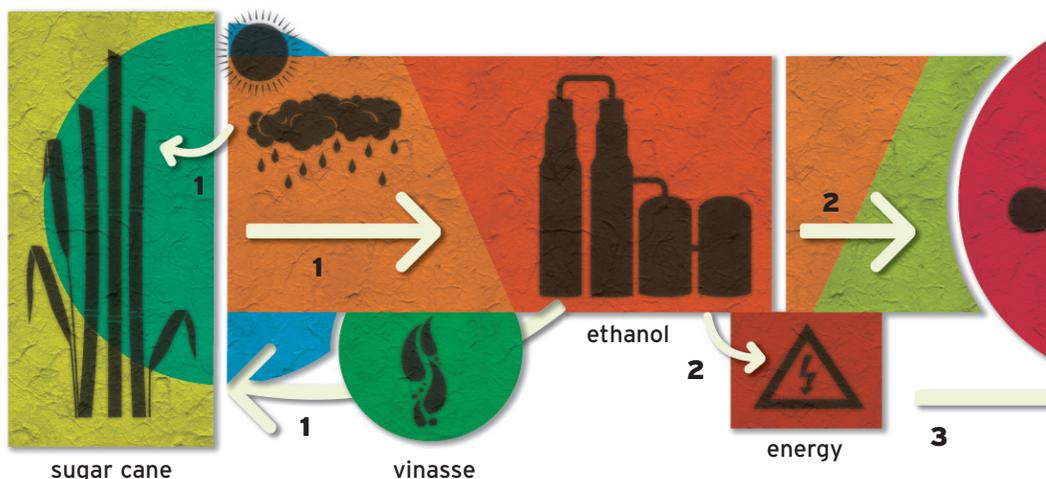
Ethanol-based polyethylene was certified by the Beta Analytic Laboratory in the USA, using the carbon-14 technique, as being a product made from

100% renewable raw material. While the raw material, in this case ethanol, is renewable, the end product is not biodegradable. "The product has identical properties to those of oil-derived polyethylene. As it is a fairly resistant and stable plastic it can be recycled and reused several times; at the end of its useful life it can be incinerated without causing environmental problems", says Morschbacher. The big environmental advantage of polyethylene from alcohol is that for every kilogram of polymer produced, roughly two and a half kilograms of carbon dioxide are absorbed from the atmosphere by the photosynthesis of the sugar cane.

Alcohol-chemical center - Dow Química is also preparing to produce polyethylene from ethanol. In July, it announced a joint-venture with Crystalsev, a Brazilian sugar and alcohol trading company belonging to the Vale do Rosário refinery, from Morro Agudo, and the Santa Elisa refinery, from Sertãozinho, in São Paulo state, for setting up an integrated alcohol-chemical center that should go on-stream in 2011, with capacity to produce 350,000 tons of low density polyethylene a year; its commercial name is Dowlex and it will be used for making flexible packaging, industrial films and injected articles. At first, the product will be sold in the domestic market, which is growing at six to seven percent a year. The material is already produced by Dow from

Integration

1. As sugar cane grows it absorbs carbon dioxide from the atmosphere through photosynthesis. The vinasse, a waste liquid resulting from the crushing and fermentation process, will be used as a fertilizer for cane growing.
2. The transformation of ethanol into ethylene is conducted through a dehydration process, with the addition of catalysts. The water released during the process will be used for producing power-generating steam.



SOURCE: DOW QUÍMICA

oil-derived naphtha at plants in Asia and Europe.

To transform ethanol into polyethylene, Dow also uses the dehydration process. Modern catalysts enable the firm to obtain an ethylene that is as pure as that produced from oil. The water released during the process of transforming ethanol into polyethylene will be used for producing steam for power generation. It is estimated that the undertaking will create some 3,200 direct jobs, plus hundreds of indirect ones in the agricultural, industrial and manufacturing sectors. The polyethylene plant will consume seven hundred million liters of alcohol a year, which corresponds to eight million tons of sugar cane.

The two companies will be partners at all the stages, beginning with the planting of a 120,000 ha. sugar plantation to the manufacture and marketing of the plastic. Complete integration of the cycle means that the center will be self-sufficient from the energy point of view, generating enough surplus energy from cane bagasse to power a city with half a million inhabitants. The location of the alcohol-chemical center is yet to be defined but locations in the mid-south of Brazil are being analyzed. "The price of ethanol polyethylene will take into account the same supply and demand forces that affect naphtha polyethylene", says Diego Donoso, Plastics Director for Dow -Latin America. "The end customer will get a product with

THE PROJECT

Obtaining and characterizing environmentally degradable polymers (PAD) from renewable sources: sugar cane

MODALITY

Technological Innovation in Small Companies Program (Pipe)

COORDINATOR

JEFTER FERNANDES DO NASCIMENTO - Industrial PHB

INVESTMENT

R\$ 338,686.30 (FAPESP)

the same technical and *performance* characteristics as conventional polyethylene, but will gain in the added value of the production. "

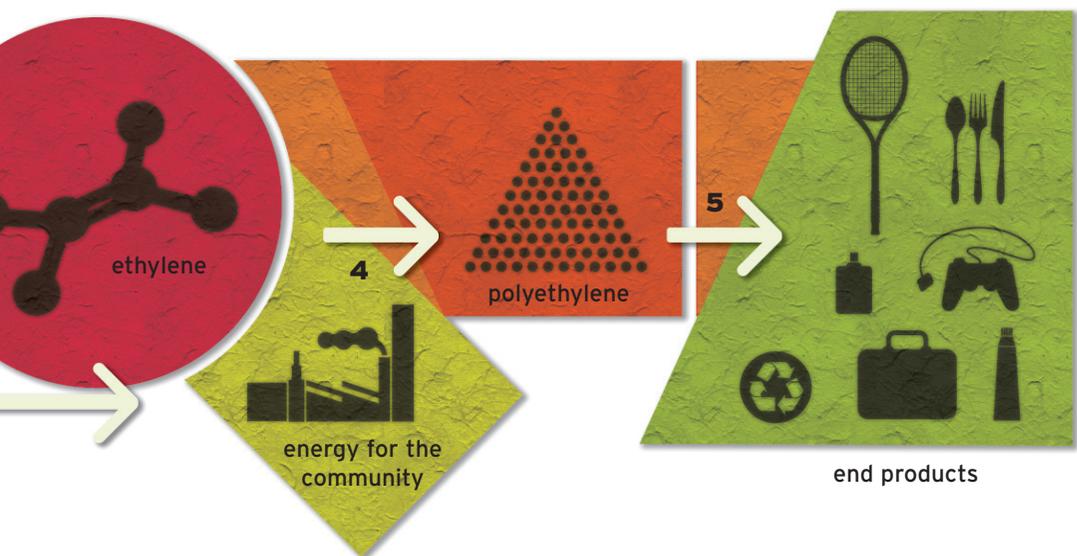
Acid hydrolysis - Oxiteno, which is part of the Ultra Group, has a similar project to Dow's for building a bio-refinery for the production of sugar and alcohol from sugar cane bagasse, straw and tips, using a technology called acid hydrolysis. This has not yet been mastered on a commercial scale; it consists of breaking up cellulose molecules by adding sulfuric acid to the waste. The future unit will also produce alcohol-chemical products from non-conventional technology.

Since November 2006, the company has maintained a partnership arrange-

ment with FAPESP for developing research projects in the technology area for the production of sugar, alcohol and derivatives. In January 2007, during the first phase, twenty-three projects were chosen in partnerships with research institutes and universities, of which seven were approved in the second phase in July.

While the petro-chemical companies are wagering their money on ethanol plastics, PHB Industrial, part of the Pedra Agroindustrial Group, from Serrana, and the Balbo Group, from Sertãozinho, both in São Paulo state, have been making, since December 2000, a biodegradable plastic produced by natural bacteria, in a pilot plant. The product is sold in small quantities under the trade name of Biocycle to the USA, Japan and European countries. The raw material has been used mainly in the manufacturing of rigid plastics produced by the injection-mold process and also in foams that can replace Styrofoam. Biocycle is also used for the production of polyurethane substitutes, as well as for bioplastic sheets and thermoformed products.

The industrial plant for production on a large scale, expected to be ready in 2010, will be installed in the Ribeirão Preto region. "The production of biodegradable plastic should reach some ten to thirty thousand tons a year", says physicist, Sylvio Ortega Filho, Executive Director for the development of biodegradable plastics at PHB, in which



3. Ethylene is converted in a process similar to that used for manufacturing raw material from fossil sources.
4. The alcohol-chemical center will be self-sufficient from the energy standpoint and will generate a surplus sufficient to power a city of half a million inhabitants.
5. Once the polyethylene has been produced, it is possible to make a range of plastic products.



MIGUEL BOYAVAN

the Institute of Technological Research (IPT), the Sugar Plantation technology Center (CTC) and the Institute of Biomedical Sciences (ICB) of the University of São Paulo also took part, with funding from FAPESP's Technological Innovation Program in Small Companies (Pipe).

Natural polyester - The polymer is produced by growing the *Alcaligenes eutrophus* bacteria, currently called *Cupriavidus necator*, in a culture with the saccharine from sugar. The saccharine is transformed into glucose to feed the bacteria. "The carbon chain from the glucose is transformed by the bacteria into poly-2-hydroxy butyrate (PHB)", explains Professor Elisabete José Vicente, from the Institute of Biomedical Sciences (ICB) at USP, who took part in the studies that resulted in the biodegradable plastic and is currently supervising research into the production of polymers from bacteria. PHB belongs to the group of polymers called polyhydroxyalkanoates (PHA), which are polyesters accumulated by microorganisms in the form of intracellular granules.

Their thermoplastic properties mean that, after being extracted from the interior of the producing cell with organic solvents, they can be purified and processed, generating a biodegradable, compoundable and biocompatible product. These polymers may have many applications, such as the production of films or rigid structures, in addition to medical and veterinary uses, such as making sutures, supports for growing tissue, implants, the encapsulation of controlled release drugs and other applications that use nanotechnology.

"So far, more than 150 different bacteria that naturally accumulate this cytoplasmic granule have been identified", says Elisabete. The *C. necator* bacterium stands out because it can

Pilot PHB plant, where products sold under the Biocycle trade name (right) are produced

accumulate a large amount of polymer – from eighty to ninety percent of its dry weight. To grow, it needs fructose or glucose. “The first genetic improvement of the bacteria, which was carried out many years ago, obtained a mutant that was capable of growing in glucose, which is cheaper than fructose”, says Elisabete. In Brazil, the researcher, along with Professor Ana Clara Guerrini Schenberg, also from ICB, started working on the project in 1992. This resulted in a new mutant bacteria that can grow in sugar cane saccharose and in another recombinant bacteria with a better production yield of the PHB-V co-polymer, which is more malleable.

Genetic modifications - The bacteria manufactures the polymer naturally, but the genetic improvements allow for a considerable increase in production to take place. In the project, involving PHB and partner institutions, some genetically modified bacteria were developed and patented. “We’re only using natural bacteria to produce the biopolymer, because Europe prohibits genetically modified organisms”, says Ortega. The demand for polymers from renewable sources comes basically from three major applications in the global market. The first is the packaging market. The second is the automotive industry, which is trying to replace products used in cars by others that do not contribute to global warming, as European markets demand. The third application is in the medical area (*see box* Integration).

The partnership with PHB resulted not only in a product that is already in the market, but also in on-going research at the university. The group, coordinated by Professor Elisabete, from ICB at USP, is working on two fronts. On one, the researchers are looking for bacteria that can produce polymers from carbon sources other than saccharose, such as the industrial waste. “This would lower the production costs of the biomaterial, which is as much as three times that of oil-derived plastic”, says Elisabete. At the same time, the group is also studying applications for the biopolymer after it has been purified, such as a substrate for growing stem cells, a line of research carried out jointly with

Professor Radovan Borojevic, director of the advanced program of Cell Biology as applied to Medicine at the Federal University of Rio de Janeiro. Another line is studying the use of the biopolymer for immobilizing enzymes and pharmaceutical drugs, in partnership with Professors Mário Politi, from the Institute of Chemistry at USP and coordinator of the Nanotechnology Research Group at the National Council of Scientific and Technological Development (CNPq), and Carlos Alberto Brandt, a member of the same research center.

At USP’s ICB, another group, led by Professor Luiziana Ferreira da Silva, who also took part in the development of the production of biodegradable plastic from PHB, but who is linked to the IPT technical research institute, is working on lines of research that involve the production of biodegradable materials. In 2002, Luiziana concluded a process for the use of sugar cane bagasse to produce PHB. Bacteria were selected that, after being broken down into smaller molecules through acid hydrolysis, are capable of growing in cane bagasse and not in the wash where the saccharose is found. Another line of research is studying the development of a hybrid plastic produced by bacteria, except that instead of being fed with sugar cane they receive the fatty acid from six carbons. “As oil is offered to the bacteria, they start producing an elastomer that is very like rubber”, says Luiziana. The objective of this study is to obtain another type of plastic material plastic that can be used, for example, in the covering of diapers, disposable carpets and other uses. ■

Medical applications

Sutures for surgery, reinforcing mesh used in operations for correcting hernias, membranes for repairing venous and arterial lesions and tubes for arterial implants are just some of the products developed by the Biopolymer from Sugar Cane Research Group, a partnership between the Federal University of Pernambuco (UFPE) and the Rural Federal University of Pernambuco (UFRPE). “All these products have been used in experimental research with excellent results”, says Professor José Lamartine de Aguiar, the group’s coordinator. The research started in 1990, when Francisco Dutra, a chemical engineer from UFRPE, identified polymeric formations in the fermentation process for alcohol production. The biopolymer is obtained from sub-products of sugar cane, such as molasses. The physical and chemical characteristics of the biopolymer after it has been purified aroused the interest of researchers from various areas. “Initially, the material was applied in test animals after cytotoxicity and biocompatibility tests had been performed”, says Aguiar. Production of the biopolymer, which has been patented by UFPE, will be the responsibility of a bioplant that is in the final set-up phase at the Experimental Sugar Cane Station of Carpina, an off-site campus of UFRPE in the Pernambuco countryside.

PHB INDUSTRIAL

