VIEWPOINT

Practical Approaches to Green Solvents

Joseph M. DeSimone

Solvents are widely used in commercial manufacturing and service industries. Despite abundant precaution, they inevitably contaminate our air, land, and water because they are difficult to contain and recycle. Researchers have therefore focused on reducing solvent use through the development of solvent-free processes and more efficient recycling protocols. However, these approaches have their limitations, necessitating a pollution prevention approach and the search for environmentally benign solvent alternatives. This report highlights opportunities for the practical implementation of such green solvents.

Solvents, and dissolution in general, have been integral to many industries for hundreds of years. In the 1400s, alchemists had already focused on solvents and the dissolution process as they searched for "menstruum universale," the universal solvent that possessed the powers to remove all seeds of disease from the human body (*1*). Today, almost all manufacturing and processing industries—automotive, electronics, pulp and paper, chemical, mining, food, cleaning—depend on the extensive use of solvents or water. To satisfy this dependency, almost 15 billion kilograms of organic and halogenated solvents are produced worldwide each year (*2*). The solvents are used as process aids, cleaning agents, and dispersants. They inevitably end up leaching into our ecosystems. An even larger amount of water is used and contaminated in related processes.

For example, the textile industry may require almost 100 liters of water to dye a kilogram of fiber (*3*). The aqueous effluent from such dyeing processes must be treated, but most local municipalities' regulations in the United States allow it to be returned to its natural source (often a local stream or river) in a contaminated condition. Furthermore, many fiber materials, such as cotton, polyamides (nylon), and polyesters, absorb large amounts of water. Because the heat of vaporization of water is high, a large amount of energy is needed to dry the dyed fibers. Indeed, water-based processes are usually very energy intensive.

The dry cleaning industry is also highly dependent on solvents (*4*, *5*). Most dry cleaners—approximately 100,000 worldwide—use perchloroethylene (perc) as the primary processing solvent. Numerous studies have shown perc to be highly toxic, affecting plant workers and consumers who use dry cleaners; landlords and financial institutions who hold title to contaminated land; and people whose homes are in close proximity to dry cleaning establishments. Everything perc comes in contact with in a dry cleaning plant must be handled as "hazardous waste," except for the dry-cleaned clothes we wear.

Water and solvent usage is also required for the precise fabrication of device elements for state-of-the-art microprocessors (*6*, *7*). A typical microelectronics fabrication facility processing 5,000 wafers per day will generate almost 5 million liters of organic and aqueous solvent waste per year. For example, chemical mechanical planarization (CMP), an increasingly important operation in such facilities, uses ultra-purified water and supported silica slurries to polish wafer levels for improved manufacturability. A standard CMP tool will use 40,000 liters of ultra-pure water per day.

Even the food industry is not exempt from solvent usage and emissions (*8*). Hexane is use to extract most of the 8 million tons of oil isolated per year from soybean seeds and for the isolation of millions of tons of oil from other seeds and grain commodities in the United States. The U.S. Environmental Protection Agency (EPA) categorizes hexane as a HAP (hazardous air pollutant). Yet according to EPA Toxic Release Inventory (TRI) statistics, more than 20 million kg of hexane are released to the atmosphere because it is used in the solvent extraction of vegetable oils.

Since the 1960s, a number of events have raised international concern about the release of toxins into the environment. Publication of *Silent Spring* by Rachael Carson in 1962 led to a public outcry to regulate pesticides (*9*). Health concerns were linked to contamination at the Love Canal in Niagara Falls, NY. The Cuyahoga River in Ohio was so polluted that it caught fire (*10*). Laws in the United States attempting to tackle these problems initially focused on treatment of wastes before their release or neutralization of the waste subsequent to their release. The U.S. Pollution Prevention Act in 1990 refocused national environmental policy on preventing the formation of waste at the source. An initiative focused on pollution prevention by researchers in the chemical industry, often referred to as "green chemistry," grew out of these legislative efforts (*11*).

As a result of the above changes in the law and because of the growing public sentiment in support of our environment, there has been a significant focus for industry to reduce or eliminate the use of water and organic solvents during manufacturing and processing. Approaches to mitigate the release of solvents and contaminated water into our ecosystem include reduction and/or recycling; switching to "solvent-free" processes that are not dependent on the use of solvents or to processes that do not generate contaminated water; and conversion of processes that use organic solvents and water to "solvent alternatives."

Reduction and/or Recycling

Many of the industries mentioned above have made remarkable progress in implementing "closed-loop systems" that reduce solvent and/or water use and improve their ability to recycle. Industries throughout the world have been quite effective in reducing their emissions of solvents through such process improvements. This activity has been popularized by corporate stewardship programs like 3M's "3P" program, whose premise suggests that solvent reduction and recycling is not only important for the environment, but that such "Pollution Prevention Pays" (*12*).

Switching to Solvent-Free Processes

Several industries have eliminated solvents from key process steps. Examples include the elimination of organic solvents and other volatile organic compounds from many paints and coatings, resulting in dry, solvent-free powder coatings (*13*) and 100% solid ultraviolet curable coatings (*14*). The use of water in emissive applications like coatings is a preferable alternative to organics. (In contrast, water used in nonemissive applications, for example, as a reaction medium in chemical transformations or as a dyeing medium for textile fibers, inevitably gets contaminated and is hard to clean up without substantial costs.) Polycarbonate producers increasingly use a solvent-free, melt-phase polymerization technology (*15*), based on diphenylcarbonate and bisphenol-A, instead of the traditional interfacial route, based on phosgene and bisphenol-A carried out in methylene chloride and water. Many other solvent-free processes are sure to emerge as scientists and engineers

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Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599–3290, USA; Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695, USA; and co-founder, Micell Technologies, 7516 Precision Drive, Raleigh, NC 27613, USA. E-mail: desimone@unc.edu

respond to customer demands for "dry" processes. Indeed, recent research efforts have succeeded in achieving important chemical transformations using solvent-free processes including for efficient catalytic entioselective syntheses of unsaturated amines (*16*) and for Wittig reactions (*17*).

Solvent Alternatives

Despite such advances, many processes have been shown to require process "liquids" of some kind. This is especially true for industries that are dependent on operations involving coatings, separations, or reactions. In such situations, some solvents are preferable to others. For example, homogeneous solvent-based coatings may be replaced with water-based heterogeneous emulsions, or chlorinated organic solvents with hydrocarbon-based solvents. Water may be used instead of organic solvents for conducting chemical reactions (*18*, *19*), toluene instead of benzene (*20*), cyclic siloxanes instead of tetrachloroethylene (*21*), or biodegradable esters instead of nonbiodegradable solvents (*22*). Over the last 15 years, additional, less conventional solvent alternatives have attracted much attention from academia and industry. They include supercritical water (*23*, *24*), ionic liquids (*25*–*27*), fluorous phases (*28*–*30*) and carbon dioxide (*31*–*35*).

Supercritical water. Water exists in the supercritical state at temperatures above 374°C and pressures above 221 bar. Supercritical water behaves as a nonpolar solvent primarily because hydrogen bonding is lost under these extreme conditions. The dielectric constant of water decreases from 80 at ambient conditions to <5 above the critical point. Salts are not soluble in supercritical water, whereas nonpolar organics are completely soluble, as is O_2, and can be rapidly and efficiently oxidized to CO_2 and H_2O. Supercritical water oxidation (SCWO) was first developed in the 1970s for the destruction of organic waste (*36*). Oxidation reactions in supercritical water have been extensively studied, especially for chemical demilitarization and the disposal of organic waste such as nerve agents and mustard gas. However, the design of a suitable reactor poses significant challenges. Under the extreme conditions required, trace amounts of halogens lead to extensive corrosion of most reactor materials. Despite extensive research efforts, corrosion problems have not been satisfactorily solved. SCWO has not been successfully commercialized and will probably never become a practical solvent alternative.

Ionic liquids. Ionic liquids have recently received increasing attention as an environmentally preferable solvent alternative, because they have very low vapor pressures and may be used to replace volatile organic solvents. Several authors have shown (*37*–*39*) that chloroaluminate compounds such as 1-butylpyridinium chloride/aluminum(III) chloride mixtures can exist as liquids at room temperature. Such ionic liquids are being considered as solvents for a wide range of separations and as reaction media for processes including catalysis. The author is not aware of a successful commercialization of ionic liquids as a reaction or separation medium. However, a collaboration between academia and industry, QUILL, is actively pursuing the discovery and development of ionic liquids for such applications. The researchers associated with QUILL have shown that a variety of ionic liquids are good solvents for a wide range of inorganic, organic, and polymeric molecules. Moreover, a number of organic reactions have been shown to be compatible with these designer solvents, including cationic polymerizations, electrophilic alkylations and acylations, and pericyclic reactions. Despite this progress on the scientific pursuit of reactions in ionic fluids, there is public skepticism (*40*) as to their characterization as preferable solvents for reasons of environmental stewardship, simply because of their low volatility.

Fluorous phases. Solvent extraction is widely used in organic chemistry to separate substances from mixtures, to isolate dissolved compounds from solutions, and to remove soluble impurities from mixtures. Solvents commonly used for this purpose include diethyl ether, methylene chloride, chloroform, acetone, and water. This process is usually accomplished by exploiting the immiscibility of two liquid phases, usually one aqueous and the other organic. Highly fluorinated (fluorous) compounds are referred to as the "third liquid phase," because organics, water, and fluorous compounds are mutually immiscible (Fig. 1). This property is often a strong function of temperature, presenting an important new opportunity for separations and for solution-phase organic synthesis (*41*–*43*). Because of their ability to be used in an integrated way that allows for product isolation, analogies can be drawn between fluorous-phase synthesis and solid-

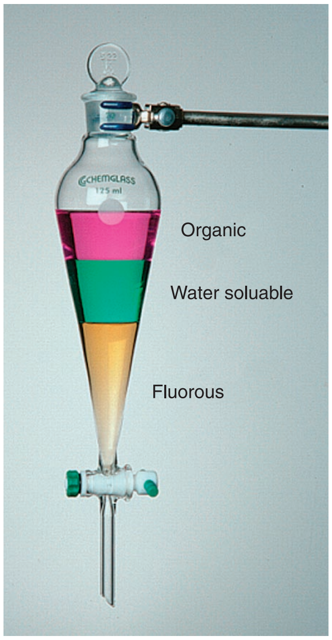

Fig. 1. A photograph of a typical three-phase liquid-liquid extraction is shown with an organic (yellow), inorganic (blue), and fluorous (clear) phases. [Illustration from (*65*)]

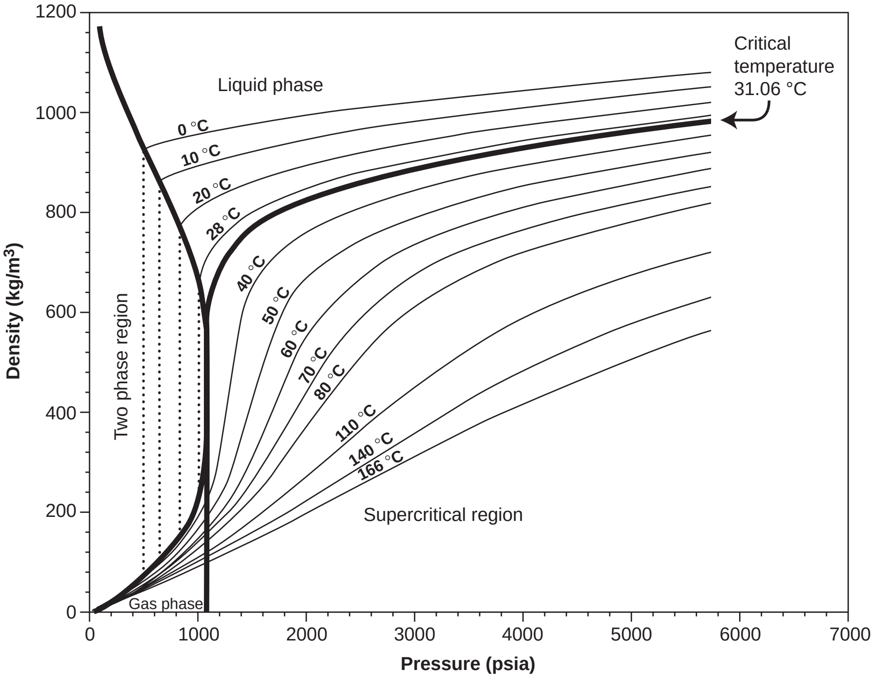

Fig. 2. Density versus pressure isotherms for liquid and supercritical carbon dioxide.

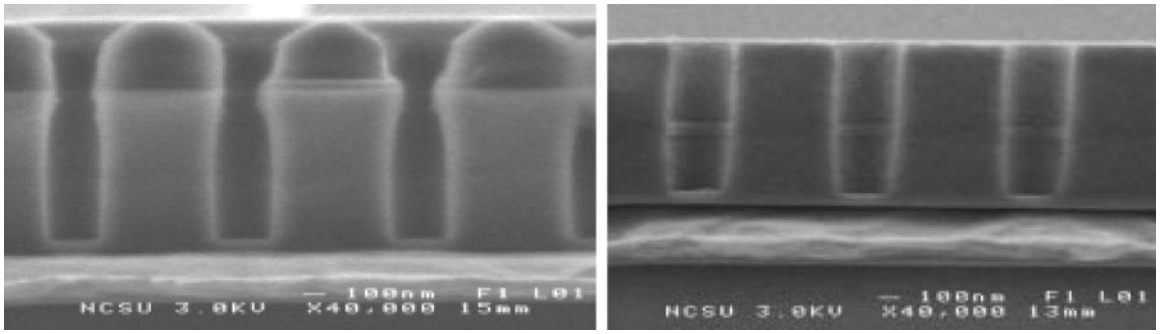

Fig. 3. Electron micrographs of reactive-ion etched dual Damascene deep via structures before (left) and after (right) CO_2-based stripping and cleaning process to remove photoresist and photoresist residue. [Provided by Micell Technologies (*66*)]

phase synthesis with supports such as polymer resins. Solid-phase synthesis has been extensively adopted for automated synthesis and combinatorial chemistry and has revolutionized chemical synthesis while reducing the need for large amounts of solvents, especially for the separation of compounds. Fluorous phases may achieve similarly widespread adaptation and enjoy increased utility, especially with the burgeoning commercial interests from companies such as Fluorous Technologies, Inc.

Carbon dioxide. Carbon dioxide (CO_2) is an attractive solvent alternative for a variety of chemical and industrial processes, especially because it is plentiful and inexpensive, and has properties that are between those of many liquids and gases. At room temperature and above its vapor pressure, CO_2 exists as a liquid with a density comparable to organic solvents but with excellent wetting properties and a very low viscosity. Above its critical temperature and pressure (31°C and 73.8 bar), CO_2 is in the supercritical state and has gas-like viscosities and liquid-like densities. Small changes in temperature or pressure cause dramatic changes in the density (Fig. 2), viscosity, and dielectric properties of supercritical CO_2, making it an unusually tunable, versatile, and selective solvent**.**

Processes that use CO_2 do not contribute directly to the greenhouse effect associated with global warming. Most CO_2 sold today is isolated as a by-product from primary sources, such as from the production of ethanol, ammonia, and hydrogen (*44*). Because of the low heat of vaporization of CO_2, energy costs can be substantially reduced relative to water-intensive processes, which often demand large amounts of energy associated with drying operations.

The potential of CO_2 as an environmentally preferable solvent is now being realized in several areas, including separation processes in the food industry, coatings in the automotive and furniture industries, polymer production and processing, and cleaning processes for the garment care (that is, dry cleaning) and microelectronics industries. For example, supercritical CO_2, instead of chlorinated organic solvents, is used extensively to decaffeinate coffee beans and tea (*45*). Union Carbide has pioneered its use as a diluent for coating processes, dramatically lowering the amount of volatile organic compounds needed in coating operations (*46*). DuPont has commercialized the manufacturing of certain grades of polymers based on tetrafluoroethylene (Teflon), using CO_2 as the solvent instead of 1,1,2-trichloro-1,2,2-trifluoroethane or water (*47–49*). Micell Technologies and Global Technologies have commercialized liquid CO_2 dry-cleaning processes that eliminate the use of perc (*50*). Micell Technologies has extended their process know-how to include precision cleaning unit operations for the manufacture of integrated circuits (Fig. 3), eliminating the need for organic solvents and water (*51*).

Beyond simple extensions of CO_2 usage into additional areas, it is expected that the unique physical properties of CO_2 will be exploited in entirely new ways. Nowhere is this potential more exciting than in the microelectronics and biomedical industries.

Several challenges facing the electronics industry as it reduces feature sizes to the nanometer-length scale, may be overcome with CO_2-based processes. For example, "image collapse" is a significant problem as feature sizes on integrated circuits approach 100 nm (*52*). Structures derived from organic polymers with feature sizes on the order of 150 to 50 nm and aspect ratios of 3 or greater do not have the mechanical integrity to withstand the powerful and destructive forces associated with high surface tension liquids, especially water. Carbon dioxide, with its excellent wetting properties in both the liquid and supercritical states, can be used to eliminate image collapse (Fig. 4) (*53*).

Precision coating may also exploit the exceedingly low surface tension and low viscosity of liquid CO_2. Through the precise

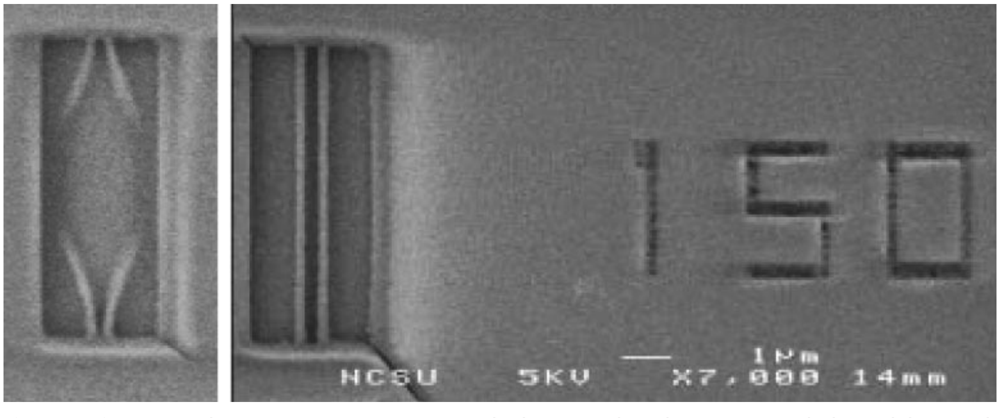

Fig. 4. Development of 150 nm features with a 6:1 aspect ratio using standard aqueous-based processing with thermal drying, which leads to structural damage and image collapse (left) versus aqueous-based development followed by CO_2-based drying process which eliminates image collapse (right). [Provided by Micell Technologies (*66*)]

control of the evaporation rates of liquid CO_2 in a novel spin-coating tool, one can generate extremely uniform, thin films of photoresists on silicon wafers (Fig. 5) (*54*). Processes based on CO_2 are essentially "dry" processes despite the fact that, under certain conditions, gaseous CO_2 can be condensed into use as a process liquid. The extensive use of such dry processes could eliminate the need to shuttle wafers between benches for wet processes and closed-loop dry process tools. Because totally dry processes can utilize massively interfaced manufacturing tools, the replacement of water and organic solvents with CO_2 in the microelectronics industry may dramatically reduce the need for expensive, state-of-the-art clean room facilities.

In the biomedical arena, many opportunities for CO_2-based processes are emerging. Researchers at the University of Nottingham are using CO_2 to facilitate the impregnation and modification of biocompatible polymers to improve the wear properties of implants and to provide scaffolds for tissue engineering (*55*). Cooper and co-workers (*56*) have pioneered the use of high internal-phase supercritical fluid emulsions for the preparation of well-defined porous materials that have the potential to be widely used for the manufacture of controlled release devices and biological tissue scaffolds. Other researchers (*57*, *58*) are pioneering the use of CO_2 to facilitate the production and delivery of pharmacologically active materials. In particular, Johnston and colleagues (*58*) have developed a process for precipitating solutes dissolved in an organic solvent by using carbon dioxide as an antisolvent. Not only is there a significant environmental advantage for using CO_2, but this process offers a means of tuning the particle size and shape of the products to generate nano- or micrometer-scale sphere and fibrils.

Carbon dioxide is also used as a solvent in catalysis (*59–62*). The most advanced project of this kind, at the Thomas Swan plant in the United Kingdom, uses supercritical CO_2 in the synthesis of trimethylcyclohexanone, a derivative of acetone used in styrene products (*63*). The plant has also been used to hydrogenate alkenes, aldehydes, nitro compounds, ketones and oximes. Reaction rates with heterogeneous catalysts were enhanced in the high-diffusivity and low-viscosity supercritical environment, and selectivity was increased. They and others (*64*) have shown the benefits of carrying out reactions in supercritical fluids in continuous flow reactors instead of conventional batch equipment. Continuous processes offer significant advantages over simple batch process, including allowing one to run the reactor at steady state, enabling the feed to assume a uniform composition throughout the reactor by which a uniform reaction product is achieved, and obtaining great temperature control.

Conclusion and Outlook

Environmental advantages alone probably will not enable alternative solvents to achieve widespread applicability. The continued commercialization of pollution prevention technologies must include not only environmental or "green" advantages, but also advantages related to performance, health, and cost. The cost of ownership associated with the continued use of water and organic solvents is no longer a minor issue. Finding an appropriate solvent that is environmentally preferable can be a challenge, as the design criteria need to converge to include solubility issues, inertness to the relevant chemistries, cost, safety of handling, and environmental preferability. Solvent recycling and solvent-free processes, where appropriate, will continue to gain market share. As for the implementation of solvent alternatives, industry will increasingly choose solvents on the basis of environmental demands in the future. However, the full potential of alternative solvents will only be reached if researchers exploit the advantageous properties of such alternatives beyond their intrinsic environmental advantages. Carbon dioxide has made particular inroads as a solvent alternative because of its transient "dry" nature, which enables it to transform from a liquid to a gas, its excellent wetting characteristics, its low viscosity, and its tunable nature, especially in the supercritical state. Time will tell if carbon dioxide and the other solvent alternatives will achieve widespread utilization.

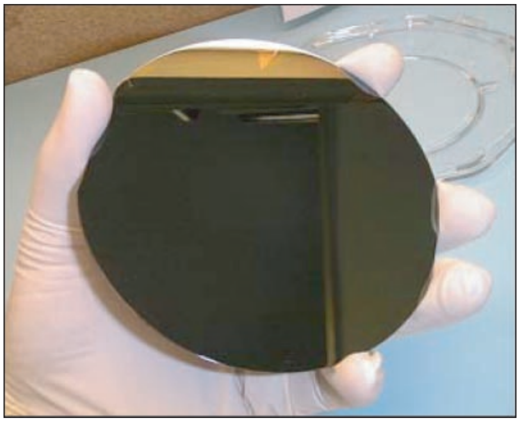

Fig. 5. A silicon wafer coated with a 193-nm photoresist system using a liquid CO_2 spin coating tool operating at slightly below room temperature. [Provided by the NSF Science and Technology Center for Environmentally Responsible Solvents and Processes: (*67*)]

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VIEWPOINT

Biodegradable Polymers for the Environment

Richard A. Gross and Bhanu Kalra

Biodegradable polymers are designed to degrade upon disposal by the action of living organisms. Extraordinary progress has been made in the development of practical processes and products from polymers such as starch, cellulose, and lactic acid. The need to create alternative biodegradable water-soluble polymers for down-the-drain products such as detergents and cosmetics has taken on increasing importance. Consumers have, however, thus far attached little or no added value to the property of biodegradability, forcing industry to compete head-to-head on a cost-performance basis with existing familiar products. In addition, no suitable infrastructure for the disposal of biodegradable materials exists as yet.

Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. Built for the long haul, these polymers seem inappropriate for applications in which plastics are used for short time periods and then disposed. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers (BPs) disposed in bioactive environments degrade by the enzymatic action of microorganisms such as bacteria, fungi, and algae. Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. BPs are often derived from plant processing of atmospheric CO_2. Biodegradation converts them to CO_2, CH_4, water, biomass, humic matter, and other natural substances. BPs are thus naturally recycled by biological processes (Fig. 1).

The worldwide consumption of biodegradable polymers has increased from 14 million kg in 1996 to an estimated 68 million kg in 2001. Target markets for BPs include packaging materials (trash bags, wrappings, loose-fill foam, food containers, film wrapping, laminated paper), disposable nonwovens (engineered fabrics) and hygiene products (diaper back sheets, cotton swabs), consumer goods (fast-food tableware, containers, egg cartons, razor handles, toys), and agricultural tools (mulch films, planters). BP commercialization is, however, hampered by competition with commodity plastics that are inexpensive and familiar to the customer. Also, an infrastructure for the disposal of BPs in bioactive environments must be developed and will require capital investments. Without an extensive network of efficient composting and other bioconversion facilities that, in addition to compost, yield other valuable chemical intermediates, BPs and other biodisposables (food, yard-waste, nonrecycled paper) are destined to be entombed in dry landfill environments designed to retard biodegradation.

In this Viewpoint we report on progress, technical and social challenges, and environmental benefits of BPs. We describe what we view as highly promising biodegradable polymers that are either in development or already marketed (Fig. 2). For comprehensive reviews that include more detailed descriptions of research on biodegradable polymers for environmental applications, see (*1–3*).

Biodegradable Plastics from Starch and Cellulose

Starch is an inexpensive, annually renewable material derived from corn and other crops. The biodegradation of starch products recycles atmospheric CO_2 trapped by starch-producing plants. All starches contain amylose and amylopectin, at ratios that vary with the starch source. This variation provides a natural mechanism for regulating starch material properties.

Starch-based BPs can be produced by blending or mixing them with synthetic polymers. By varying the synthetic blend component and its miscibility with starch, the morphology and hence the properties can be regulated easily and efficiently. This approach has been successfully implemented by Novamont under the Mater-Bi trademark (Tables 1 and 2) (*4*). Blends containing thermoplastic starch (destructurized starch that is noncrystalline, produced by the application of heat and work) may be blended or grafted with biodegradable polyesters [such as polycaprolactone (PCL)] to increase flexibility and resistance to moisture. These materials are mainly formed into films and sheets. Blends with more than 85% starch are used for foaming and injection molding. The foams can be used as loose-fill in place of polystyrene; the starch-based loose fills have an average density of 6 to 8 kg/m^3, compared with 4 kg/m^3 for expanded polystyrene loose fill (*5*). Loose-fill materials from starch are

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Polytechnic University, National Science Foundation Center for Biocatalysis and Bioprocessing of Macromolecules, Six Metrotech Center, Brooklyn, NY 11201, USA. E-mail: rgross@duke.poly.edu