MATERIALS SCIENCE

Cleaner Manufacturing of Plastics—With a Bit of Bubbly

Environmentally speaking, plastics have a bad rep. They generally don't degrade in landfills. And producing them generates huge amounts of hazardous waste in the form of organic solvents such as toluene and chlorinated hydrocarbons, along with contaminated water. Going without plastics, however, is almost unimaginable, given the number of different guises in which they appear in contemporary culture.

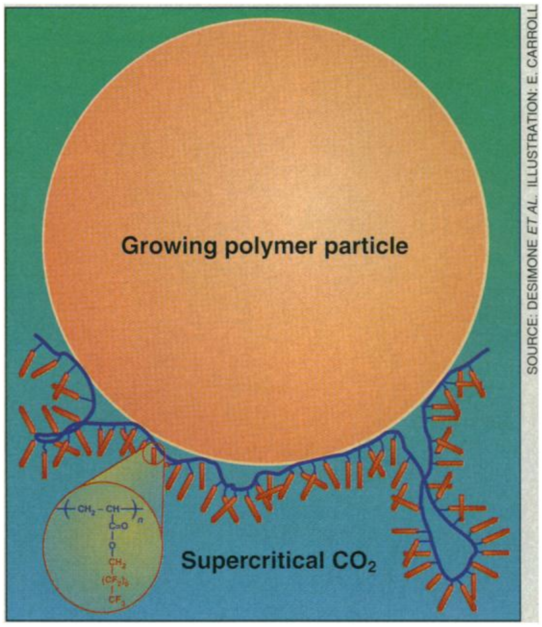
So how can the environmental burden be reduced? Lately, industry has taken to cleaning up the production waste, but that can be very costly. An alternative is to find ways of making plastics that are environment-friendly from the start. One strategy has focused on tinkering with the production process to reduce the amount of waste. Now, on page 356 of this issue, Joseph DeSimone and his colleagues at the University of North Carolina, Chapel Hill, present a more radical modification that might eliminate one source of waste altogether: They have gotten rid of harmful solvents and made quality polymers using relatively harmless—and inexpensive—carbon dioxide.

DeSimone's group has demonstrated their innovation on one common plastic, but they expect that it will apply to others. And their strategy is not only cleaner than conventional techniques; it may also give chemists more control over the molecular weight and composition of the product than conventional techniques allow. "This is really interesting work," says chemical engineer Eric Beckman, who does similar research at the University of Pittsburgh and teaches a pollution prevention course there. "They show they can make plastics as good or even better in carbon dioxide."

That's quite different from the way plastics are usually made. Conventional manufacture begins with a solution of the monomer—the plastic's chemical building block —dissolved or dispersed in an organic solvent or water. An initiator compound encourages the monomeric molecules to link end-to-end, forming a polymer containing hundreds or thousands of units. These long-chain molecules form tiny spheres that then get pressed or molded into useful shapes.

What's left from this process is the solvent, which may be hazardous on its own, together with leftover monomer and initiator. Even if the original solvent was plain water, the waste is considered environmentally dangerous, says DeSimone. In fact, lightly contaminated water is one of the plastics industry's biggest cleanup headaches.

DeSimone's group set out to relieve that headache by changing the solvent. Two years ago, DeSimone showed that fluoropolymers, which are teflon-like materials, could be produced in a new kind of solvent: supercritical carbon dioxide (*Science*, 14 August 1992, p. 945). A supercritical gas is one at a pressure so high its density resembles a liquid's, while its viscosity remains close to that of a gas. Transforming the gas into its supercritical form can be done at room temperature, creating a liquidlike medium for chemical reactions. And unlike water, carbon dioxide is easy to separate from any leftover monomer or initiator: Simply relieve the pressure and allow the gas to escape.



Double duty. Fluorine-containing tails on a surfactant molecule remain in solution while its backbone clings to a growing polymer sphere, keeping it suspended.

Unfortunately, says DeSimone, "most polymers don't dissolve in carbon dioxide. Fluoropolymers were the exception to the rule." For example, monomers of methyl methacrylate (MMA)—the basis of plexiglass—dissolve easily in carbon dioxide, but the polymers fall out of solution once the molecular chains grow beyond 10 units or so. And while 10 units is, officially, a polymer, it's not "poly" enough for use as a plastic.

So DeSimone's group had to find a way to keep the growing polymers dissolved. They turned to surfactants—an old chemical standby for keeping molecules evenly suspended in solution. Surfactants, which are the basis of detergents, are split-personality molecules with one end that is at home in the solvent and another that tends to bind to the substance being dissolved—grease, in the case of a detergent. DeSimone and his colleagues designed a special surfactant with a fluorine-containing end that was CO_2-philic (carbon dioxide–loving) and dissolved readily in the carbon dioxide. The other end was CO_2-phobic and wanted to fall out of solution like the poly(MMA). The CO_2-philic side kept the surfactant and its cargo in solution, while the CO_2-phobic side adsorbed to the growing polymers.

Thanks to the surfactant, the MMA polymers grew to lengths of up to 3000 units—squarely in the useful size range—and formed tiny plastic beads a few micrometers across. Besides the technique's environmental advantages, chemical engineer Keith Johnston of the University of Texas thinks it could offer more control over polymer size. Many solvents have a tendency to squelch polymer growth at random, when a stray solvent molecule binds to the end of the growing chain. Carbon dioxide, however, doesn't interact with the growing molecule at all.

Moreover, says Johnston, because the carbon dioxide can slip in between the molecules of the growing polymer, it can keep the poly(MMA) sphere pliable, like a sponge full of holes. By diffusing other monomers into the plastic, engineers could create highly specialized polymers. The porous spheres could also serve as tiny vessels for drug delivery. And DeSimone thinks these advantages might not be limited to poly(MMA). The same surfactant might work for other acrylic polymers, and surfactants designed on the same principles could work for other classes of polymers.

The strategy requires few changes in the manufacturing process, which should appeal to the chemical industry, said a chemical engineer at Air Products and Chemicals in Allentown, Pennsylvania. One adjustment, however, could be a major stumbling block: the need to run the polymerization at high pressure. While carbon dioxide is one of the cheapest solvents—at 4 cents a pound, it's second only to water—"high pressure is always capital intensive," says DeSimone. But if the cleanup savings outweigh the added capital costs, he and his colleagues may have opened the way for the plastics industry to make a break from conventional solvents—and helped plastics change their rep once and for all.

–Karen Celia Fox

Karen Celia Fox produces the radio show "Science Report" for the American Institute of Physics.