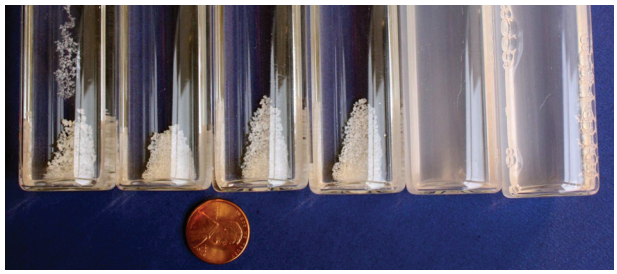
Perfluoropolymer degrades in decades, study estimates

The breakdown of fluorotelomer polymers, the main fluorinated ingredient in stain repellants and paper coatings, is a significant source of perfluorooctanoic acid (PFOA) and other fluorinated compounds in the environment, U.S. Environmental Protection Agency (EPA) scientists conclude in a study recently published in *ES&T* (**2009**, DOI 10.1021/es9002668). The finding could impact the future of these and myriad other products that rely on fluorotelomer polymers, because the agency is moving to tighten its rules on the basis of this study and other research.



EPA

EPA scientists tried different solvents to dissolve the acrylate-linked fluorotelomer polymer used in the experiments.

PFOA occurs at low levels in the environment and in human blood. It remains in people's bodies for years and causes developmental problems and other adverse effects in laboratory animals. Last year, high levels of perfluorinated chemicals found in Decatur, Ala., prompted EPA to issue a short-term drinking-water advisory for PFOA, and New Jersey has issued guidance for chronic drinking-water exposure of 0.04 parts per billion.

Other chemicals break down to form PFOA, but few attempts have been made to determine whether fluorotelomer polymers biodegrade. These polymers represent a potentially large source of PFOA and other perfluorocarboxylates, because they constitute about 80% of total fluorotelomer production.

But experimentally determining whether perfluorotelomer polymers degrade is fraught with difficulties. The EPA study has its share of problems, including few data, insufficient controls, and a leap from the laboratory results to broad conclusions, according to some scientists who study these chemicals.

Ideally, chemists strive to monitor biodegradation of a particular chemical by measuring both decreases in its weight and increases in the breakdown products, says environmental chemist Linda Lee of Purdue University. But the polymer is too big to analyze, so chemists are left trying to track the breakdown products, which include fluorotelomer alcohols and PFOA.

But even at the very start of the experiment, the polymer contains fluorotelomer alcohols as residuals from the manufacturing process. These residuals complicate the experiment because they act as background noise that can swamp the signal of degradation. A two-year-long study by DuPont scientists concluded that degradation was a very slow process, but the report was criticized by some academic and industrial chemists for starting with too high a fluorotelomer alcohol residual signature.

EPA research scientist John Washington used an acrylate-linked fluorotelomer polymer custom made to minimize residuals. He also completely dissolved duplicate samples of the polymer at the start of the experiment and then at 497 days and 546 days to make sure he analyzed all the chemicals. "A key feature of our work is the extraction," he says. "The DuPont study was very good, but they did not understand the need for total extraction." The DuPont scientists declined to comment for this story.

But the custom polymer, with a grain size similar to table salt, is more than 100 times bigger than fluorotelomer polymers in commercial use. Washington attempted to account for this with a model that allows for the much greater surface area, and consequently greater degradation rate, of smaller particles. The conversion drops his experimentally determined polymer half-life from roughly 1000 years to about 10−17 years. While Lee agrees that small particles may degrade more rapidly than large ones, she cautions that Washington's conversion is too simplistic.

Other scientists say the EPA study makes a significant contribution. "This is an important question, and the EPA study advances the science by finding a better way to deal with the problem of residuals," says chemist Scott Mabury at the University of Toronto.

"We believe that at this point in time this is the best data available to the agency," says Cathy Fehrenbacher, chief of EPA's exposure assessment branch. "The relatively short half-life is consistent with other unpublished studies that have been submitted to the agency."

In 2006, EPA proposed that it should review new perfluorinated polymers before they are made, because they could break down to produce PFOA and other perfluorochemicals. The rule has languished for over three years, but EPA now expects to finalize the rule this year, according to spokesperson Dale Kemery.

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