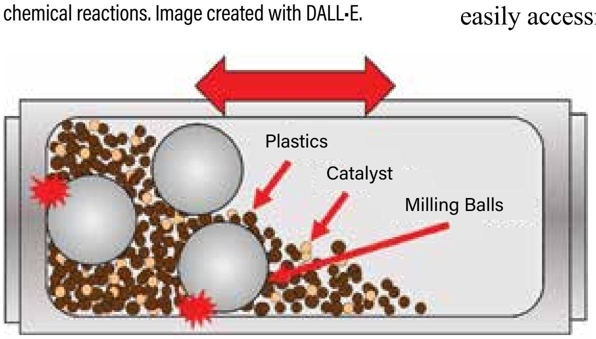
Eliminating End-of-Life Plastics by Mechanochemical Recycling

The accumulation of plastics in landfills and the environment is among the most pressing problems facing engineers. Efficient chemical recycling processes would provide an opportunity to valorize these waste streams and create an economic incentive to reduce landfilling and pollution. However, many of the desirable properties for plastic applications make efficient upcycling difficult. For example, low chemical reactivity and solvent-resistance are critical properties that prevent material failure but impede many chemical recycling processes, which typically break waste plastics into their constituent monomers or blendstocks. Monomers formed by chemical recycling are particularly attractive because they can be purified and used to make new plastic products that are chemically identical to the originals.

▲ **Figure 1.** The high impact between the metal balls in a ball mill reactor and the polymer surface is sufficient to momentarily liquefy the polymer and facilitate chemical reactions. Image created with DALL•E.



▲ **Figure 2.** This diagram of a ball mill reactor demonstrates how the collisions between milling balls and plastics can create reactive environments.

With support from the U.S. National Science Foundation (NSF), Carsten Sievers and his collaborators at the Georgia Institute of Technology are addressing these challenges. They are developing plastics upcycling processes that use mechanical forces in ball mill reactors instead of heat (Figure 1). When the milling balls collide with solid plastic particles, catalysts, and reactants, they create contact between these solids that normally require all but one component to be in the liquid or gas phase. In addition, the collisions provide enough energy to initiate chemical reactions that would otherwise require heat. These reactions, which occur near room temperature, convert the polymers into monomers or molecules that can be used to make new polymers or chemicals (Figure 2).

In a recent paper, the research team showed that polyethylene terephthalate (PET) can be depolymerized into its monomeric building blocks via mechanochemistry within 7 min by milling it with sodium hydroxide. The critical step in this process is creating easily accessible interfaces between the solid PET and solid sodium hydroxide particles. To illustrate the translational potential for progressing these lab-scale experiments to an industrial scale, the researchers modeled the trajectories and impact forces of thousands of balls. A technoeconomic analysis showed that the process could be economically viable if PET waste can be collected for less than $500 per ton.

Mechanochemical depolymerization can also be applied to other polymers, but the reaction path needs to be tailored to the feedstock. For example, the process of depolymerizing polystyrene into styrene monomers without additional reactants generates mechanoradicals by rupturing polymer molecules. Styrene monomers can be eliminated from these radicals in the inverse reaction of radical polymerization. However, for this reaction to occur to a significant extent, the mechanically activated energetic reaction environment must be maintained for as long as possible, and generated products must be continuously removed from the ball mill to prevent repolymerization.

While harsher reaction conditions are required to depolymerize polyethylene, it can be broken into fragments in a two-step process. The polyethylene is oxidized by milling it with a catalyst and hydrogen peroxide, and once oxidized, the polymer chain can be deconstructed much more readily.

The results from the NSF-supported project have led to a new project sponsored by the Toyota Research Institute of North America and industrial support to scale up the volume of the batch process from lab to pilot scale. "The success of mechanochemical recycling at the lab scale with its potential for industrial-scale application highlights the importance of continued investment in such innovative recycling technologies," says Oscar Daoura, Associate Research Scientist at Dow Chemical. CEP

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