Mechanochemistry

A new route to sustainable polymer recycling

Plastics and rubbers are some of the most important materials in advanced societies, and hundreds of millions of tonnes are produced every year. Devising efficient and cost-effective ways to recycle these materials has become a crucial environmental concern. Although degradable plastic-based materials can be produced, their practical use is limited by their vulnerability under environmental stress. Professor Junpeng Wang and his team at the University of Akron, USA, have developed a new strategy that allows them to control the stability of a polymer. Their mechanochemistry approach locks the polymer into a stable non-depolymerisable state during material operation and unlocks it for recycling at its end of life.

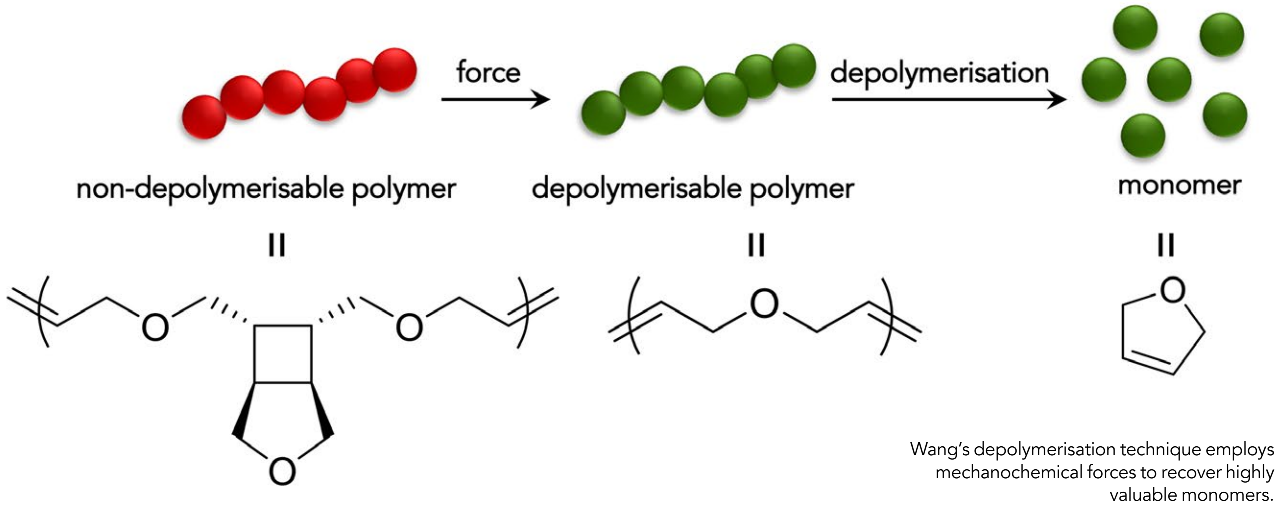
Plastic is one of the most common classes of man-made materials, finding various applications in a wide range of industries, from packaging to piping and plumbing, automobiles, toys, and furniture, to name but a few. Modern plastics are typically synthesised through relatively inexpensive processes starting from fossil fuel-based chemicals, like petroleum oil and natural gas. They form stable, lightweight, durable, and flexible materials, which can be moulded into solid objects of virtually any shape and size.

PLASTIC POLLUTION

The global production of plastic materials has continuously and dramatically increased since the synthesis of the first example, Bakelite, in the second decade of the 20th century. Around 359 million tonnes of plastics were produced in 2018, roughly two orders of magnitude more than the total production in 1950. This has led to a growing concern for the environmental impact of plastic. A large component of the plastic produced every year is in fact not reused, and its very slow decomposition rate causes widespread pollution, particularly in major water bodies.

POLYMERS

Plastic materials have a polymeric structure: they are composed of long chains of repeated subunits called monomers, each of which is made up of a relatively small number of atoms. These macromolecular chains can arrange themselves next to each other or form chemically bonded networks. Macromolecular chains are linear polymers, or thermoplastics. They include materials like polyethylene and polypropylene, which alone account for more than 60% of the world's thermoplastic production, along with polystyrene and polyethylene terephthalate (PET). Chemically crosslinked polymers, or thermosets, include epoxy resin (ER) and polyurethane. Because of the presence of chemical bonds among the polymer chains, these materials exhibit higher stability than thermoplastics and they are more difficult to degrade and recycle. Several natural polymers are also known, which include natural rubber, wool, silk, and cellulose, the main constituent of wood and paper.



Wang's depolymerisation technique employs mechanochemical forces to recover highly valuable monomers.

RECYCLING PLASTIC

Materials recovery strategies to recycle used plastic have been in use since the 1930s. All of them exploit either mechanical or chemical recycling techniques. Mechanical recycling is conceptually simple, but its application is limited by its cost and by the inevitable degradation in the quality of the materials obtained at the end of the recycling process. In contrast, chemical recycling attempts to decompose the polymeric chains into their constituent monomers, which can then be used as starting chemicals for the synthesis of new chains. This approach, based on chemical depolymerisation, makes it possible to produce new plastic with no need for additional chemical feedstock. As such, it offers a promising route toward a closed-loop plastic economy, which does not rely on fossil fuels or oil.

> **A large component of the plastic produced every year is not reused and its very slow decomposition rate causes widespread pollution.**

MECHANOCHEMICAL DEGRADATION

Despite their inefficiency, mechanical degradation processes can achieve partial depolymerisation, by mechanically breaking some of the chemical bonds within a polymer. However, for most plastic materials, these processes cannot yield the pristine monomers, which are required to synthesise new plastic. To achieve a mechanical conversion of a polymer into its monomers, chemical modifications must be carried out to increase the sensitivity of the polymer to mechanical degradation. This can be accomplished by incorporating specific chemical moieties, known as mechanophores, within the structure of the polymer. These mechanophores increase the response of the material to externally applied forces, triggering the cleavage of the chemical bonds holding the monomers together. This approach is investigated by Professor Junpeng Wang and his team at the University of Akron, USA.

DEPOLYMERISATION TECHNIQUES

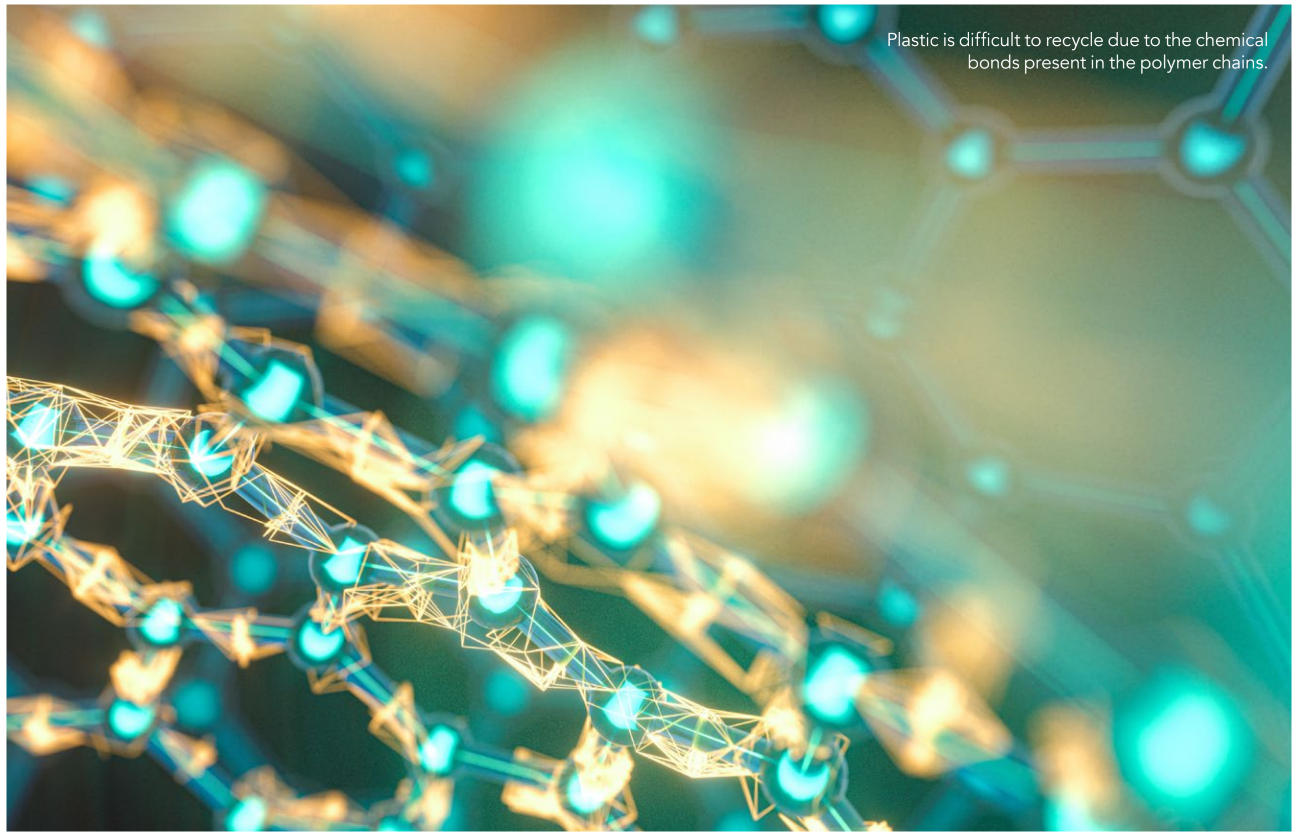
'Mechanochemical recycling', explains Wang, 'is a unique type of chemical recycling, which leverages chemical reactions induced by mechanical forces to recover highly valuable monomers.' Mechanochemical degradation can be achieved for both bulk polymers and for polymers in solution. For bulk materials, mechanical forces can be applied using a variety of techniques, including extension, compression, swelling and ball milling. In the case of polymers in solution, the most common method is ultrasonication, which exposes the polymer solution to ultrasonic frequencies. During ultrasonication, forces on the polymer chains are generated by the cavitation effects created by the sound-induced nucleation, growth, and collapse of microbubbles in the solvent. Polymer segments closer to the microbubbles move faster than those far away from them, and different regions of the chain experience different forces. Eventually, this leads to chain breaking, typically at mid-chain, where the force is highest.

CONTROLLING POLYMER STABILITY

Although the chemical modification of a polymer can enhance its degradability, it can also negatively impact its stability during production, storage, and use. Various techniques to address this reduced resistance to environmental effects have been proposed, but typically these approaches lack generality, and they substantially increase the costs of the polymer production. Wang and his collaborators have pioneered the use of a novel approach in which the degradability of a polymer is 'locked' during storage and usage and 'unlocked' when the polymer needs to be decomposed into monomers.

LOCKED DEGRADABILITY

In Wang's approach, locking is achieved through the introduction within the polymer structure of specific chemical groups that act as locking moieties. The locking moieties keep a polymer intact even when easily cleavable chemical bonds break in response to environmental effects, such as changes in the acidity of the solvent surrounding the polymer, which, in normal conditions, could trigger its degradation. This makes the material virtually insensitive to environmental changes and very stable. On the other



Plastic is difficult to recycle due to the chemical bonds present in the polymer chains.

hand, when the polymer needs to be degraded, an on-demand transition to its unlocked state can be induced mechanochemically, by ultrasonicating the polymer solution or grinding the polymer solid. After unlocking, degradation can easily occur, as the breaking of cleavable bonds in the polymer chains can now occur in response to chemical changes in the polymer environment.

MECHANOCHEMICAL SYNTHESIS

A polymer's stability is related to a property referred to as 'ceiling temperature', which is defined as the temperature at which polymerisation, that is the formation of bonds between monomers to form a polymer chain, and its inverse reaction are in equilibrium. Polymers with high ceiling temperatures exhibit enhanced stability, whereas polymers with low ceiling temperatures are metastable and can be easily degraded. In recent work, Wang has shown how the concepts of mechanochemistry and chemical locking can be used together to achieve the preparation of degradable polymers that would otherwise be too challenging to synthesise using standard synthetic routes.

> ***Mechanochemical recycling is a unique type of chemical recycling, which leverages chemical reactions induced by mechanical forces to recover valuable monomers.***

TRIGGERING CHEMISTRY WITH MECHANICAL FORCES

Mechanochemical activation can be used, as demonstrated in Wang's research, to convert a polymer with high ceiling temperature to a more easily degradable low ceiling temperature one. In his work, he has been able to mechanochemically generate poly(2,5-dihydrofuran) (PDHF), an easily degradable but hard-to-synthesise polymer, by converting an unsaturated polyether precursor containing cyclobutane-fused tetrahydrofuran groups in each monomer. This precursor, which represents the locked state of the polymer, has a high ceiling temperature and is extremely stable. Using ultrasonication on the polymer solution or bulk polymer grinding in a ball mill, the unlocked PDHF state can easily be accessed. This species can then be easily and completely decomposed into its (2,5-dihydrofuran) monomers in the presence of a ruthenium-based catalyst.

The results obtained in this work also indicate that mechanochemical methods can be used to regulate and fine tune the ceiling temperature of diverse classes of recyclable polymers. 'The mechanochemical generation of otherwise difficult-to-synthesise PDHF', says Wang, 'highlights the power of mechanochemistry – initiating chemistry with force in polymers – in accessing elusive structures.' The ability to create new easily degradable polymers by mechanochemical means may provide a crucial step forward in the creation of next-generation polymers for the sustainable and environmentally friendly production of new synthetic plastic and rubber materials.

Behind the Research

Professor Junpeng Wang

E: jwang6@uakron.edu **T:** +1 3309725345 **W:** junpengwanglab.org

Research Objectives

Junpeng Wang investigates how mechanochemistry and chemical unlocking can be used in combination to prepare degradable polymers that are otherwise too challenging to synthesise using standard synthetic routes.

Detail

Bio

Junpeng Wang received his PhD in Chemistry from Duke University in 2015 and conducted postdoctoral studies at University of Chicago and MIT. In 2019, he started his independent career at University of Akron. His research aims to address challenges in materials science by applying physical organic chemistry approaches.

Funding

- University of Akron
- National Science Foundation, grant no CHE-2204079

Collaborators

- Kayla Williams Pavlantos and Professor Chrys Wesdemiotis for mass spectrometry analysis.

References

Hsu, T-G, Liu, S, Guan, X, et al, (2023) Mechanochemically accessing a challenging- to-synthesize depolymerizable polymer. *Nature Communications*, 14, 225. doi.org/10.1038/s41467-023-35925-2

Zhou, J, Hsu, T-G, Wang, J, (2023) Mechanochemical degradation and recycling of synthetic polymers. *Angew Chem Int Ed*, e202300768. doi.org/10.1002/anie.202300768

Hsu, T-G, Zhou, J, Su, H-W, et al, (2020) A polymer with "locked" degradability: superior backbone stability and accessible degradability enabled by mechanophore installation. *J Am Chem Soc*, 142, 2100–2104. doi.org/10.1021/jacs.9b12482

Personal Response

What are the advantages of mechanochemical depolymerisation compared to traditional mechanical and chemical plastic recycling strategies?

" Traditional mechanical recycling typically causes degradation in the mechanical properties. Mechanochemical depolymerisation, or mechanochemical recycling in general, can be viewed as a unique type of chemical recycling in that it allows for recovery of useful building blocks, which can be reused to make plastic materials with quality comparable to virgin polymers. Compared to other chemical recycling approaches, the use of mechanical processing techniques, such as ball milling, is advantageous as it is more efficient in energy use. "