News & views

Sustainable chemistry

Mixed plastics upcycled dynamically

Mathieu L. Lepage & Jeremy E. Wulff

Waste plastics contain immiscible polymers, making recycling challenging. A new additive enables the thermal reprocessing of mixed plastics into recyclable, high-performance materials. See p.731

Humanity has a plastics problem. Our society relies on inexpensive polymers for a multitude of applications, from packaging and consumer electronics to aerospace engineering. However, dealing with the mountains of waste that are generated when these plastic items are discarded remains one of the most pressing global challenges. On page 731, Clarke *et al.*[1] report a class of additive that enables the conversion of mixed plastic waste into recyclable, value-added materials through the simple application of heat.

A major obstacle in plastics recycling originates in the diversity of materials that become mixed together in waste. Because plastics have such a wide range of uses, they must be produced to different specifications and have varying properties, such as heat resistance, transparency and mechanical stiffness. Manufacturers use various 'commodity' polymers in their products to meet these requirements – materials produced and discarded on a multi-megatonne scale annually, such as polyethylene, polypropylene and polyesters. Increasingly, plastic objects are being made from biomass-derived and biodegradable polymers such as polylactic acid.

Separating these materials from collected waste remains difficult, but mixed polymers cannot be directly reprocessed into materials that have the same properties as the original plastics. This is partly owing to differences in the molecular structures of the polymers, which cause them to separate into distinct phases at the microscopic level when blended (Fig. 1a). The process is analogous to what occurs when water and oil are vigorously mixed – tiny droplets of one are dispersed into the other. For blended polymers, mechanical failure (such as crack formation or other types of breakdown) at the boundaries between immiscible polymers results in poor performance of the reprocessed material.

Clarke and co-workers describe an innovative strategy for joining together, or compatibilizing, dissimilar plastics by forming new covalent bonds between the polymer chains. The process involves the addition of about 5% by weight of a new compatibilizing agent, relative to the mass of the polymer substrate. Remarkably, the agent stabilizes highly immiscible blends, such as mixtures of polyethylene and polylactic acid, turning them into uniform composites (Fig. 1b).

Most commodity plastics are thermoplastics, which consist of linear or branched chains, mainly of carbon atoms, that are otherwise not interconnected. Thermoplastics can be melted and reprocessed as viscous liquids. They are distinct from thermosets, which are 3D molecular networks that arise from the formation of chemical bonds (crosslinks) between the polymer chains. Such crosslinking essentially turns a polymer object into one gigantic molecule, greatly improving the material's performance but rendering it insoluble and non-meltable. As a result, most thermosets cannot be recycled and are either burnt as fuel or diverted to landfill.

The researchers' key innovation is to modify a previously described small molecule[2] that can crosslink the chains of almost any commodity plastic. The modifications produce new agents that install dynamic crosslinks – chemical groups that can break and re-form connections – between polymer chains, producing a type of material called a vitrimer. Polymeric vitrimers can exhibit

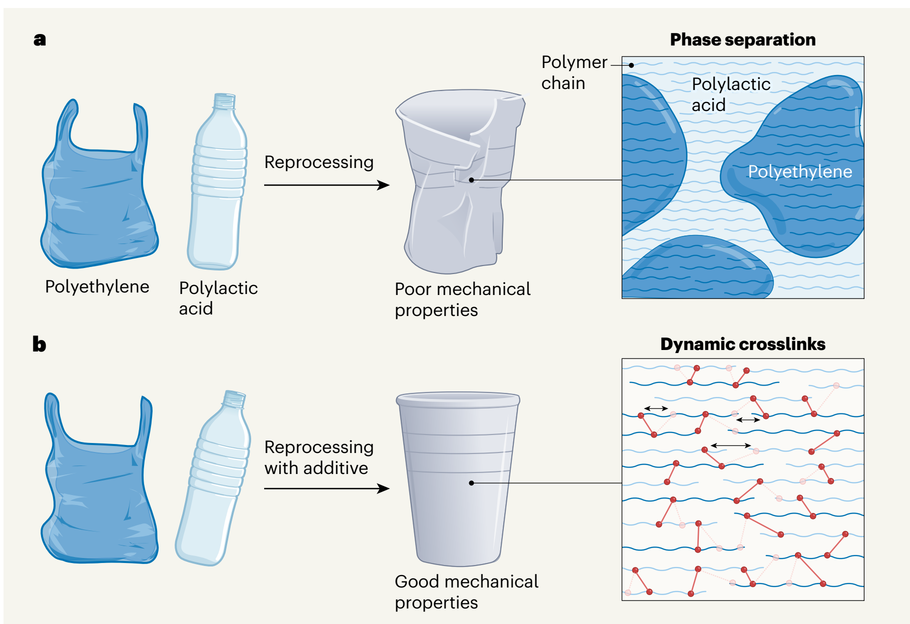

Figure 1 | Compatibilization of polymers enables recycling of mixed plastic waste. a, Mixed plastic waste cannot be efficiently recycled as a blend because many of the polymers in the waste are incompatible: they separate into distinct phases at the microscopic scale during reprocessing, producing materials with poor mechanical properties at the macroscopic scale. **b**, Clarke *et al.*[1] report additives that form dynamic crosslinks between the polymer chains of various plastics, thereby producing composites that do not undergo phase separation and have better mechanical properties than the original polymers. The crosslinks can break and re-form to relieve mechanical stress, allowing the composites to be further reprocessed and recycled.

similar mechanical properties to those of thermosets (because they are crosslinked), but remain processable at high temperatures because the dynamic linkages can exchange their positions, allowing the material to be remoulded[3,4].

Using their dynamic crosslinking agents, the authors demonstrated a simple method to convert mixtures of cheap commodity thermoplastics (less than US$5 per kilogram) into multi-component vitrimers. In doing so, the mechanical and high-temperature performance of commodity plastics such as low- and high-density polyethylene can be upgraded. Even more excitingly, stable, reprocessable composites were formed from polyethylene and polyesters. In one particularly compelling example of upcycling, a composite was created using low-density polyethylene from a plastic bag together with polylactic acid from a plastic drinking cup. The presence of dyes and other additives in the two materials was not detrimental to the chemistry, which bodes well for the use of this technology for recycling post-consumer waste.

To understand the potential impact and limitations of this work, it is helpful to consider the scale of worldwide production and use of plastics. Around 460 megatonnes of plastics were used in 2019, 40% of which consisted of polyethylene and polypropylene[5]. Only 9% of manufactured polymers were recycled[6], and the Organisation for Economic Co-operation and Development projects that the amount of plastic waste could almost triple by 2060 if policies are not implemented to address the issue[5]. It is to be hoped that regional and global actions could mitigate this increase, but large-scale recycling will be key to reaching a sustainable, circular plastic economy[7].

The technology developed by Clarke *et al.* has the potential to greatly ease the recycling of post-consumer plastics by lessening the stringency of waste sorting. However, the typical concentration of the crosslinking agent used in the study is still much too high for large-scale application. For example, the compatibilization of 100 megatonnes of mixed-waste plastics (about one-quarter of 2019's global waste) would require the production of 5 megatonnes of dynamic crosslinker — an unrealistic goal, especially given the lengthy synthetic sequences (and expensive reagents) that are used to generate the three prototypical crosslinking reagents. Moreover, the high number of fluorine atoms in the crosslinking agents might be problematic, given concerns about the persistence of highly fluorinated compounds in the environment[8].

Nevertheless, Clarke *et al.* have made an important advance by showing that simple processes for the dynamic compatibilization of mixed plastic are viable. Follow-up work will no doubt improve on the initial discovery and uncover applications for the reported composites — each of which is a fundamentally new material with the potential for use in engineering and manufacturing.

Mathieu L. Lepage is at the Fundamental and Applied Heterochemistry Laboratory (UMR CNRS 5069), Paul Sabatier University, 31062 Toulouse Cedex 9, France. **Jeremy E. Wulff** is in the Department of Chemistry, University of Victoria, Victoria, V8W 3V6, Canada.
e-mails: mathieu.lepage@cnrs.fr; wulff@uvic.ca

1. Clarke, R. W. *et al. Nature* **616**, 731–739 (2023).
2. Lepage, M. L. *et al. Science* **366**, 875–878 (2019).
3. Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. *Science* **334**, 965–968 (2011).
4. Röttger, M. *et al. Science* **356**, 62–65 (2017).
5. OECD. *Global Plastic Outlook: Policy Scenarios to 2060* (OECD, 2022).
6. Geyer, R., Jambeck, J. R. & Law, K. L. *Sci. Adv.* **3**, e1700782 (2017).
7. Royal Society of Chemistry. *Science to Enable Sustainable Plastics — A White Paper from the 8th Chemical Sciences and Society Summit* (Royal Society of Chemistry, 2020).
8. Stahl, T., Mattern, D. & Brunn, H. *Environ. Sci. Eur.* **23**, 38 (2011).

The authors declare no competing interests.

Tumour biology

Extrachromosomal DNA appears before cancer

David H. Wang

A type of circular DNA called extrachromosomal DNA was thought to be found exclusively in cancer. Its discovery in non-cancerous tissue suggests that it might have an early active role in malignant transformation. **See p.798**

A type of circular DNA not found on chromosomes, termed extrachromosomal DNA, can aid cancer growth by harbouring cancer-promoting genes (oncogenes)[1]. The unique structure of extrachromosomal DNA and its associated protein complex, called chromatin, boosts the efficiency of its transcription, and the inheritance pattern of this DNA, resulting in many copies in a single cell, supports rapid amplification of oncogene content and tumour evolution[2,3]. Although present in many types of human cancer, extrachromosomal DNA was thought to be non-existent in normal tissues. On page 798, Luebeck *et al.*[4] report their finding of extrachromosomal DNA in non-cancerous oesophageal tissue that is predisposed to cancer development, and provide evidence that this DNA might help to drive non-cancerous tissue to become cancerous.

Barrett's oesophagus is a condition in which the cells lining the oesophagus (Fig. 1) change their identity as a complication of the reflux of acidic contents from the stomach and intestinal bile back into the oesophagus (gastro-oesophageal reflux)[5]. A minority of people with Barrett's oesophagus go on to develop cancer after the cells have progressed through low-grade and then high-grade dysplasia — precancerous states in which cells acquire an increasing number of genetic abnormalities and structural changes. Large-scale genetic abnormalities can arise during dysplasia from mutations or loss of genes that function as tumour suppressors, such as *TP53*, and such mutations or loss can lead to whole-genome duplication, genomic instability or catastrophic chromosomal rearrangements called chromothripsis[6,7].

Luebeck and colleagues sought to answer the key question of whether extrachromosomal DNA found in oesophageal cancer is a consequence of genomic instability or a causal event responsible for the transition from dysplasia to cancer. The authors did this through computational analysis of whole-genome sequencing results of oesophageal biopsies from UK and US patients. Oesophageal biopsies from a single time point were examined for 226 individuals who had a diagnosis of one of the following: Barrett's oesophagus; Barrett's oesophagus with low-grade dysplasia; Barrett's oesophagus with high-grade dysplasia; early-stage cancer; or late-stage cancer. Longitudinal biopsies (those taken at different times) from at least two time points and from at least two locations in the oesophagus were analysed for a separate group of 80 people in the United States who had Barrett's oesophagus. This group consisted of 40 individuals who developed oesophageal cancer (67.5% had high-grade dysplasia) and 40 who did not (7.5% had high-grade dysplasia).

For the UK group, none of the people with Barrett's oesophagus or Barrett's oesophagus with low-grade dysplasia had extrachromosomal DNA. However, 4% of individuals with high-grade dysplasia, 25% with early-stage cancer and 43% with late-stage cancer had