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A critical review on the sustainability of inverse vulcanised polymers

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With increasing environmental pollution and climate change there is an urgent need for innovative solutions to tackle these challenges. However, especially since we live in the age of plastics with a linear economy it is important to not only look at their recyclability, biodegradability or that they are made from renewable resources, but also their whole lifecycle from resourcing to end-of-life treatment in order to achieve circularity. Inverse vulcanised polymers are claimed to be a green and more sustainable alternative to a wide range of materials for applications in energy storage, separation systems, construction and agriculture to just name a few. The use of waste material for their synthesis as well as the unique properties of these materials might be a game changer. But the path to large scale industrial production and application is still far as the scale-up comes with its own set of challenges. Herein, we take a closer look at the individual milestones in the lifecycle of inverse vulcanised polymers and how they can fit in as a more sustainable material along the road.

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Sustainability spotlight

Due to a large overproduction of sulfur from fossil fuel refinement, it is often stockpiled in huge pyramids in the open where it can cause environmental pollution. Inverse vulcanised polymers offer a solution for the utilisation of elemental sulfur and simultaneously provide beneficial properties for a large range of applications from energy storage to environmental remediation. However, the type of monomer and its processing has a huge impact on the system sustainability. The focused development of these materials could ultimately contribute to the UN sustainability goals 6 through waste water remediation, 7 with better energy storage systems, 9 through innovative construction materials, and 12 due to economic symbiosis and waste valorisation.

Introduction

The world is facing an escalating environmental crisis, with the depletion of natural resources and increasing pollution levels as two major aspects. These challenges stem from our reliance on a linear economic model, where resources are extracted, used, and discarded as waste. This approach is not only wasteful but also unsustainable in the face of finite resources and growing environmental pressures. To ensure a sustainable future, we must accelerate transformation to a circular economy, which emphasises the reuse, recycling, and regeneration of resources, harnessing both existing materials and renewable resources to minimise waste and environmental harm.

Among the most pressing environmental issues is pollution caused by plastics and hazardous chemicals. In nature, these pollutants persist for decades, harming wildlife, ecosystems, and human health. Addressing this issue requires innovative solutions, including the development of cleaner, safer, and more sustainable materials. In this regard, legislative frameworks play a key role in driving the systemic changes needed to

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tackle these challenges. Policies and regulations encourage industries to adopt greener practices and develop sustainable innovations. The European Green Deal,[1] and the associated 2020 chemicals strategy introduced by the European Commission,[2] is a prime example of such an initiative, demanding change from the chemical sector and broader economy through stringent environmental standards, ambitious sustainability goals, and support for technologies that are safe and sustainable by design. These legislative efforts are essential for achieving a balance between economic growth and environmental protection, paving the way for a more sustainable future. Over 80 measures—including product innovation, avoiding poor or unsustainable products and processes, and compliance with REACH and CLP regulations—help ensure rigorous scrutiny of chemical use, regulation, and data requirements. This strategy has been met with significant opposition from industry,[3] as the new restrictions could limit chemical diversity with rapid bans on new chemicals arguably preventing the development of future technologies. Equally, these measures can also fuel the development of new and more sustainable materials that are built from renewable resources and designed to recirculate in chemical product streams.

One emerging class of innovative materials are polymers with high sulfur content. Similar to other historical developments in the field of materials chemistry, their development was sparked by the utilisation of low-value waste products which otherwise are expensive to dispose or store. Traditionally, the use of sulfur in polymer science has been associated with the vulcanisation process, a process used to strengthen rubber.[4] Inverse vulcanisation (IV) flips this concept on its head, using sulfur as a major building block to create entirely new classes of polymers, often with remarkable properties.[5] Inverse vulcanised polymers have been called revolutionary in the context of sustainable materials since their production exploits industrial waste, is solvent-free and simple, and allows for incorporation of renewable resources.[6,7] The scope of this review article is the investigation of these claims, exploring the advantages and disadvantages associated with the use of inverse-vulcanised materials, with a goal to identify the challenges that must be overcome for the sustainable industrial-scale application of these polymers. To gain full understanding of the environmental impact of a product, one should not only consider their production and the respective carbon footprint but also assess the full lifespan of the product (Fig. 1). Therefore, the individual phases in the lifecycle of inverse vulcanised polymers are analysed herein, from synthetic challenges in the lab, their scale-up and their use-phase, and potential end-of-life treatments followed by a sustainability consideration for each section.

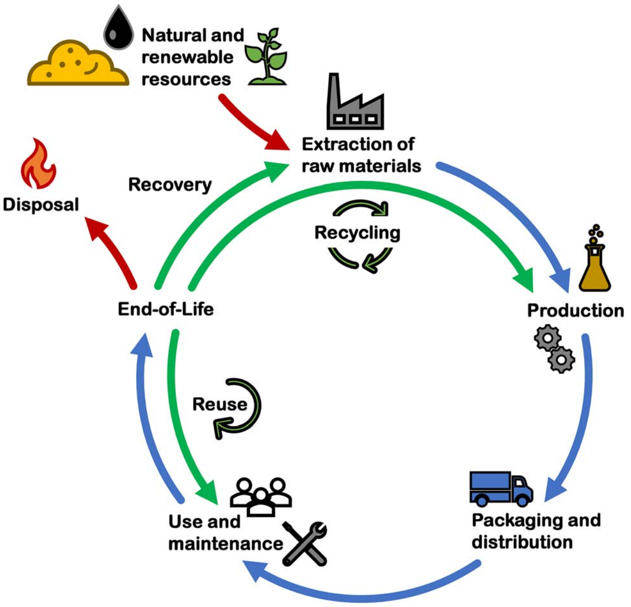


Fig. 1 Potential product lifecycle of IV materials from sourcing to production, packaging, use-phase to the end-of-life with possible options for recycling and recovery of the materials.

The lifecycle of inverse vulcanised materials

Resourcing: waste sulfur

Elemental sulfur originates from both natural and anthropogenic sources. Natural sources include volcanic emissions and biological processes in sulfur-rich environments, such as wetlands. Meanwhile, anthropogenically sourced sulfur is a by-product of industrial activities, including the refining of fossil fuels, natural gas processing, and mining (Table 1).[8] Over the last decade, global sulfur production has remained relatively stable at about 85 million metric tons per year.[9] However, due to worldwide regulations limiting sulfur content in diesel, gasoline, and natural gas, a continuous rise of the global sulfur surplus is expected in the foreseeable future. Even though the natural deposits for oil and gas will be depleted at some point in the future, the current surplus production of sulfur poses enormous challenges for existing producers, leading to reduced sulfur prices and even disposal costs in some regions. This becomes relevant especially when the depletion of natural oil reserves with low sulfur content (so-called sweet crude oil) leads to the use of formerly untapped deposits that were avoided due to high sulfur contaminations (sour crude oil).[10] Sulfur is primarily used to produce sulfuric acid, one of the world's most widely used base chemicals. However, this use competes with sulfuric acid recovered from ore smelting, since it is essential

Table 1 Sulfur sources and the respective annual production[8]

Sulfur source	Mass equivalents [10^6 t]
Frasch sulfur	1.1
Natural sulfur	0.7
Pyrite	4.2
Sulfide ore	11.6
Natural gas desulfurisation	7.9
Tar sand	15.9
Crude oil	11.2
Unspecified	4.6
Total	57.3

Fig. 2 Sulfur pyramids in Alberta, Canada. Source: https://www.enersul.com/operations/.

for processing phosphate rock and metallurgical ore leaching. Other existing utilisations of sulfur, such as in pigments, pesticides, and rubber vulcanisation and use as an agricultural nutrient, are well established and offer limited opportunities for consuming significant new sulfur supplies.[11]

As the amount of sulfur deposited in large piles increases, so could its environmental impact, particularly due to the exposure of elemental sulfur to weathering.[12] However, only a few studies discuss the environmental impact of sulfur piles, which are considered the main source of sulfur for inverse vulcanisation in this article. Wagenfeld *et al.* argued that long-term storage of elemental sulfur in blocks, as done in *e.g.* Kazakhstan and Canada, results in minimal environmental impact (Fig. 2).[13]

Nevertheless, potential risks remain, including groundwater contamination and the release of volatile sulfur dust, especially if the highest safety measures are not implemented.[13] Since research on the environmental impact of elemental sulfur is limited, we will transfer results from studies on its agricultural use and general exposure to weathering. While elemental sulfur is considered non-toxic in the environment and non-accumulative in the food chain, complex biological, chemical, and physical processes influence its fate and potential environmental effects.[14] The most common transformation is the oxidation of elemental sulfur into sulfates, which are readily available for plant uptake. This process is primarily biological, driven by diverse microorganisms such as chemolithotrophs (*e.g.*, *Thiobacillus* species), heterotrophic bacteria, and fungi. *Thiobacillus* species, in particular, are key sulfur oxidisers frequently detected near sulfur piles, potentially causing soil acidification and groundwater contamination through sulfuric acid production if rainwater runoff is not properly managed.[12,15,16] Several factors influence microbial sulfur oxidation, including soil texture, pH, organic matter content, nutrient availability, microbial interactions in the rhizosphere, temperature, and moisture levels. Therefore, examining soil composition and pH near sulfur piles and mining plants is crucial for assessing environmental harm.[13] Given that these sulfur piles are exposed to all weather conditions, heavy rainfall and wind can intensify their environmental impact.[12,13] Studies indicate that heavy rains can alter the biogeochemical cycle by causing lateral subsurface sulfur transport, leading to soil acidification, loss of soil fertility, depletion of base chemicals, and water acidification.[12] However, the question of toxicity to plants, fungi, aquatic animals, and humans remains complex. While elemental sulfur is generally considered harmless, existing data and studies are incomplete. Kuklińska *et al.* reported that sulfur toxicity has been detected in certain fungi, some plants, animals, and humans. In humans, sulfur exposure can cause skin irritation, allergic reactions, respiratory issues, and eye irritation. Toxicity can occur through ingestion of contaminated food or inhalation of sulfur dust, fumes, and smoke.[12,14] More critical to human health are volatile sulfur compounds such as hydrogen sulfide and sulfur dioxide, which are highly toxic and can additionally contribute to air pollution and acid rain.

Given these potential negative impacts, further research is necessary to fully understand potential consequences.[14] Despite these uncertainties of environmental harm, it is critical to reduce the amount of sulfur stockpiled in the environment. One part of the solution could be sulfur-rich polymers prepared by inverse vulcanisation, a relatively recent advancement in materials science, which has gained significant attention for its potential to contribute substantially to the field of polymeric materials with simultaneous beneficial effects on environmental pollution.

Production phase: technical and economic challenges

Lab-scale synthesis. One of the first applications of elemental sulfur was in the vulcanisation of natural rubbers.[4] Since crude rubber contains unsaturated C=C bonds, making it vulnerable to oxygen, ozone, and light with low resistance to aromatic, aliphatic, and halogenated hydrocarbons, their properties are insufficient for industrial applications. To improve its resistance to degradation, natural rubber is vulcanised. During this process, crude rubber such as natural and synthetic rubber or acrylonitrile-butadiene-rubber is mixed with about 3 wt% ground sulfur, along with accelerators and activators, and then heated to around 150 °C.[17] This process converts raw gum-elastic polymeric material into a rubber-elastic end product with adjustable properties like hardness and elasticity, as a function of the degree of vulcanisation for applications in tires for cars, trucks, bikes, and airplanes. With higher sulfur loading and under controlled conditions, vulcanisation produces ebonite, a hard rubber first created by Charles Goodyear through prolonged vulcanisation. Ebonite contains about 30–40 wt% sulfur and was originally used as a substitute for ebony wood.[18] Further increasing the amount of sulfur, *i.e.* reversing the ratios, results in inverse vulcanisation, first established in 2013. Despite the extensive research on inverse vulcanisation in the last decade, there are still many unknown factors that influence reaction mechanisms and kinetics, and material properties such as solubility and colour, exacerbated by challenging characterisation as the products are often both amorphous and insoluble.

Understanding of kinetics, thermodynamics and the mechanism

A full understanding of the kinetics of the inverse vulcanisation process will help to better predict the outcome of such reactions and the properties of the materials obtained thereof. This can support the focused development of materials for specific applications with consistent and predictable properties. In this regard, fewer trial-and-error approaches are needed so the development becomes more efficient and environmentally friendly. Early work on the study of stable polymer materials made from elemental sulfur is based on anionic sulfur copolymerisation with propylene sulfide following an anionic ring-opening polymerisation pathway.[19] The weak bond enthalpy of the S–S bond of around 266 kJ mol^{-1} (C–C bond: 346 kJ mol^{-1}) results in faster bond dissociation compared to that of C–C bonds. Homolytic and heterolytic S–S bond cleavage mechanisms have been proposed (Fig. 3), depending on the applied temperature. Cleavage of the S–S bonds at elevated temperatures forms $^{\bullet}S–[S]_6–S^{\bullet}$ diradicals, which further polymerise towards high-molecular weight polysulfides above temperatures of 159 °C.[20,21] Heterolytic S–S bond cleavage under formation of zwitterionic polysulfides in the form of $+S–[S]_n–S–$ has been proposed to take place above 200 °C.[22–24] The role of homolytic *vs.* heterolytic S–S bond fission in (inverse) vulcanisation is not fully clarified yet and is still a topic of discussion in the literature.[25] However, sulfur homopolymers are prone to depolymerisation due to the thermodynamically and entropically favoured conformation of cyclic $S_{5\leq n\leq 12}$ allotropes, resulting in unstable materials.[26] The invention of inverse vulcanisation in 2013 significantly changed the impact of sulfur polymer chemistry in the scientific community. Stable high sulfur content materials became available by the straightforward reaction of elemental sulfur with unsaturated organic comonomers (so-called "cross-linkers") at high temperatures. The irreversible addition of sulfur to C═C double bonds under formation of C–S bonds yielded stable materials with up to 90 wt% sulfur.[27] Inverse vulcanisation can be seen as a bulk free-radical polymerisation where sulfur acts as the initiator, monomer, and solvent all at once. Yet, under certain conditions, nucleophilic mechanisms also contribute, particularly

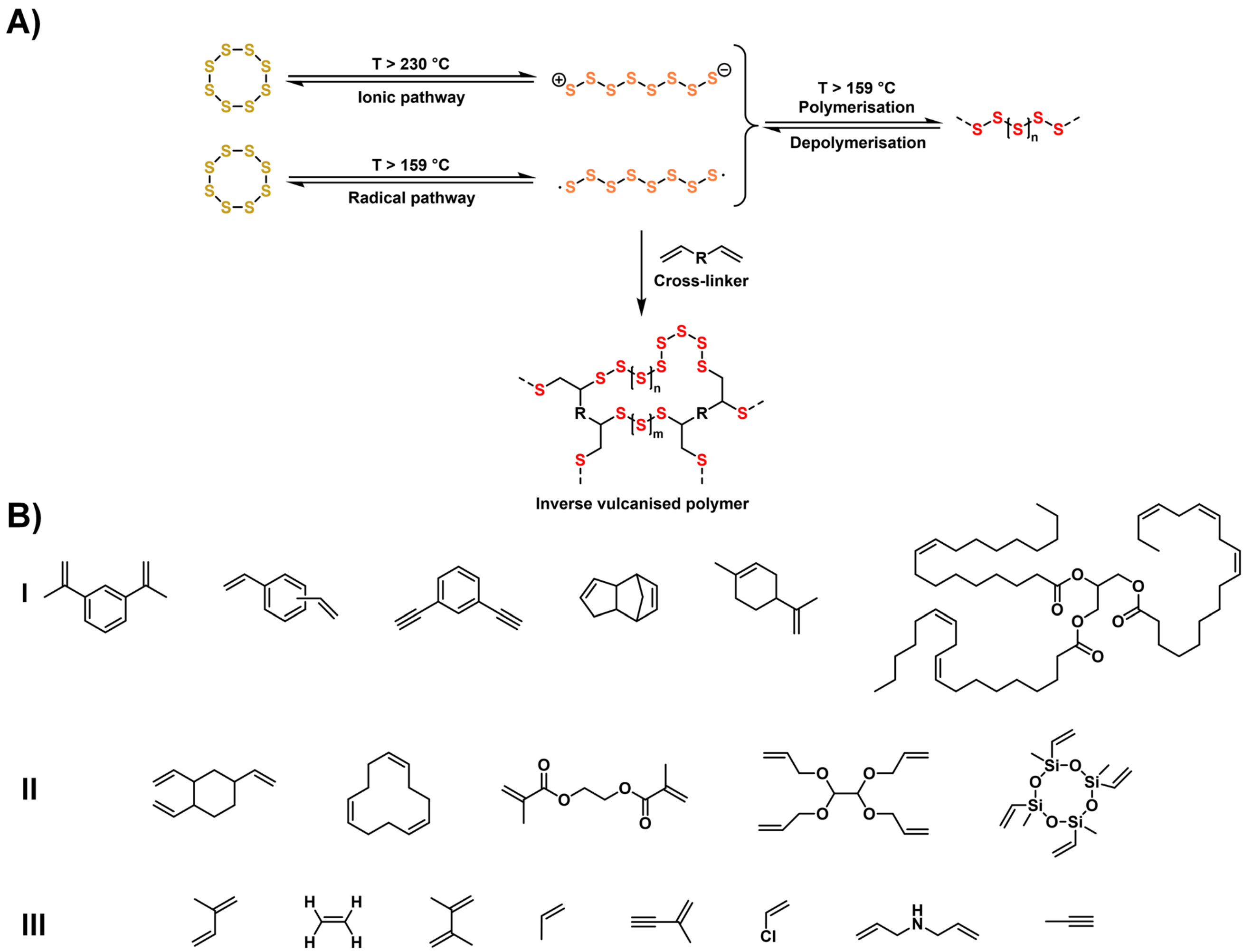


Fig. 3 (A) General scheme of IV *via* an ionic or radical reaction pathway. (B) Selection of reported cross-linkers suitable for IV. Group I: cross-linkers reactive without a catalyst in conventional IV; Group II: cross-linkers reactive with a catalyst; Group III: cross-linkers applicable in photoinduced IV.

when trace impurities, additives or initiators favour the formation of polysulfide anions. Thus, inverse vulcanisation is better understood as a mixed-mode polymerisation, where the dominant pathway depends on the specific monomer chemistry, reaction temperature, and presence of catalytic or environmental factors. With the easy to perform synthesis, low-cost input materials and a wide range of possible monomers, inverse vulcanisation offers inherent economic and ecological advantages in terms of sustainability:

- The use of elemental sulfur comes with the benefit of low cost and facile manageability. As of May 2024, the sulfur price was £224 per ton on an industry scale.[28] For comparison, the price of styrene could be assumed to be £787 per ton in August 2024.[29]
- The use of solvents or initiators is not necessary and reactions exhibit outstanding atom efficiency with potentially low-complexity reaction protocols, though significant control measures could be required for consistent results.[30]
- In its most basic form, an inverse vulcanisation reaction mixture comprises only elemental sulfur and a cross-linker, which are both consumed during the polymerisation. In the case of quantitative reactant conversion, extensive purification steps (*e.g.* precipitation, washing, *etc.*) can be avoided and the obtained polymers can be used directly.[27]

Even though many commercial polymer building blocks (propylene: −48 °C, vinylchloride: −13 °C, methacrylate: 80 °C; methyl methacrylate: 101 °C, and styrene: 145 °C) have a lower boiling temperature than the melting temperature of sulfur, it has been shown that gaseous monomers can be passed through molten sulfur to polymerise.[31] Direct polymerisation of sulfur and gaseous monomers in the gas phase was also proven to successfully produce sulfur polymers.[32] Despite the drawbacks that come with high temperatures, this opens pathways to a new group of monomers based on renewable resources, such as glycerides, fatty acids, terpenes, rosin, phenols and benzoxazines. A concise overview of renewable resources for inverse vulcanisation has been recently published by Shen, Zheng, and Zhang.[33]

Ground-breaking advancements in recent years were the invention of "catalytic", photoinduced and mechanochemical inverse vulcanisation, which will be discussed briefly in the following section. The addition of accelerators, most prominently amine nucleophilic activators or metal diethyldithiocarbamates, was shown to significantly decrease the temperature and time required for full conversion of reactants in IV reactions.[34] In contrast to conventional catalysis, the accelerator may not be regained after the reaction as it is believed to remain bound in the material.[35] The concept of photoinduced inverse vulcanisation was introduced in 2022 by Jia *et al.* and marked the first report of the successful reaction of highly volatile and gaseous cross-linkers that are long established as monomers in conventional polymerisations but were not available for inverse vulcanisation, such as isoprene, ethylene, dimethyl butadiene, and propene among others.[36] However, more research is necessary to convert the applicability of gaseous cross-linkers from surface polymerisation to the generation of multigram, macroscopic bulk materials. Mechanochemical inverse vulcanisation uses the mechanical energy applied by a ball mill to drive the polymerisation without the need for external heat, therefore allowing polymerisation of volatile cross-linkers that would not be accessible in a conventional inverse vulcanisation.[37–39] Given the dramatically lower energy consumption on one hand and the extended range of usable cross-linkers on the other, these methods represent an important advancement in terms of sustainability.

Characterisation of inverse vulcanised materials

Special considerations must be made in terms of material characterisation and analysis, which differ from conventional carbon-based polymer science. Whereas in a conventional, purely organic polymerisation, the monomer conversion and degree of polymerisation can be determined relatively easily with established and widespread methods such as nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC), the evaluation of IV reactions is more intricate.[40] Typically, the conversion of organic cross-linkers can be monitored and validated by ^{1}H NMR and infrared (IR) spectroscopy, which allow the detection of characteristic $C{=}C$,[41,42] $C{\equiv}C$,[43,44] oxazine,[45–47] and epoxide[48,49] bonds among others. However, to fully validate the progress of inverse vulcanisation, the irreversible conversion of cyclic elemental sulfur into polysulfide chains is at least as important as the conversion of organic cross-linking groups. Methods to evaluate the incorporation of crystalline sulfur into stable amorphous polysulfides mainly focus on differential scanning calorimetry (DSC) and powder X-ray diffraction (PXRD) where residual crystalline phases can be identified by melting or refraction, respectively.[27,50] The total amount of sulfur in a material may be inferred by thermal gravimetric analysis[27] and elemental analysis,[51] and the qualitative presence of oligosulfides can be confirmed by energy-dispersive X-ray spectroscopy (EDX),[50,52] time-of-flight secondary ion mass spectrometry (ToF-SIMS),[51,53] and X-ray photoelectron spectroscopy (XPS).[54] Nevertheless, the exact determination of the sulfur rank and the long-term stability of polysulfides remain challenging due to the dynamic nature of S–S bonds, which can cause undetectable depolymerisation.[55] However, recent work by Chalker *et al.* on high resolution Raman spectroscopy of high sulfur containing polymers showed that in some cases di-, tri- and tetrasulfides can be distinguished giving insights into the respective sulfur rank.[56,57]

One major problem of inverse vulcanisation is the inapplicability of SEC as a fast and effective tool to determine average chain lengths and distributions of polysulfides prepared by this method. The lack of control makes the preparation of narrowly distributed polymers one of the major future challenges.[51] Additionally, given the inherent insolubility of cross-linked polysulfides, solution-based analyses are limited, and often solid-state alternatives required. We believe that one key advancement in polysulfide characterisation will be the increased use of ^{33}S NMR spectroscopy. Due to the low natural abundance of the ^{33}S isotope (0.76%), its low gyromagnetic ratio, and low sensitivity compared to protons, ^{33}S NMR spectroscopy has been a niche analysis method in the past. Further challenges that complicate the sulfur NMR analysis are the fact that ^{33}S is quadrupolar which might require solid state NMR with its own set of limitations due to availability and know-how. However, with improvements of ^{33}S enrichment and NMR instrumentation in recent years, we expect that ^{33}S NMR spectroscopy can become a key method to gain further insights into the mechanisms of inverse vulcanisation and the nature of high sulfur content polymers.[58]

Advancing inverse vulcanisation with computational chemistry

To drive the development of inverse vulcanisation on a chemical level, a deeper understanding of the underlying reaction mechanism is vital.

Some of the most detailed mechanistic studies of inverse vulcanization have focused on the polymerizations of sulfur with 1,3-diisopropenylbenzene (DIB) or styrene.[59–61] However, the comonomer can also play a crucial role in the reaction mechanism and insights into reactions occurring at different functional groups will allow a more elaborate choice of cross-linkers. Understanding the influence of environmental conditions such as moisture, oxygen exposure, *etc.* will also improve the production of these materials on both the laboratory and industrial scale by improved reaction management. In this regard, computational methods are often applied to understand reaction mechanisms and kinetics. Although to date, they have not been applied extensively in the field of inverse vulcanisation, this may change as the field attracts a greater number of researchers. Some noteworthy articles that have applied density functional theory (DFT) to inverse vulcanised polymers exist already and may serve as starting points or blueprints for future research.[62,63] Tonkin *et al.* and Kleine *et al.* used DFT to understand the infrared absorption of their target comonomers and polymers, towards better infrared optical imaging lenses.[31] Meanwhile Dodd *et al.* used DFT to understand the Raman spectra of inverse vulcanised polymers and tried deciphering their structure.[64] Whilst not a direct probe of the polymers themselves, Smith *et al.* used computational chemistry to calculate the Fukui indices of different atoms on a target comonomer, indicating their likelihood of undergoing radical attack and thereby shedding some light on the mechanism of polymerisation.[65] An extensive DFT study was performed by Zheng *et al.*, focusing on DIB.[42] Their work represents the most in-depth application of computational chemistry to inverse vulcanisation to date, and gave insights into the chemo- and regioselectivity of thiyl radicals with α-methyl styrene. The latest DFT calculations on the photo-induced polymerisation of sulfur species provided further insight into the mechanisms and further predicted – and later validated – the thermal depolymerisation of sulfur species, which is crucial data for the advancement of recycling methods for high sulfur polymers.[66]

The aforementioned publications demonstrate that there is a wealth of exciting results available from computational chemistry, in relation to inverse vulcanisation. Optical properties can be predicted, directing research to finding the best comonomers to use for highly transparent infrared components, or even elucidating the source of the colour of inverse vulcanised polymers. The reactivity of comonomers can be predicted, explaining why some comonomers are readily reactive and others are recalcitrant, or which moieties of a comonomer are likely to be reactive. This could guide comonomer selection or inform catalysis of inverse vulcanisation by identifying reasons why comonomers are unreactive and how a catalyst could lower the activation barrier. In relation to this, machine learning models could analyse reactivity trends in comonomers and suggest new comonomers that could be reactive. Finally, although it would be a particularly challenging and time-consuming undertaking, it is possible that DFT could be used to calculate intermediate species' energy levels as well as the energy levels of the transition states that connect them. This could then be used to elucidate reaction pathways, as in the work of Pople *et al.* and explain experimental observations, or with enough investigation, suggest mechanisms for inverse vulcanisation.[62]

DFT is not the only computational approach that could benefit inverse vulcanisation. Molecular dynamics could provide ways to predict a variety of bulk properties for inverse vulcanised polymers of different comonomers at different degrees of cross-linking, resulting in potential structure–property relationships. The glass transition temperature can be predicted by molecular dynamics, which can be used to confirm the inverse vulcanised polymer structure from experimental data. The refractive index can be calculated, which is a value of great importance in the optical applications of inverse vulcanised polymers. A variety of mechanical properties can be predicted by molecular dynamics, which are important to know where durability or elasticity in the applications is important. Several properties important for battery applications of inverse vulcanised polymers can be calculated, such as the dielectric constant and the rates of mass transport of electrolytes through a polymer matrix. Similarly, the migration of elemental sulfur through a polymer matrix could be examined to predict the rates of sulfur bloom. Finally, molecular dynamics could be used to model interfaces, relating experimentally determined surface tension to predicted values of hydrophobicity.

A core issue in applying computational chemistry, particularly molecular dynamics, to inverse vulcanisation, is choosing an appropriate model system. This can be challenging when the structures involved are not explicitly understood; even when developing hypothetical polymer units, significant care must be taken. There are computational methods for modelling polymer units, considering them as part of a repeating chain of infinite length, without having to model the entire chain. However, these methods may not be so easily applied to an inverse vulcanised polymer, which is thought to be both highly cross-linked, and have no defined repeating unit. A single inverse vulcanised polymer encounters dramatic variability in its structure from factors like varying numbers of sulfur atoms in each sulfur chain; unreacted double bonds; sulfur loops (where a sulfur chain that would otherwise cross-link, actually connects to the same comonomer unit); by-product functionalities (*e.g.* 1,2-dithiole-3-thione rings); different distributions of cross-linking units within the same chain; and many more complications.

The next best approach then is to abbreviate this model. Good examples of this can be found in the work of Zheng *et al.*,[42] Tonkin *et al.*,[31] Kleine *et al.*,[63] and Dodd *et al.*.[64] These studies demonstrate the use of chemical intuition to rationalise sensible abbreviated models for inverse vulcanised polymer units. This allows DFT studies on these units, although it must be remembered that these units cannot take into account the effect of an extended polymer structure or long range interactions, a necessary compromise to develop a model that is small enough to undergo calculations in a reasonable timeframe. This compromise of reducing the complexity and size (in terms of number of atoms) in exchange for reasonable computation times with the trade-off of reduced accuracy and applicability to the real-world system is commonly encountered in most DFT studies. However, due to the high complexity of inverse vulcanised systems and their large size, such simplifications may lead to reductions in their accuracy and applicability. It is paramount to carefully consider the model to be used to get the best accuracy and applicability possible. For molecular dynamics, this problem would be expanded. One of the primary sources of error in molecular dynamics is a model that is too small and therefore not representative of the true system. Molecular dynamics would also require a relatively high degree of understanding of the structure of the polymer chains, to build sensible models that encapsulate the interaction between those chains. As such, it is likely that an intellectual breakthrough regarding the building of digital models of inverse vulcanised polymers would be necessary before molecular dynamics could be applied with a useful degree of accuracy.

Taking computational chemistry a step further, recent breakthroughs in the field of AI-based protein structure prediction, in particular the development of AlphaFold and its latest iteration, AlphaFold 3, could be a game changing tool for polymer-based material innovations. This cutting-edge model is capable of accurately predicting the joint structure of biomolecular complexes, including proteins, nucleic acids and small molecules. By significantly surpassing traditional docking methods and physics-based approaches, AF3 enables highly precise modelling of protein–ligand, protein–nucleic acid, and antibody–antigen interactions. The ability to generate high-accuracy predictions across diverse molecular types marks a transformative step in computational chemistry and molecular design.[67] While AlphaFold primarily focuses on biological macromolecules, its underlying deep-learning framework could be generalised to synthetic polymer chemistry. This advancement would bridge the gap between computational chemistry and experimental polymer science, leading to breakthroughs in fields ranging from sustainable materials to high-performance composites. By harnessing AI-driven molecular prediction, polymers could be designed with unprecedented precision, revolutionising the development of novel materials with tailored functionalities. Beyond structure prediction, AI-driven approaches could accelerate the discovery and optimisation of advanced polymeric materials by training on vast polymer libraries to rapidly screen and identify materials with the desired chemical and physical properties.[68] In the relatively young field of inverse vulcanised polymers, however, this would require a massive extraction of materials data from the literature – another possible application for AI – since the data availability for these materials is quite limited.

Transferring such approaches to the synthetic world of polymer chemistry also comes with major challenges. With the limited amount of building blocks in the natural world, specifically 20 natural amino acids, the number of possible combinations and interactions is much lower compared to the amount of synthetic building blocks available to date. Additionally, proteins and enzymes are confined molecules with specific purposes and limited interactions between each other. In a polymeric material which is an assembly of macromolecules, they strongly interact with each other physically and chemically, determining their macroscopic properties. The combined effects of a massive monomer library and macromolecular interactions make it very difficult to predict their properties.

In terms of sustainability, computational chemistry has many cited benefits that would be applicable to inverse vulcanisation. Computational chemistry is often used to accelerate experimental chemistry by identifying the most promising avenues through computational predictions followed by a small subset of experimental validation, requiring fewer experimental resources Further benefits could arise from the prediction of bio-based substitutes that produce precisely tuned chemical and physical properties. A more promising and far-reaching application of AI in polymer science is the development of biodegradable and chemically recyclable polymers. This area would narrow down the available building blocks and therefore facilitate calculations and predictions. Furthermore, AI-driven models could help predict the biodegradability of polymers by identifying molecular structures that are more susceptible to enzymatic breakdown. In reverse, AI-assisted protein and enzyme design enables the development of completely new biomolecules that can help to break down polymers that are to-date not biodegradable. Specifically high sulfur containing polymers that already could be susceptible to biological attack are a low hanging fruit for such approaches. It is important to highlight that the energy and water demands of AI are ever increasing. Calculations should be conducted with purpose, with computational tools designed for efficiency in the same way that we would expect from synthetic optimisations, so as to not replace one problem with another.

Even though computational methods can help to make better reaction choices and improve the overall reaction outcome, it is not enough to develop more sustainable materials including less toxic and renewable reactants and products as well as their recyclability on the lab-scale and beyond. A general guideline for the sustainable development of chemicals and materials are the "12 Principles of Green Chemistry", which we will introduce in the context of inverse vulcanisation.

Synthesis of inverse vulcanised materials in the context of circular economy and the 12 principles of green chemistry

Since the Green Deal was launched in 2020, the term circular economy has gained traction by advocating for a production and consumption model which strives to extend the lifetime of products by using the 10 R principles.[69] The 10 R principles (Refuse, Reduce, Resell or Reuse, Repair, Refurbish, Remanufacture, Repurpose (Rethink), Recycle, Recover and Remine) transform the common linear model of "take-make-consume and dispose" into a circular model which considers waste as a resource, drives to eliminate or reduce waste as much as possible, considers every step of the lifecycle of a product to enable multiple use cases of products, and decouples economic growth from product consumption.[69,70]

Within polymer science, additives in plastics or difficult separation of complex composite- and multi materials, can impose limits on circularity, especially in terms of recycling.[71] Some solutions include the reduction of complexity or the change towards chemicals that are "optimal adapted – better – safer" as in mono-materials.[71] To approach these solutions, green chemistry design principles are essential.

While green chemistry is originally designed to integrate sustainability into linear process models, the literature states that with its twelve principles, their revaluation and the focus on the environmental pillar, green chemistry can contribute to circular economy.[70,72] Defined as "the design of chemical products and processes that reduce or eliminate the generation of hazardous substances"[72] it focuses on the technical part of chemical and material development. Therefore, it plays a crucial part not only in a circular economy but also in sustainable chemistry, where the development of safer chemicals in all life cycle stages is evaluated economically and socially.[72] Green chemistry principles are a guideline for a wide range of practices aimed at making chemical processes more sustainable, energy-efficient, and environmentally friendly. This guideline is summarised in 12 key principles, first outlined by Paul Anastas and John Warner in their 1998 book "Green Chemistry: Theory and Practice".[73] This should be a concept for all research and development of new chemicals and materials to decrease the environmental impact of the modern chemical industry. In the following section we briefly describe the 12 principles and how the synthesis of inverse vulcanised materials is in alignment with these principles to underline their potential as more sustainable alternatives to state-of-the-art materials:

(1) Prevention: it is better to prevent waste than to treat or clean up waste after it has been created.

Since sulfur is a waste product from the oil industry, inverse vulcanisation turns a potential environmental burden into an economic and ecological opportunity. By addressing waste generation at its source, it is in alignment with the principle that prevention is better than clean-up, minimising environmental risks while creating more environmentally friendly materials that could contribute to a circular economy. Furthermore, inverse vulcanisation can be conducted as a solvent-free copolymerisation, which reduces the formation of chemical waste during production.

(2) Atom economy: synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

Inverse vulcanisation can be driven to an atom economy of almost 100% making it a highly promising synthetic method from a sustainability standpoint. This can guarantee a near complete upcycling of sulfur waste into useful products, besides minimal by-products which can be suppressed by adjusting reactants and reaction conditions. The requirement for high atom economy reinforces the aim to reduce potential H_2S by-products by the control of reaction conditions, in addition to safety concerns.

(3) Less hazardous chemical syntheses: wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Even though inverse vulcanised materials are mostly bench stable, they may potentially release small molecule sulfur compounds, which could indicate a negative environmental impact. To-date they are not known to be toxic, but for a full understanding of the human and environmental toxicity, long-term studies must be conducted.

(4) Designing safer chemicals: chemical products should be designed to serve their desired function while minimising their toxicity.

Preliminary studies with limonene-based polymers showed no leaching of toxic compounds into water, proven by a cell viability test with liver cells. Similar to the aforementioned bullet point, a full environmental study should be conducted to understand their impact, especially due to the variety of comonomers which might show different degradation and leaching behaviours.[74] It is worth noting that some inverse vulcanised polymers are indeed flammable and can release toxic gases. However, in certain composites, these polymers can provide flame retarding properties.[75]

(5) Safer solvents and auxiliaries: the use of auxiliary substances (*e.g.*, solvents, separation agents, *etc.*) should be made unnecessary wherever possible and, when used, innocuous.

In most inverse vulcanisation reactions solvents are not necessary. However, due to the strong exothermicity of the reaction, solvents may offer a chance for heat dissipation during large-scale synthesis, benefiting safety. Potential high boiling solvents need to be non-toxic and recyclable to be in alignment with the 12 principles.

(6) Design for energy efficiency: energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.

Inverse vulcanisation is a highly exothermic reaction, and therefore energy input for heating is only required to initiate the reaction. Subsequently, the process heat could be used for initial heating of the reaction in a flow system or for the distillation of solvents on the industrial scale. Additionally, reactions can be conducted more energy efficiently at lower temperatures when using catalysts like metals or amines.

(7) Use of renewable feedstocks: a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

The use of unsaturated organic compounds such as plant oils, limonene, *etc.* has been shown and proves the accessibility of renewable resources for inverse vulcanisation. An important aspect of renewable feedstock – especially with plant oils – is the competition with the food chain, and therefore products such as used cooking oils,[76–78] peanut shells[79] and cellulose[80,81] hold promise for sustainable production. A detailed review on the applications of used cooking oil can be found elsewhere.[82]

(8) Reduce derivatives: unnecessary derivatisation (use of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

The polymer properties can be tuned with the choice of comonomer. More sensitive functional groups such as halogenides,[83] additional double bonds[53] or epoxides,[49,84] should be introduced by orthogonal post-polymerisation modification methods to avoid side reactions.

(9) Catalysis: catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Inverse vulcanisation can be catalysed by organic and inorganic materials such as amines and metal oxides. This can reduce the temperature needed for the reaction and therefore increase the safety of potential scale-up processes. Additionally, inverse vulcanisation has been shown to be initiated by ultraviolet (UV) irradiation or mechanochemical processes. This brings the reaction temperature down to ambient conditions and reduces the evolution of toxic by-products such as H_2S.

(10) Design for degradation: chemical products should be designed so that at the end of their lifetime break down into innocuous degradation products and do not persist in the environment.

Due to the inherent dynamic behaviour of the S–S bonds in polysulfide containing materials, they can be recycled mechanically and chemically. Although these materials are highly resistant to acids, bases and a range of solvents, it has been shown that the S–S bonds can be degraded.[56,85] Further research has to be devoted to the full recovery of the organic components as well as potential by-products, weathering behaviour, biodegradation and their toxicity.[86,87]

(11) Real-time analysis for pollution prevention: analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

The main analytical tool for the characterisation of sulfur compounds is Raman spectroscopy. Its incorporation as an online monitoring method can be used to identify certain sulfur species in the polymer as well as sulfur by-products. Other methods such as infrared (IR) spectroscopy can be implemented to follow the consumption of double bonds and therefore drive the reaction to full conversion.

(12) Inherently safer chemistry for accident prevention: substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions, and fires.

Auto acceleration of inverse vulcanisation poses a safety issue, mostly due to potential explosion of the reaction setup and the evolution of toxic H_2S. This is the major hurdle for the industrialisation of inverse vulcanised materials, since process safety is of utmost importance. The use of catalysts, photochemistry, mechanochemistry and solvents/additives may alleviate this issue; however, more research is required in order to apply these concepts on a larger scale and to gain a better understanding of the causes of H_2S being produced as a by-product and how to stop it.

These principles demonstrate the inherent simplicity of the inverse vulcanisation process and are a good example of how to put these principles in practice. Simultaneously it highlights the crucial role green chemistry plays, not only in a circular economy, but also in sustainable chemistry.[72] As a quantitative measure of the environmental and economic impact of products and processes, life cycle assessment (LCA) proved to be an efficient tool which enables the identification of potential environmentally friendly technologies including the principles of green chemistry.[72,88,89] This will be further discussed in later stages of this article.

To demonstrate the potential of inverse vulcanisation and its future viability, the process has to be transferred to the industrial scale. Here, the 12 principles can help to translate synthetic procedures from lab-scale to the industrial level, *i.e.* by reducing waste or simplifying the used chemicals. However, scale-up will reveal several challenges that must be addressed in order to commercialise high sulfur polymers for a broad range of applications. In the following section we discuss challenges on the laboratory and industrial levels and possible solutions.

From the lab to industrial scale-up

Although small scale (tens of grams) syntheses are acceptable for specialty applications, in order to truly address the excess sulfur problem, inverse vulcanisation must achieve mainstream use wherein the polymers would be applied on the scale of tonnes. The reaction must be scaled up from the grams scale to the kilograms scale, and further, to the tonnes scale. With this in mind, the reaction must be adapted to industrial reactor designs and processing formats, which carry their own considerations not encountered on the lab-scale. In addition, consistent product quality is of utmost importance for real-world applications.

The road so far

The majority of studies on inverse polymerisation mention the need for efficient up-scaling in some way, but to date, only very few publications have explicitly addressed it. In particular, Griebel and Li *et al.* were the first to report kilogram scale inverse vulcanisation.[90] By choosing a reaction temperature as low as $T = 130$ °C, the authors were able to produce a poly(sulfur-*random*-(1,2-diisopropenylbenzene)) (poly-S-*r*-DIB) copolymer in the 1 kg scale from S_8 (90 wt%) and DIB (10 wt%) using 1,2-dichlorobenzene (50 wt% with regard to the total monomers) as a solvent. Other approaches by Chalker *et al.* used sodium chloride as the porogen and a heat sink to control the exotherm on the kilogram scale.[91] Due to its electrochemical properties, the copolymer was suggested for application as an active cathode material in Li–S batteries. Meanwhile Clean Earth Technologies synthesised 500 kg of a canola oil inverse vulcanised polymer in bulk polymerisation, but it is worth remembering that canola oil is a lower reactivity comonomer and is less prone to exothermic runaway reaction complications that other more reactive comonomers when scaled up.[92]

Challenges and possible solutions

The most prominent and prohibitive obstacle that must be overcome when dealing with the scale-up of the inverse vulcanisation reaction is its inherent exothermicity and the ensuing auto-acceleration that can occur, also known as the Trommsdorff-Norrish effect.[93] This effect becomes relevant when exothermic polymerisation emits heat during its propagation phase, which increases the rate of initiation and thus also of propagation, hereby liberating yet more heat. This cycle of increasing heat liberation can cause a runaway reaction worsened by the fact that with more propagation, the molecular weight (and degree of cross-linking if applicable) increases, which increases the viscosity of the reaction and decreases the efficiency of stirring. With poor stirring comes less effective dumping of heat out of the reaction and into the surroundings, leading to heat build-up and temperature increases within the reaction mixture, accelerating propagation, which compounds the problem. Consequently, inverse vulcanisation reactions will often undergo an auto-acceleration event when they are removed from stirring or agitation and are allowed to settle.


Fig. 4 Photograph of an inverse vulcanisation reaction after the effects of auto-acceleration. The reaction was carried out by heating 50 g or dicyclopentadiene and 50 g of sulfur at 140 °C in a 500 ml flask. Before the point where auto-acceleration occurred, the reaction mixture consisted of ~100 ml of smooth liquid being stirred and heated. After the heat generated by the exothermic reaction became too great to be lost to the surroundings, the mixture bubbled up rapidly – changing from a calm liquid to the form seen in approximately 2 seconds.

On the lab-scale, auto-acceleration looks like a sudden "bubbling up" of the reaction, accompanied by a rapid darkening of the reaction mixture, increases in viscosity, and sometimes the emission of fumes (Fig. 4). With proper control measures, a lab-scale auto-acceleration is a minimal hazard that results in a polymer with poor quality that polymerised so rapidly that it is highly inhomogeneous and not usable for its respective application. The results will likely be wastage of the tens of grams of polymer and discarding the reaction glassware. On an industrial scale, an auto-acceleration would be a catastrophic event. The severity of auto-acceleration increases with increased reaction scale, as more monomer present means there is more heat that can be liberated. This could result in a dangerous thermal expansion or explosion that poses a health hazard to nearby personnel. An industrial reactor would potentially be damaged by such an auto-acceleration event, and kilograms to tonnes of polymer would be wasted. Additionally, auto-accelerations in inverse vulcanisation tend to cause increased hydrogen sulfide production from the reaction, which is easily controlled in the lab-scale, but could be overwhelming on an industrial scale, leading to release of harmful hydrogen sulfide emissions into the surroundings and the atmosphere.

Avoiding auto-accelerations on the industrial scale is challenging, because increasing the scale of the reaction rapidly increases the likelihood of an auto-acceleration event: there is more reactive material liberating heat and the reaction volume is increased, making heat dissipation into the surroundings much more challenging. Already at the hundreds of grams scale, solvent-less inverse vulcanisations become highly prone to auto-acceleration.

One route to overcoming this auto-acceleration obstacle is using a lower reaction temperature, although this increases the reaction time and thereby makes the overall process less economical. Additionally, with a longer reaction time, there is a greater probability that some unforeseen issue, such as a power cut, could cause the reaction to fail. While this is a minor issue on the lab-scale, this could present a serious drawback for industrial scale synthesis as there is the potential to waste many kilograms or even tonnes of material along with any energy and time that was invested in the synthesis. Furthermore, simply lowering the reaction temperature does not address the root cause of the Trommsdorff-Norrish effect, and thus solely lowering the temperature may be insufficient to prevent auto-acceleration, especially since the scale inherently increases the risk of auto-acceleration as mentioned above.

A low reactivity comonomer can be used, which means choosing a comonomer wherein the alkene bonds are of high activation energy, choosing a comonomer with a lower density of reactive double bonds, or choosing a comonomer with only one reactive double bond. The choice of comonomer, however, will often be constrained by the desired application, so it is not a particularly flexible variable. Additionally, using a lower density of double bonds means that more sulfur atoms must be stabilised across fewer double bonds, often resulting in a polymer that is more prone to sulfur bloom and therefore has a shorter lifespan. This can be explained by monomers with high double bond density, such as DCPD, leading to lower sulfur ranks that are harder to degrade and therefore show higher ageing resistance.[55,94] Dodd *et al.* used Raman spectroscopy to demonstrate that polymers with higher sulfur content also exhibit higher amounts of unreacted sulfur,[64] which could be correlated with increased ageing effects.[95] However, this field is subject to further research into structure–property relations.

Catalytic activation of inverse vulcanisation has been shown to reduce the likelihood of auto-accelerations in some cases, as it permits a lower reaction temperature to achieve a similar rate to a higher temperature inverse vulcanisation.[34,96]

Process design also offers options. In particular, using a larger number of smaller reaction vessels could facilitate heat management and thus avoid undesired events induced by the Trommsdorff-Norrish effect. In-depth considerations of synthesis plant design are required to ensure realisation. Alternatively, running the synthesis in flow could be a solution. If the reaction mixture itself is constantly moving and the pipes for the flow reactor are kept to sufficiently small diameters that ensure efficient heat escape from the reaction mixture, heat accumulation in the reaction mixture can be avoided. Since to date, only batch reactions of inverse vulcanisation have been performed, more future research on flow chemistry in relation to inverse vulcanisation is suggested, with the goal of scale-up in mind. A recent study of Chalker *et al.* utilised flow chemistry for the photochemical synthesis of poly(trisulfides) from monomers derived from waste sulfur.[66] These insights can help to develop approaches for inverse vulcanisation in flow with high efficiency and minimal energy input. Herein, viscosity changes in the reaction mixture occurring as the reaction progresses need to be considered, as these potentially lead to the clogging of reactor pipes. Consequently, thorough studies on the change in reaction viscosity with time will be needed. The exact viscosity – reaction time relationship being unique for every possible combination of reaction conditions and comonomer choices calls for a case-by-case study for every reaction to be introduced into flow chemistry. Another potential solution could be to run inverse vulcanisation in a solvent in a flow reactor. What would then have to be considered is the potential of precipitated polymer clogging the reactor pipes. As inverse vulcanisation proceeds, the polymers show higher molecular weight and degree of cross-linking, making them more insoluble. Thus, as the reaction proceeds for a longer time, there is a higher chance of polymers precipitating from the solvent, causing complications in the reactor. Flow reactors are preferred in industry as they can continuously produce the product, and are more economical in terms of heating because after the initial energy-intensive heating up, the temperature only needs to be maintained. This procedure causes much lower energy costs than heating the reaction, maintaining temperature, and then cooling the reaction, as would be the case for a batch reactor. Regardless, there is significant research work to be done in the future before inverse vulcanisation can be performed in flow reactors at the industrial scale, and there will likely be many chemical engineering aspects to consider.

Using a solvent in the reaction is one of the most promising ways to decrease the likelihood of an auto-acceleration, as it dilutes the reactants and slows down the reaction and its heat generation over a larger volume. The solvent acts as a heat sink, so the heat emitted does not just increase the temperature of the reactants but also increases the temperature of the solvent, which can then dump the heat into the surroundings.

However, adding a solvent brings some complications. First of all, the solvent must be able to solvate both the comonomer and the sulfur. There are almost no solvents that can solvate solid sulfur to a degree that is useful in a reaction. Since inverse vulcanisation cannot occur without activation when sulfur is in the solid state, the miscibility of molten sulfur with hot solvents should be under scrutiny. This does limit suitable solvents to those with high boiling points, exceeding at least 120 °C (the melting point of sulfur). One publication by Ren *et al.* demonstrated the solubility of elemental sulfur with temperature in different relevant solvents.[97] They found that the solubility of elemental sulfur in all tested solvents increased over the temperature range of 20 °C to 80 °C. While this temperature range is substantially lower than the range of interest for inverse vulcanisation, it does show a promising trend that is supported by the finding that molten elemental sulfur was miscible with refluxing p-xylene (boiling point of 139 °C), from which a successful inverse vulcanisation was carried out.[44] Of the tested solvents Ren *et al.* found that purely aliphatic solvents were less effective at solvating sulfur than aromatic solvents. Of the aromatic solvents, increasing the substitution level decreased the effectiveness of the solvent.[97]

Adding a solvent also introduces concerns about the economics and sustainability, as it is another substance that must be factored into the costings. Although recycling of the solvent may enable a dramatic cost reduction, the solvent expands the quantity of material to be heated and thus the energy expenditure. This means that minimising the solvent quantity becomes a factor to consider with the trade-off that a higher reactant concentration increases the risk of auto-acceleration. Solvent recovery from polymeric materials, especially thermosets, is difficult; low percentage recovery from solvent-based reactions can have significant environmental impacts as evaluated though life cycle assessments.

Moreover, the solvent quantity will also impact the concentrations of the reaction solution, which will likely influence how much polymer can remain solvated before precipitation occurs. If not planned for, precipitation could be an undesirable complication. Any precipitated polymer could be unsuitable for solution processing, which could be a requirement for manufacture and applications: in this scenario, precipitated polymers would be uneconomically wasted. Furthermore, a precipitated polymer will still be capable of polymerising further, and since it is no longer solvated, there is the risk of auto-acceleration. Solvated inverse vulcanisations will likely require reaction windows to be quantified by research, for the minimum time a reaction can be run to obtain a suitable product, and the maximum time a reaction can be run before a precipitate is observed. These reaction windows will be governed primarily by the composition of the reaction mixture, reaction scale, and reactor design.

In some cases, it is possible to reduce the likelihood of an auto-acceleration event by performing a two-step reaction. In principle, this can be applied to any inverse vulcanisation, but it is most effective with a comonomer that has two reactive carbon–carbon double bonds, each in a different chemical environment. Such is the case for dicyclopentadiene, wherein the norbornene double bond is strained and therefore reacts at a lower temperature than the cyclopentene double bond. This allows the norbornene double bond to be consumed with a lower temperature reaction to create a linear polymer, after which the temperature is ramped up to induce the reaction of the cyclopentene double bond. This approach minimises the number of double bonds reacting at a given time, thus reducing the chance of an auto-acceleration.[98]

Another obstacle to scale-up is the production of the hydrogen sulfide by-product. Some inverse vulcanisations generate this toxic by-product, which reduces yield and atom economy whilst producing toxic fumes that can be corrosive to the reaction apparatus and cannot be allowed to reach the atmosphere. Sulfur dioxide is another gaseous by-product that could form when the reaction mixture auto accelerates and reaches temperatures above 210 °C.[99,100] Sulfur dioxide is also corrosive and toxic, though its formation can be suppressed effectively by using oxygen-free reaction conditions. Hydrogen sulfide formation is more challenging to suppress, as it can form from water in the reaction system or directly from the reaction of sulfur with the comonomer. It is hypothesised based on hydrogen acidity, though not proven, that hydrogen abstraction by thiyl radicals from the comonomer is the primary source of hydrogen sulfide emissions from inverse vulcanisation reactions. Hydrogen can be abstracted from the alpha-allyl position, but other relatively acidic hydrogens can be candidates as well. This can be suppressed by maintaining a low reaction temperature, as it seems that the energy barrier for this hydrogen abstraction is relatively high and needs significant thermal energy to surmount. Of course, using a comonomer with no acidic hydrogens can lead to no hydrogen abstraction, and theoretically, no hydrogen sulfide emissions, but this is constrained by the application that the polymer is intended for, and the desired structure of the inverse vulcanised polymer itself. Auto-accelerations are also associated with production of larger volumes of hydrogen sulfide, but this is secondary for preventing auto-acceleration itself.

It would be necessary to quantify any gas emissions in a scaled-up IV process as the outgas would need treatment to meet emission regulations. On the lab-scale, this can be done by bubbling the outgas through aqueous sodium hydroxide, which deprotonates the hydrogen sulfide and forms NaSH, which dissolves in water and is trapped. On an industrial scale, this would be impractical and expensive, as additional regulations would need to be accounted for in having large quantities of highly basic solutions. These solutions would also be depleted and require replenishment, which is an additional cost. Some form of fixed bed adsorbent, like SULFATREAT granular iron oxide, would be more preferable for the reaction outgas to pass through, purifying it of hydrogen sulfide. Alternatively, and this would require notable technical consideration, if the inverse vulcanisation synthesis plant were to be constructed near an oil refinery, then it is feasible that the reaction outgas could be directed into the Claus process, converting the hydrogen sulfide back into elemental sulfur. Oil refineries have the industrial reactors to perform the Claus process, as it is the subsequent stage to hydrodesulfurisation, with these being the two reactions that are responsible for producing the excess elemental sulfur upon which inverse vulcanisation is founded. In fact, a return of sulfur from outgassing H_2S into the educt material stream would be desirable in terms of economy, sustainability, and circularity.

Scale-up aspects regarding alternative synthetic routes

Optimising modern synthetic approaches may enable overcoming the hurdles outlined above. For instance, Yan *et al.* suggested mechanochemical synthesis as a solvent-free and comparably fast method for the production of inverse vulcanised polymers.[37] Since heating is not required during *e.g.* ball milling, auto-acceleration was found to be negligible on the lab-scale. Upscaling of mechanochemical approaches is therefore worth investigating in the future. Notably, Marshall *et al.* recently demonstrated that melt processing and moulding of sulfur copolymers made from norbornadiene dimers is a feasible approach to produce plastic lenses for long-wave infrared thermal imaging, which has been proven to react under mild conditions in a ball mill.[38,101] Furthermore, using light of a specific wavelength (either 380 nm or 435 nm, 10 W), Jia *et al.* were able to realise photoinduced inverse vulcanisation at ambient temperatures that makes long curing times redundant and does not generate H_2S that needs to be captured from waste gas.[36] In terms of economic viability, the low reaction temperatures (18–20 °C) not only decrease the energy demand but also enable the use of comparably cheap gases such as acetylene, ethylene, propylene, and vinyl chloride as carbonaceous crosslinkers. Poly(S-DIB) synthesised by means of a photoinduced IV process exhibited high sorbent capacities for mercury uptake.

When such innovative alternative syntheses are considered for full-scale technical realisation, it is of particular importance to keep in mind that the actual applications may govern the production process. Mechanochemical synthesis is expected to be highly attractive in the context of bulk products, due to low risk of auto-acceleration and H_2S evolution, which would facilitate the conversion of large amounts of educts. However, it is worth mentioning that recent studies suggested a critical impact of the reactor material that is used during mechanochemical inverse vulcanisation.[39] This has to be taken into account when designing a large-scale reactor system. In this context, the exploitation of synergies with existing interdisciplinary research networks beyond the “classical” polymerisation community could be a promising way to accelerate a technical transfer. For instance, the research network COST (European Cooperation in Science and Technology)[102] initiated the working group Mechanochemistry for Sustainable Industry, which aims at realising the sustainable production of compounds and materials of industrial interest on a medium- and large-scale (**https://www.mechsustind.eu**).

In contrast, photo-induced inverse vulcanisation is expected to play a role in the context of more specialised applications, particularly given that the light-induced reaction has been reported to take up to 72 hours.[103] Photo-induced surface coating with sulfur polymer thin films could be a particularly promising field of application, since the excellent heavy metal affinity will typically call for high surface areas of the sorbent.[104,105] A combination with other emerging technologies, such as 3D-printed substrates or mixing elements that provide additional geometric surface area, can ensure an optimal exploitation of the high sulfur polymer sorbent and maximise the contact between the solid and the fluid phase.

Beyond mechano- and photochemistry, catalytic inverse vulcanisation processes have also been suggested by means of experimental work in the lab-scale and computational efforts, *i.e.* DFT. One of the first catalysts to be suggested for inverse vulcanisation was diethyldithiocarbamate.[34,106] In addition to highly relevant aspects like increased yield and improved material properties, such catalytic routes may also solve issues that impede industrial up-scaling such as reduction of the reaction temperature and H_2S evolution. It was shown that reaction temperatures can be reduced to 100 °C for catalysts like tetramine, thiazole, thiophosphate, guanidine, mercaptobenzothiazole, thiourea, xanthate, and sulfenamides,[107] which also resulted in patents for amine-based catalysts.[96] Additionally, Mousavi *et al.* reported the copolymerisation of the bio-based cross-linker oleic acid with sulfur while exploiting titanium oxide (TiO_2) as a catalyst, which yielded high sulfur polymers with improved mechanical stability compared to non-catalysed synthesis.[108] Although catalyst-borne impurities may impede the use of such copolymers in optical applications, they are expected to be beneficial whenever high mechanical strength is required. For instance, Diniz *et al.* used 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TVTSi) to synthesise sulfur polymers (poly(S-TVTSi) that are highly water repellent, with purposefully incorporated inorganic SiO_2 and TiO_2 improving the hydrophobicity of the polymer.[109] These findings underscore the need for tailored preparation routes in order to obtain highly functional and specialised polymer products.

Claimed industrial applications of inverse vulcanised materials include their use as alternatives to Portland cement (**https://www.otbmaterials.com/**), bitumen asphalt replacements (**https://uberbinder.com/**), and for heavy metal capture (**https://www.thiotech.co.uk/**). Herein, continuous production of the material can be achieved by compounding extruders, producing pellets. Compared to conventional cement, the manufacturing of this material is claimed to produce up to 95% less CO_2, with higher strength and lower water permeability.

Ultimately, the intended application of the copolymer and its desired properties strongly govern both the synthesis route and the full-scale technical process. For example, in applications such as coating components to produce mercury absorbers, a discontinuous production process may be sufficient. However, when copolymer production is required at the tonne scale and the product will undergo further processing, a continuous production process is generally more desirable. As underscored in this section, the efficient integration of IV processes into established plants and production sites can be a vital aspect as well, particularly under consideration of transportation, infrastructure, exhaust after-treatment, circularity, and heat management.

System sustainability

From a sustainability point of view, there are several factors to be considered in any scaled-up production process as sustainability has inherent environmental, economic and social aspects. The physical flows of reagents and energy flows, the production systems and operational requirements and the consequential impacts on the ecosphere and associated environmental impacts are significant.[110] Social impacts, depending on the elementary flows from extraction of raw materials and production systems, as well as material toxicity, can be asymmetrically felt across different populations. The economic considerations discussed in this section strongly interact with both social and environmental factors.

For inverse vulcanisation, physical flows can be defined as the resources, materials, semi-products and products (inputs) as well as emissions, waste and products (outputs).[110] In the case of inverse vulcanisation, energy flows are differentiated from physical flows, *e.g.* when the heat of the exothermic reaction is recovered for energy production or to heat virgin material input. Any electricity purchased for the scaled-up production as well as the heat recovery can be defined as energy flow.[110] To-date inverse vulcanisation can be carried out with fossil-based and renewable monomers. While sulfur and its environmental impact is already discussed and it was argued why sulfur from stock piled should be used, it is important to bear in mind that sulfur also originates from fossil fuel production. Although bio-based materials, such as vegetable oils or limonene, can be used as comonomers, it is still important to mention that their production, due to extraction and purification steps and the cultivation of the bio-material, will have an environmental impact. In this regard, the greenhouse gas (GHG) emissions of common fossil-based monomers such as styrene or dicyclopentadiene (DCPD) are competitive or even lower compared to those for bio-based monomers (Table 2). This results from very refined and efficient production processes of fossil-based materials. Even though the carbon footprint might seem bad on first look, there is more to sustainability than GHG emissions. Most industrial and government policy focuses on CO_2 emission since it is easy to put numbers to it, but all impact categories are important.

Table 2 Carbon footprints of various monomers used for inverse vulcanisation

Monomer	CO_2 equivalents [kg CO_2 per kg]	Ref.
Sulfur	1.53	111
Dicyclopentadiene	1.54	112
Styrene	3.20	113
Limonene	28.2	114
Vegetable oils	0.36–15.32	115
Used cooking oil	0.167	116

A reduction in carbon footprint that leads to major harm to our land, water or health is not inherently sustainable. Often trade-offs between different scenarios occur, meaning that the prioritisation of environmental impacts must be carried out. Sustainability discussions are complex and nuanced, making it ever more important to quantify the potential consequences of different components in identifying and optimising the sustainability of processes, in this case meaning that even if dicyclopentadiene has lower GHG emissions its resource use for example could be high given that fossil fuel is a limited resource. Also, a trade-off for bio-based monomers regarding land-use could occur due to the potential competition with food sources. Here, used vegetable oil stands out with low GHG emissions and no competition with food sources. It could stand in competition with the production of biodiesel, but in contrast to this it does not need pre-treatment or transesterification, which cause human health issues due to methanol usage and high energy input during transesterification.[117]

Its real environmental impact depends on the specific scale-up processes and it is advised to conduct environmental assessments, such as LCA, when implementation will take place. The complexity of the discussion of bio-based *vs.* fossil based is debated extensively in the literature. First of all, the terminology of bio-based needs to be defined. Bio-based means that the material is made partially or fully out of biomass, while saying nothing regarding its recycling properties or degradability in the environment. Bio-degradable means that these materials can be broken down by the work of natural microorganisms at different temperatures. While often used as synonyms, these types are definitely not the same showing why the end-of-life of bio-based materials still needs to be discussed.[118] The literature indicates that many bio-based materials produce less GHG emissions compared to fossil-based alternatives, though results vary significantly between individual materials. Energy use impacts also tend to be lower, while eutrophication is often higher for bio-based options. Other impact categories, such as acidification, ozone depletion, and photochemical ozone formation, are reported to show similar results. However, these are general findings, and a meaningful comparison requires evaluating the specific bio-based materials against their fossil-based counterpart.[119]

The issue is that the carbon footprint of a potentially interesting cross-linker is often not accessible at the laboratory scale. Improved data availability and greater transparency from suppliers are necessary to better assess the sustainability of a chemical to plan the synthesis of new materials more efficiently and sustainably. The next step in this discussion is the evaluation of the entire production process to generate the most efficient, environmentally friendly process possible. A major guideline for this is the twelve principles of green chemistry with its selection of input materials attached to the concept of eco-design and the avoidance of fossil-based chemicals to improve the production processes. Critically, chemical reactions and productions are electricity and heat intensive, which leads to high GHG emissions if the electricity and heating or cooling cannot be generated through renewable energy or *i.e.* heat exchangers. This depends strongly on the infrastructure of the country where production is located, yet scenarios where chemical plants are supported by 100% renewable energies are very limited.[120] The highly exothermic reaction of elemental sulfur with double bonds holds great potential for heat recovery, hereby reducing the energy flow inputs, ultimately reducing their environmental impact. After all, this offers economic advantages, reducing costs otherwise spent for heating, electricity and infrastructure.

By using water to cool chemical reactor systems, the impact on the environment caused by water usage needs to be looked at closely. To date inverse vulcanisation processes only depend on cooling water, while modern reactors mostly use closed cooling circles to minimize water loss, and therefore the impact on water use is neglectable. Yet, depending on the process structure, solvent waste, waste water, and pollution through highly toxic H_2S occur during the production. The regulation and proper treatment of industrial waste streams are essential to prevent environmental and social harm. While modern chemical plants often adhere to strict safety standards, accidents and spills can still occur, especially in less developed countries where regulations may be less strict. Among these waste streams, solvents play a major role. Due to their chemical properties, solvents are used in large quantities across numerous chemical reactions and processes. However, their widespread use is linked to several environmental and health concerns, including increased toxicological risks to humans and freshwater ecosystems, as well as air, land, and water pollution, ozone depletion, and the emission of particulate matter. If wastewater containing solvents is not properly treated, it can lead to eutrophication, excessive water consumption, and ecotoxicity in freshwater systems. Moreover, managing solvent waste often involves energy-intensive processes, resulting in additional GHG emissions aimed at preventing environmental contamination.[121]

A further factor with a high impact on the environment but often neglected is transportation. It is well known that industrial transportation *via* airplanes, lorries, trains or transporters emits GHG emissions. This increases with travelled distance, and the type and amount of transported good. Therefore, the location of the production plant is important, not only for environmental but also economic reasons. This factor was mentioned for the production of bio-based materials already, but another example would be the transportation of the elemental sulfur towards the production plants. The logistic infrastructure by sulfur piles is mainly based on trains, so to include the sulfur transportation, new logistics are needed and therefore costly. Additionally, transporting chemicals often means a lot of bureaucracy and safety measures to prevent fine dust or other leakages, which are important for the protection of the environment but are also cost and time intensive. To avoid this, a crucial step towards a more environmentally friendly production of inverse vulcanised materials is the integration into existing plants especially in locations where sulfur is produced in the first place. Advantages would also include the fast and easy recovery of H_2S that might be produced during the reaction by the Claus process which is mostly used to produce sulfur during fossil fuel desulfurisation.

While evaluating potential risks in product development is important, the real environmental impact can only be determined when a specific process is mapped out. The more data on the individual steps, input and outputs are generated, the more transparently and specifically the environmental impacts can be analysed and different approaches be compared. Scaling up the inverse vulcanisation process and assessing emerging technologies, a prospective LCA should be carried out, which is a helpful tool to record all inputs and outputs of the new technology. By considering a distant future instead of the current state and focusing on emerging technologies, such as inverse vulcanisation, a prospective LCA could represent the environmental impact of the emerging technology better as an LCA, yet the uncertainty regarding futuristic scenarios and missing data points must be kept in mind.[122] While most industrial and government policy focuses on GHG emission, all impact categories are important: a reduction in carbon footprint that creates major harm to our land, water or health is not inherently sustainable. Often a trade-off between different scenarios occurs, meaning that the prioritisation of environmental impacts must be carried out. The major challenge is that accurate quantification is only possible with the full disclosure of operational parameters and chemicals used. Assessing and comparing different synthetic methodologies is not possible without much more transparent publishing and data sharing.

In addition to the environmental and economic aspects of sustainability, the third pillar is social sustainability which is still an underexplored part of sustainability.[123] It addresses social and socio-economic dimensions, particularly the impacts of products and processes on various stakeholders such as workers, local communities, society, consumers, and value chain actors. It is crucial to guarantee the health and safety of workers operating chemical plants by properly controlling reaction conditions and implement safety measures in case of reaction run-away or leakage of toxic gases. While in Canadian crude oil extraction plants, and other developed countries laws against forced labour and child labour are enforced, this definitely does not account for all potential plant location sites such as those in third world countries. Considering the worst case of pollution through waste or H_2S the local communities and employees surrounding the plant may be severely affected.

On the other hand, chemical plants can also generate jobs and increase the engagement of the local community. Yet, the behaviour and public relations of companies employing inverse vulcanisation at their plants significantly shape the social impact of production. The most important impact for consumers is transparency regarding the used chemicals and the properties of the produced material, in particular with bio-based feedstocks, due to emerging regulations such as the EU's supply chain law. From a broader societal perspective, production processes must aim to be as environmentally friendly as possible, as their effects extend beyond local ecosystems to global issues like GHG emissions. Therefore, accurate, site-specific data are key for assessing social impacts more transparently. To comprehensively evaluate the societal implications across all life cycle stages of sulfur polymers, a Social Life Cycle Assessment (S-LCA) can be conducted. This would capture not only aspects of human health but also broader categories such as human rights, working conditions, and cultural heritage.[123]

Use phase: applications and ageing of inverse vulcanised materials

Promising applications of inverse vulcanisation. The concept of inverse vulcanised polymers has only been around since 2013, but materials containing sulfur are among the oldest man-made polymers with the invention of vulcanised rubbers by Goodyear[4] and polysulfide polymers by Lowig and Weidmann.[124] Since then a plethora of high sulfur containing polymers have been developed.[125,126] In the following section we highlight selected applications where inverse vulcanised polymers could be applied as an alternative to commercial materials and how they can improve the environmental impact of the respective class of materials.

The properties of elemental sulfur and high sulfur content materials lead to high potential for a broad range of applications.[127–132] From an economic standpoint, however, two types of applications have to be considered: bulk materials deplete sulfur stockpiles and simultaneously develop materials with beneficial properties, and high-tech applications on small scales to replace expensive and resource intensive state-of-the-art materials. High priced monomers are not considered a problem for the low-volume/high-end applications like Li–S batteries or optical applications – where the requirement for high performance will far outweigh the cost of the materials. Since sulfur is the major component of these materials, less monomer is needed, thus reducing the overall material cost. Furthermore, replacing low-volume specialty chemicals with inverse vulcanisation-based alternatives might not have a big impact on the consumption of stockpiled sulfur. However, it can have a big impact on their respective carbon footprint since their production often requires high energy input, next to the production of waste such as solvents and unwanted by-products. For bulk applications such as sulfur concrete, cement binders or heavy metal adsorbents, which would be a major consumer of sulfur stockpiles, there will also be a real requirement to keep the cost of the comonomer down. Most vinylic monomers and cross-linkers that can be applied in inverse vulcanisation, such as styrene/acrylates, are used commercially and therefore are readily available and cheap. Due to sophisticated and highly developed production processes, they have a comparably low carbon footprint (see Table 2), especially because many C=C double bond-containing chemicals such as dicyclopentadiene are by-products from oil refining processes.[133] This highlights again the importance of focused material development for individual applications. In the following section we briefly highlight some promising applications of inverse vulcanised materials and their potential environmental impact; detailed articles on individual applications can be found elsewhere.[13,127,132]

High refractive index materials

A major specialised application of inverse vulcanised polymers often highlighted in the literature is in high refractive index lenses for IR optics.[134,135] This arises from S–S bonds and C–S bonds (note that carbon and sulfur have the same Pauling electronegativity) exhibiting low infrared absorbances, as their stretching modes either do not, or very weakly, satisfy the selection rule for infrared spectroscopy, namely that infrared vibrational modes must cause a change in dipole moment.[136] In addition, sulfur is a highly polarisable atom, and a high proportion of polarisable atoms within a material's structure increases its refractive index.[135] Since inverse vulcanised polymers are comprised mostly of such bonds (S–S and C–S), they equally show high refractive indices and are therefore promising materials in applications for IR optics (Fig. 5). This renders inverse vulcanised polymers as potential next-generation materials for infrared optics, *i.e.* for application in thermal imaging devices. Compared to conventional materials, their high refractive index allows for thinner lenses that maintain the same optical power, reducing costs and weight.[135] These polymers are already much cheaper than the current industry standards, like chalcogenide glasses and crystalline semiconductors. Thinner lenses not only cut costs and weight but also help preserve the lens shape, which is crucial for maintaining optical precision over time. Chalcogenide glasses in contrast require rare, highly pure raw materials and energy-intensive processes, making them expensive. Inverse vulcanised polymers on the other hand are cost-effective, scalable, and often don't require purification, while still being mechanically robust, melt-processable, and highly transparent and refractive in the IR spectrum. Additionally, they offer the benefits of thermal healing and recyclability, providing a major advantage over traditional materials in terms of sustainability and reusability. Pyun *et al.* were the first to demonstrate the applicability of fully polymer-based lenses in thermal imaging that can be remoulded and show good thermomechanical properties that suppress reflow of the material.[137] They additionally provide insights into the characterisation of such materials.[101] Boyd *et al.* on the other hand reported the first inverse vulcanised organometallic hybrid materials as IR transparent lens with easy processability.[138] This further demonstrates the versatility of the potential of sulfur polymers for optical applications. The development of advanced manufacturing processes for inverse vulcanised materials, such as 3D-printing, can further expand applications as individualised products for IR optics.[139]

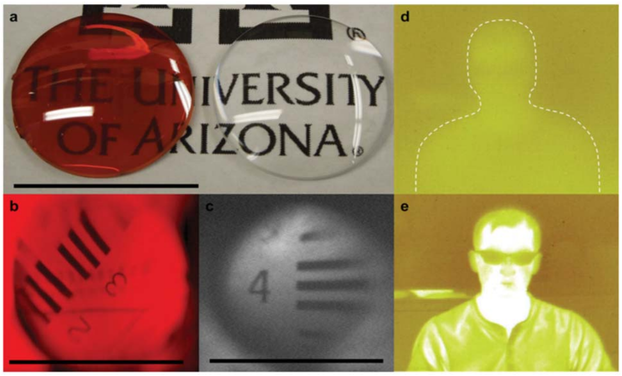


Fig. 5 (a) Digital image of lenses: (left) poly(S-*r*-DIB) copolymer (80 wt% S 8) and (right) glass, (b) digital image of a USAF target through copolymer lens in visible wavelengths and (c) image captured with a near-infrared camera of the USAF target illuminated with a 1550 nm laser (scale bars = 25.4 mm). (d) Thermal imaging of a human subject through a PMMA film (~1 mm) in the mid-IR (3–5 μm) regime (dotted white line highlights the area where the subject is sitting). (e) Thermal imaging of a human subject through an 80 wt% S_8 poly(S-*r*-DIB) copolymer film (~1 mm) in the mid-IR (3–5 μm) regime. (Images are false colored, sepia tone: white corresponds to ~37 °C and brown corresponds to ~24 °C). Reproduced with permission from *Adv. Mater.*, 2014, 26, 3014–3018. Copyright 2025, John Wiley and Sons.

Possible sustainability impact. Inverse vulcanised polymers offer a potentially more environmentally friendly alternative to cost-intensive rare earth materials like germanium and chalcogenide glass, which are commonly used in IR optics. They usually require rare and expensive raw materials of extremely high purity, which significantly increases their cost as well as environmental footprint due to the energy-intensive processes for extraction, refinement, and fabrication. Inverse vulcanised polymers on the other hand use widely available and low-cost materials, which not only reduces the dependence on rare earth elements but also promotes circular economy principles by repurposing industrial by-products.[7]

Another aspect that makes IV-based IR lenses more sustainable than current materials is their easy repairability. Traditional materials like chalcogenide glass and germanium are difficult or impossible to repair, calling for full replacement in case of damage. This generates waste that is harmful to the environment and also requires energy and resources required to remanufacture and dispose these materials. In contrast, high sulfur polymers can be thermally healed when damaged, restoring their functionality without the need for replacement. This ability to self-repair extends the lifespan of IR lenses and reduces material waste, contributing to a more sustainable product lifecycle. Furthermore, the recyclability of these materials allows them to be fully reprocessed at the end of their use phase, reducing landfill waste and environmental damage.

Energy storage

Li–S (lithium–sulfur) batteries operate through reversible redox reactions between lithium and sulfur (S_8). During discharge, lithium at the anode is oxidised, releasing lithium ions and electrons that travel to the sulfur cathode, where sulfur is reduced to form lithium sulfide. The reverse occurs during charging. The discharge process involves a two-stage transformation: cyclic S_8 forms soluble Li_2S_8, which is further converted to Li_2S_6 and Li_2S_4 (yielding 25% of sulfur's theoretical capacity) and then to solid Li_2S_2 and Li_2S (yielding 75% of capacity).[140] This type of battery shows many advantages such as high energy density (theoretical specific capacity of 1675 mA h g^{-1}; energy density of 2600 Wh kg^{-1}), which is significantly higher than that of conventional lithium-ion batteries.[140] Also, elemental sulfur is a very abundant and cheap raw material, which could reduce the cost of battery materials. Furthermore, sulfur is a very lightweight material which, in combination with the high energy density, translates to lower weight of the battery with the same energy storage capacity. These properties are highly beneficial for applications in vehicles and transportable electronics.

Despite all these advantages, there are some drawbacks that have to be considered: Both sulfur and lithium sulfide (Li_2S), the discharge product, have poor electrical and ionic conductivity. This results in sluggish redox kinetics at the cathode, leading to low sulfur utilisation and limited specific capacity. Also, depending on the used electrolyte, the intermediate lithium polysulfides formed during discharge might be soluble in the electrolyte. These polysulfides can diffuse to the anode, causing the so called "shuttle effect", which leads to a loss of active material, low coulombic efficiency, and capacity fading over time.[140] Another issue is the change in volume during charge and discharge processes, since sulfur undergoes a significant volume expansion (~80%) upon full lithiation to form Li_2S. This expansion can cause mechanical stress and pulverisation of the electrode, resulting in poor cycling stability and reduced battery lifespan. Side reactions of polysulfides with lithium metal at the anode can influence the battery performance. In reverse, an uneven lithium deposition can lead to dendrite formation, which can penetrate the separator, causing short circuits.[140] Inverse vulcanised polymers could be a solution to these challenges: cross-linkers such as DIB, divinylbenzene, and styrene have been employed to form high sulfur polymers for Li–S batteries, but these polymers often have low conductivity, which limits rate capability. Even larger scales up to 1 kg were synthesized to demonstrate industrial application for energy storage (Fig. 6).[90] To improve their performance, conductive building blocks can be incorporated. Advanced copolymers from poly(*m*-aminothiophenol) (PMAT) and sulfur yield cp(S-PMAT), combining high sulfur content with improved conductivity and excellent cycling stability. Benefits of these materials include the inhibition of LiPS shuttling and therefore increased cycling stability as well as safety, due to the possible flame retardancy of certain inverse vulcanised materials as composites.[75] By improving safety and flame retardancy, the incorporation of flame retarding comonomers could be addressed.[141,142] Generally, inverse vulcanised polymers outperform sulfurised polymers electrochemically. The production is straightforward, using elemental sulfur without solvents or catalysts. However, further optimisation through materials design and multifunctional cross-linkers is needed to enhance performance and facilitate large-scale synthesis of high sulfur content polymers.

Possible sustainability impact. The high sulfur content in these polymers, combined with their ability to facilitate efficient Li-ion transport, contributes to maintaining high capacity without the risk of leakage, evaporation and flammability, which is a risk in liquid electrolytes. The absence of liquid electrolytes lowers the environmental impact related to the production, disposal, and recycling of toxic solvents, also minimising the need for complex containment and cooling systems, further reducing the weight and material costs of battery systems.

Reducing weight is directly linked to a lower environmental footprint. Lower mass results in reduced energy consumption during the production, transport, and operation of devices powered by these batteries. This can be especially advantageous for applications in low distance electric planes and helicopters, where weight is a crucial factor.

From a sustainability perspective, eliminating solvents decreases the energy and water usage associated with solvent manufacturing and recycling, contributing to a greener battery lifecycle.

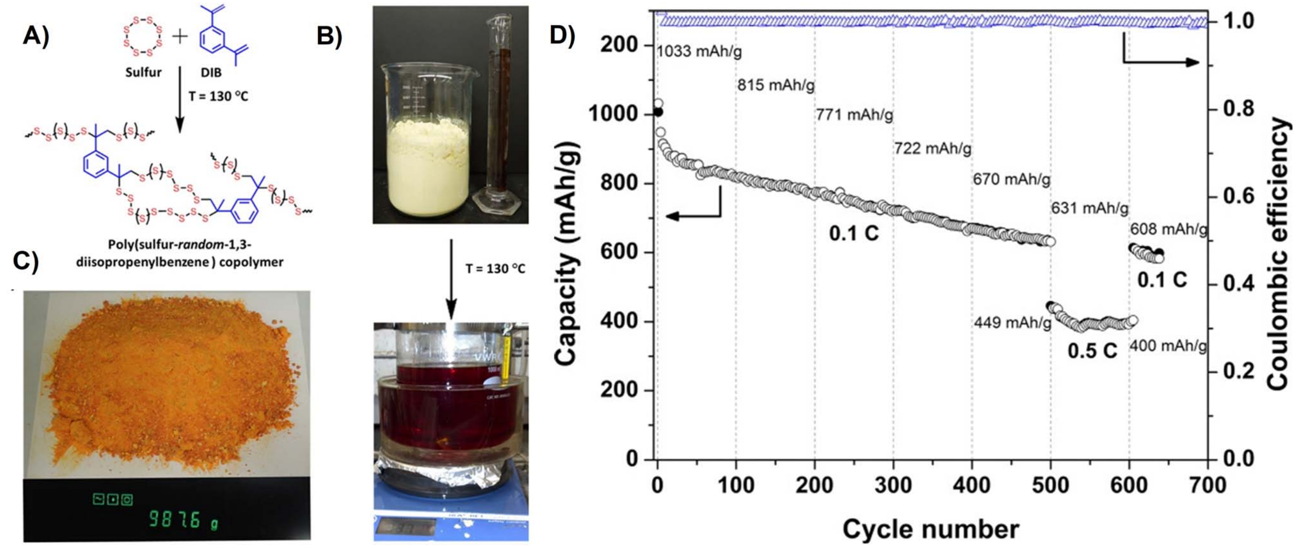


Fig. 6 (A) Synthetic scheme for the synthesis of poly(S-*r*-DIB) at $T = 130$ °C; (B) pictures of scaled-up polymerisation (1 kg, 10 wt% DIB); and (C) image of 1 kg poly(S-*r*-DIB) with 10 wt% DIB. (D) Cycling performance of a Li–S battery using a poly(S-*r*-DIB) copolymer (10-wt% DIB, 1 kg scale) for 640 cycles with charge (filled circles) and discharge (open circles) capacities, as well as coulombic efficiency (open triangles). Cycles 1–499 are run at a rate of C/10 (167.2 mA g^{-1}); cycles 500–599 are run at C/2 (836 mA g^{-1}); and cycles 600–640 are run at C/10 (167.2 mA g^{-1}). Reproduced with permission from *J. Polym. Sci. Part A: Polym. Chem.*, 2015, 53, 173–177. Copyright 2025, John Wiley and Sons.

The potential low-cost, scalable nature of inverse vulcanisation is critical for making Li–S batteries more commercially viable, which promotes the broader adoption of energy storage technologies with a lower environmental impact compared to current lithium-ion systems.

Even though lithium sulfur batteries are among the most promising future battery systems, to be more sustainable than current technologies, their recycling and circularity has to be considered as well. Due to the challenges discussed above, no recycling methods have been established yet, although initial approaches were reported in the literature employing thermal and hydrometallurgical methods.[143,144] A major challenge in the recycling of the sulfur-containing parts of a Li–S battery is the formation of Li-polysulfide intermediates during charge and discharge processes.[145] As previously discussed, IV-based cathode materials can actually inhibit or reduce the formation of Li-polysulfides, which in return should improve their recyclability. Additionally, recent studies showed that all solid-state Li–S batteries hold great potential for long-lasting energy storage with high capacity,[146] as life time is one of the most important factors – over repairability and recycling – when it comes to sustainability.[147] However, it was mentioned that future work should mainly focus "on cathode structure engineering to improve density and areal loading"; here cathode materials based on inverse vulcanised materials could be a major contributor.[143]

Separation technology

Environmental pollution of water and soil is amongst the most urgent challenges we currently face. Specifically heavy metals such as mercury have raised great concerns due to their high environmental and human toxicity, causing irreversible health issues, such as kidney damage, neurological disorders, and birth defects.[148] Anthropogenic emission of mercury by solid waste incineration (municipal and medical wastes), coal and oil combustion, and metal production (iron, lead, and zinc) is a major concern. State-of-the-art technology for mercury capture from aqueous and gaseous systems includes chemical precipitation, ion-exchange, adsorption and membrane filtration.[149] From an economic standpoint, adsorption, *e.g.* with activated carbon, is a low-cost and widely applicable process. Sulfur-based materials on the other hand show much higher efficiency but the morphology and crystallinity of elemental sulfur makes its processing into useful materials difficult. Even though the interaction of heavy metals with sulfur materials is not fully understood yet, it is generally accepted that sulfur functionalities have a strong affinity to heavy metals.[150] As a result, sulfur-doped carbon materials are widely used for heavy-metal adsorption from aqueous solutions.[150]

Sulfur polymers are a promising alternative, since they consist of a very high fraction of sulfur and can be processed into any shape with a wide range of techniques, depending on the final application. The first reported inverse vulcanised materials for heavy metal uptake were developed by Chalker *et al.* using limonene as the comonomer.[74] While the uptake of the final product only showed an efficiency of 55%, the mercury was bound tightly. Since then, the efficiency of these materials could be improved tremendously by employing hydrophilic comonomers to increase the interaction of the polymer with water and individual metal ions.[92,151–154] Further advances were made by increasing the surface area of the adsorbent by coating of microporous support materials, foaming with supercritical CO_2,[155] or the use of porogens such as sodium chloride.[156] In the latest report from the group of Chalker, they demonstrated the effective adsorption and recovery of gold from different waste sources. Importantly, this method relies on polysulfide-based polymers – analogous to inverse vulcanised polymers – which are therefore free of cyanide and mercury, which is a crucial step towards more sustainable gold production and recycling. Recovery of gold from the sorbent could be achieved by depolymerisation or pyrolysis, where the latter has to be contained carefully to avoid the release of toxic gases.[57]

Beside heavy metals, oil and hydrocarbon fuel spills pose significant threats to soil and water ecosystems, impacting the environment, economy, and human health. The Deepwater Horizon disaster in 2010, which released approximately 4.9 million barrels of crude oil into the ocean, is just one example of many and highlights the devastating impact of such incidents.[157] Smaller spills of diesel fuel and gasoline occur more frequently and are particularly concerning in developing regions where limited resources hinder effective responses, endangering groundwater, drinking water, and other vital food sources like fish. These environmental catastrophes emphasise the importance of research into cost-effective technologies to enhance spill response technologies. Hence, skimming technology and sorbents, which can be produced and deployed on a large scale, have gained significant interest. Ideally sorbents are hydrophobic with a high surface area for effective adsorption of hydrocarbons and float on water so they are easy to recover.[91] Electro-spinning provides further opportunities to increase the surface area of adsorber materials. Thielke *et al.* demonstrated the co-spinning of poly(methyl methacrylate) (PMMA) and a sulfur-rich copolymer based on poly(sulfur-*stat*-diisopropenylbenzene) yielding a fiber mesh with a high surface area, suitable for the removal of mercury.[158]

Inverse vulcanised polymers offer great potential to solve these problems as shown by many studies, where these materials could be synthesised at kilogram scales and at low cost. Chalker *et al.* demonstrated the synthesis of porous polysulfides derived from canola oil, which was found to absorb roughly twice its weight in crude oil by forming oil-polymer aggregates, and could easily be separated from water (Fig. 7).[91] Additionally, the absorbed oil could be removed from the porous polysulfide through mechanical compression, enabling the material to be reused in oil spill remediation.

Further enhancement of the adsorption and separation efficiency of IV-based materials could be achieved by coating of highly porous support structures such as porous carbons, MOFs or zeolites. It has been shown that by the addition of for example silicon containing comonomers, sulfur polymers can coat almost any surface, thereby strongly increasing their range of applications.[35,159]

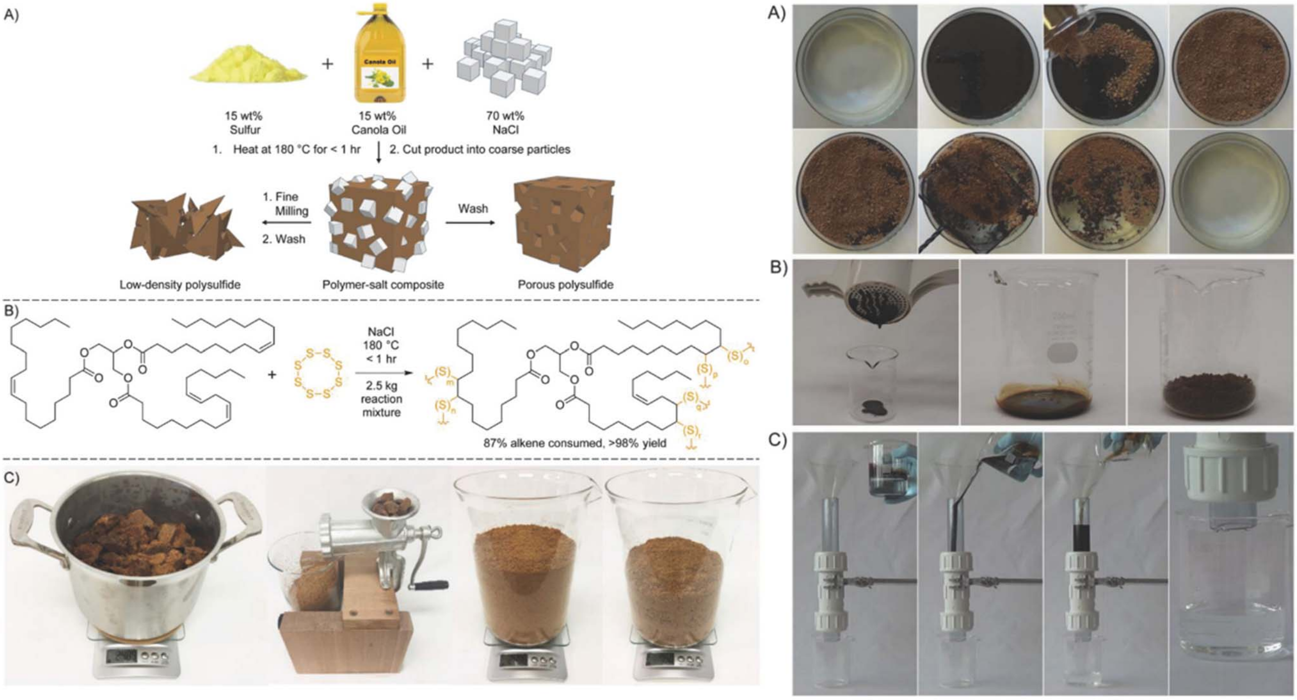


Fig. 7 Left: (A) elemental sulfur and canola oil (or used cooking oil) react directly to form a polysulfide copolymer. The polymer, equal mass in sulfur and canola oil, is a friable rubber. The inclusion of sodium chloride in the reaction mixture results in a polymer-salt composite. The sodium chloride can be removed with a water wash to introduce pores into the polymer. If the polymer is ground finely (0.5–3.0 mm particle size) and then washed with water, the void spaces formed after sodium chloride removal no longer appear as pores. In this case, the polymer tears at the salt interface where a pore would otherwise form. This finely milled polymer is referred to as a "low-density polysulfide" rather than a "porous polysulfide". (B) The polysulfide copolymer is formed by ring-opening polymerisation of elemental sulfur and reaction of the resulting thiyl-radical end groups with the Z-alkene of the unsaturated cooking oil triglyceride (primarily oleate and linoleate in the oils used in this study); 87% of the alkenes are consumed in the polymerisation, as determined by ^{1}H NMR spectroscopy. (C) Left to right: The polymer-salt composite was prepared on a 2.5 kg scale and ground finely before washing with water. After washing with water and drying, 750 g of the low-density polysulfide was obtained (far right image). Right: (A) crude oil (100 ml) was added to 1.50 L of seawater. The low-density polysulfide (100 g) was then added to the oil–water mixture. In less than 1 min, the oil and polymer form an aggregate that can be removed from the water by skimming with a net. (B) The crude oil can be recovered from the low-density polysulfide by mechanical compression and the recovered polymer can be reused in oil sorption. (C) A filter was constructed in which 30 g of the low-density polysulfide was packed into polyvinyl chloride (PVC) pipe. The polymer was immobilized using PVC mesh on the inflow end and cotton fabric on the outflow end. A mixture of crude oil (10 g) and seawater (100 g) was poured through the filter. The oil remained bound to the polymer while the purified seawater passed through the filter. Adapted from *Adv. Sustainable Syst.* 2018, 2, 1800024 with permission.

Possible sustainability impact. Activated carbon is typically produced from fossil-based materials like coal, petroleum coke, or even natural gas. This production process is energy-intensive, contributing to carbon emissions and resource depletion.

By choosing the right comonomers during the IV process, the polymer's structure and functionality can be optimised for selective absorption of different contaminants. For example, certain comonomers can improve the polymer's capacity to absorb heavy metals like mercury, cadmium, or lead, making the material more efficient and reducing the need for large quantities. It was also shown that bio-based comonomers can be utilized to produce efficient adsorber materials.[81]

Rather than being disposed of in landfills, the loaded sulfur polymer can be repurposed, contributing to the circular economy by transforming waste into valuable construction materials. The sulfur-based binder could enhance the mechanical properties of concrete while providing an environmentally friendly disposal route for the contaminants it absorbed.

Even though long term studies still need to be conducted, sulfur has a strong affinity for heavy metals, forming stable bonds that prevent leaching into the surrounding environment.[160] In contrast, activated carbon binds heavy metals more weakly, which could lead to the release of these pollutants over time in landfills, posing risks to soil and groundwater.

Construction materials

Binders and asphalt. Polymers with high sulfur content such as polysulfides have a long history in construction materials.[11,161] The commercial availability of sulfur as a by-product of the oil and gas industry, its low cost and the unique properties described above, makes it a viable large-scale construction material alternative to Portland cement, asphalt, mortars, and concretes, with the term "sulfur concrete" referring to mixtures of sulfur as the binder with various aggregates like sand, gravel and stone chips.[11,162] Sulfur concrete is created by cooling mixtures of aggregate and molten sulfur, which solidifies to form a product with hardness comparable to conventional concrete. It offers unique properties, such as rapid strength development and high final strength, low permeability, and superior resistance to strong acids and saline solutions.[11,162,163] However, a significant drawback of sulfur concrete, when using unmodified elemental sulfur, is the high shrinkage volume upon cooling, leading to distortion and inaccurate final dimensions. Sulfur can be transported to constructions sites both in the solid form and in the liquid form. Transferring sulfur to the molten form facilitates its handling since it can simply be pumped in and out of a heated tanker. Transportation over short distances can be done in insulated containers, where the low thermal conductivity of sulfur helps to retain its temperature and minimise heat loss. At longer distances however, keeping the sulfur molten is just impractical due to energy consumption; secondly these tankers are not easy to clean, so they can only transport materials one way, which makes it economically not feasible. Therefore, the sulfur industry has spent many resources developing methods to produce solid sulfur granulate with regular size that can be handled easily and limit environmental pollution.[164] Furthermore, the manufacturing of concrete blocks, railway sleepers, tubing or other parts for infrastructure is much easier and is an emerging application for sulfur-based concrete.[165]

To address transportation issues, sulfur-based cement formulations have been improved by adding modifiers. Sulfur polymer cement consists of elemental sulfur and organic modifiers, such as DCPD, and oligomers of cyclopentadiene, styrene, and mixtures of these, enhancing long-term durability. The proportions of these stabilisers/additives vary depending on the desired properties and use of the sulfur cement, typically between 1% and 14% by weight of the total sulfur.[11] This modification process to stabilise elemental sulfur can be seen as one of the first approaches to "inverse vulcanisation". However, since the load of the modifier usually does not exceed 14%, plenty of unreacted sulfur remains in the material, whereas inverse vulcanisation aims at complete sulfur conversion in order to prevent a recrystallisation and therefore maintain structural integrity of the final product. Even though so-called modified sulfur was successfully tested as a concrete binder in the 1970 s, modern approaches to sulfur as a concrete binder go by a different pathway: Sulfur is used in its elemental state, whereby the filler materials, such as gravel and sand, are coated with a binder-like material to prevent recrystallisation of the sulfur.[165] However, recent development of new bitumen-like binders based on sulfur polymers show promising results as a more sustainable alternative for concrete and building materials. Since inverse vulcanisation provides a wide range of possible comonomers, physical and chemical properties can be precisely tuned to fulfill necessary requirements for application as concrete binders or even in road surfacing.[79,166–168]

Insulation materials and flame retardancy. Beyond potential applications as concrete binders, high sulfur polymer composites were tested as insulating materials with additional flame retarding properties. One example is the work of Chalker *et al.*, who developed a sulfur, canola oil, and wool composite material that demonstrates exceptional insulating and flame-retarding properties. The thermal insulation benefits from the sulfur-polymer matrix, which retains the low thermal conductivity of elemental sulfur ($\sim$0.2 $\mathrm{W m^{-1} K^{-1}}$) while retaining high mechanical strength. The composite achieves even lower thermal conductivity (0.09 $\mathrm{W m^{-1} K^{-1}}$) due to the integration of wool, hereby outperforming typical bulk polymers and lightweight concretes. Wool also enhances the material's flame resistance; composites exhibit rapid self-extinguishing properties without dripping molten material, unlike the base sulfur-polymer. This performance is most likely attributed to the rapid formation of a protective char layer and wool's inherent high ignition temperature and nitrogen content, which synergistically suppress flames. These sustainable and efficient properties position the material as a promising candidate for energy-saving insulation and safe construction applications.[169]

In another example by Pyun *et al.* flame retarding sulfur was integrated directly in the polymer structure by synthesising sulfur-containing polyols by inverse vulcanisation. These prepolymers could then be applied in chain extension reactions and polyaddition with urethans to form segmented polyurethanes. The incorporation of sulfur introduces a flame-retardant quality, which can self-extinguish rapidly upon ignition, achieving the highest UL-94 V0 flame retardancy rating. Even though commercial segmented polyurethanes burn upon ignition, hence failing the flammability test, and sulfur also burns with a blue flame, the combination of both materials yields synergistic flame retarding properties. The adjustable mechanical performance and thermal stability of these materials underlines their broad utility in high-performance applications especially for the construction and insulation industry.[75]

Possible sustainability impact. Through high energy use and inherent CO_2 production during the calcination reaction, the production of building materials such as steel and concrete is one of the biggest CO_2 emitters worldwide.[170,171] Partial replacement of concrete and insulating materials such as stone wool for construction with sulfur-based polymers could help to reduce CO_2 emissions as well as waste produced by side reactions.

Furthermore, the repairability of construction materials, and thereby their lifespan, could be strongly improved with the use of sulfur materials due to their inherent dynamic and self-healing properties. However, the thermally and UV-light induced metathesis of S–S bonds might also limit the areas of application where high heat resistance is required or prolonged exposure to sunlight cannot be excluded.

It was also shown that sulfur-based materials have been proven to exhibit a higher resistance against water, pH and biofouling compared to conventional binders and insulators which would help the longevity of buildings and infrastructure.

Fertilisers

Historically, sulfur received minimal scientific attention because it was sufficiently available from the atmosphere, soil, and as a by-product in mineral fertilisers. However, the use of highly concentrated fertilisers with little or no sulfur in modern agriculture has drastically reduced sulfur availability in soils.[15] Studies have indicated that adding sulfur to soil improves crop yield, drought tolerance, nitrogen efficiency, and phosphorus uptake.[11,172] The addition of elemental sulfur pellets shows only minor effects due to the slow microbial oxidation and therefore slow plant uptake. Hence, agriculture represents a significant, however slowly growing market for sulfur-based compounds either as fertilisers or as controlled release systems. By delaying nutrient release, such fertilisers allow for gradual uptake following application and provide sustained nutrient availability over longer periods compared to traditional fertilisers. Slow- and controlled-release fertilisers are typically achieved using coatings that control fertiliser solubility, with sulfur-coated urea, often further coated with polyolefins or resins, being a common example.[173–175] This can reduce the caking tendency of various fertilisers during storage and transportation and delay nutrient release, while also serving as a secondary plant nutrient essential for plant growth. However, the crystalline nature of sulfur and exposure to higher temperatures in the soil lead to the formation of microscopic pores, resulting in brittleness and higher friability, which causes an abrupt release of nutrients. To enhance the overall performance of phosphorus fertilisers and support their conservation, "smart" fertilisers have been explored. Chalker *et al.* demonstrated that inverse vulcanised polymers can also serve as controlled-release fertilisers.[87] In their study, elemental sulfur was copolymerised with canola oil, incorporating three components of NPK (Nitrogen–Phosphate–Potassium) fertilisers: ammonium sulfate, calcium hydrogen phosphate, and potassium chloride. A small-scale plant growth study using tomato plants (*Lycopersicon esculentum*) as a model revealed that after 10 weeks, plants treated with the sulfur polymer composite were significantly taller, had greener foliage, and produced more fruit compared to those treated with free NPK (Fig. 8). A similar approach by Valle *et al.* showed an improved sulfur oxidation and thereby sulfate release from an inverse vulcanised polymer consisting of soybean oil as the comonomer compared to sulfur pellets. It is suggested that the triglycerides might act as a nutrient source for sulfur oxidising fungi, which leads to continuous sulfate release.[86] They further investigated the diffusion of phosphorous fertilisers and the oxidation of the sulfur species in the polymer to further optimise the delivery of nutrients in a Petri dish experiment as well as soil.[176,177]

Possible sustainability impact. Sulfur is a vital secondary macronutrient. Using sulfur in inverse vulcanised materials as a smart fertiliser system not only repurposes industrial by-products but also provides a sustainable nutrient source that enhances crop yields and improves soil quality.

Bio-derived comonomers, like canola oil or used cooking oil, offer a renewable and biocompatible alternative to fossil-fuel-based materials in inverse vulcanised polymers, promoting resource sustainability. These plant-based components could be biodegradable, reducing environmental pollution and supporting more eco-friendly agricultural practices.

Smart fertilisers with controlled-release properties reduce nutrient waste by delivering nutrients to plants over time, improving crop yields and minimising environmental damage. This efficient nutrient management helps farmers produce more food with fewer inputs, addressing the challenge of feeding a growing global population sustainably.

Ageing and wear

Due to the early stages of development, inverse vulcanised polymers are yet to be considered for their lifespan and use phase of commercial products as ageing might lead to a reduction of lifetime or a variation in the properties of an active material. For example, if used as an additive for Portland cement, a polymer that loses mechanical strength during the ageing process would not allow for the longevity of buildings and structures, and the change in physical properties could create danger for consumers if a material ages too quickly. Initial studies into the ageing of sulfur/polymer composites for the construction industry exhibit no swelling, water uptake or deterioration of mechanical properties even after soaking in aqueous sulfuric or hydrochloric acid for 24 h.[163] Another example closely related to high sulfur polymers is the ageing of vulcanised rubber, where high temperatures can result in a curing effect increasing the cross-link density and thus the brittleness of the material.[178] This is an important concept to investigate for any polymer that is being applied in a system that requires consistent mechanical properties *e.g.* concretes, car tyres, *etc.* Indeed, the Automotive Association in the UK suggests the maximum lifespan of a car tyre to be between 5 and 10 years.[179]

Next to thermal ageing, sunlight is one of the major contributors to ageing effects in polymer materials. Approximately 42% of solar radiation is in the infrared range (wavelengths greater than 800 nm), contributing to the heating of irradiated objects, but usually does not initiate photochemical reactions that degrade polymeric binders. UV light with wavelengths between 280 and 400 nm on the other hand, is responsible for many changes in polymeric materials exposed outdoors, significantly influencing polymer degradation.[180] Typical photochemical ageing reactions include chain scission, cross-linking, formation of low-molecular weight compounds and introduction of new functional groups.[181] Chain scission and cross-linking are the predominant ageing processes, where depending on the type of material and additives, one dominates over the other. When chain scission dominates, the material becomes softer over time, whereas cross-linking leads often to brittle materials. Chain scission can also lead to the degradation into smaller low molecular weight compounds and with further weathering can then be extracted and washed out, causing loss of strength, localised loss of volume, and shrinking and cracking of the material surface.[182] Similar to commercial materials like PIMS (polymers of intrinsic microporosity), inverse vulcanised polymers age over time and their performance properties change. Since S–S bonds can be cleaved and healed with UV irradiation,[36] it can be suggested that sunlight can affect the physical properties of these polymers over time, even though it has been shown that, depending on the comonomer used, they can also show UV stability and even blocking properties.[109,183] Van Os and colleagues investigated this

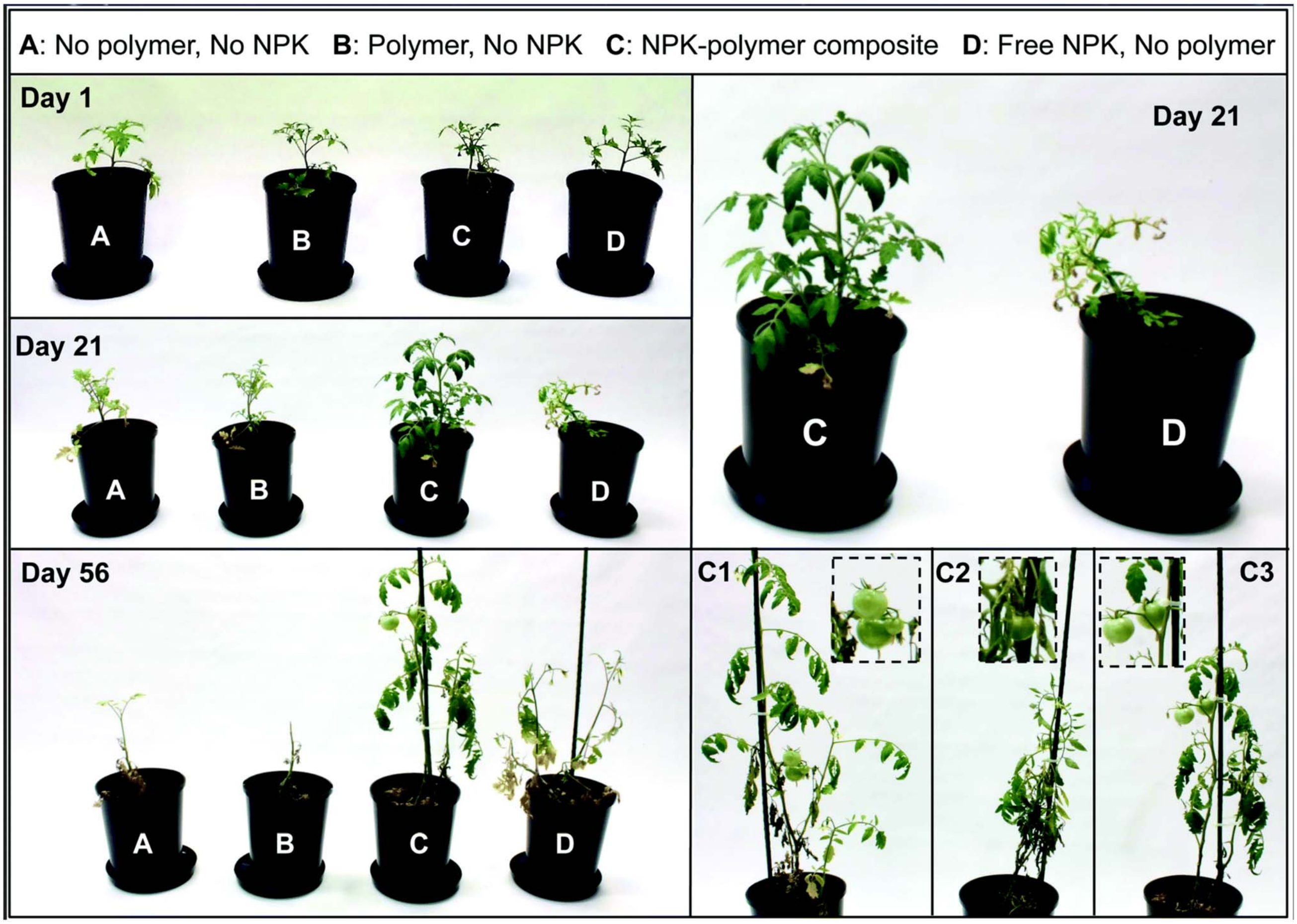


Fig. 8 Day 1: transplanted tomato plants. Day 21: the controlled-release NPK sulfur polymer composite produced consistently green and healthy plants (Group C) while the plants with the free NPK suffered from nutrient burn (Group D). Day 56: the controlled-release NPK sulfur polymer composite (Group C) promoted more rapid growth and more fruit than the plants with free NPK (Group D). Plants C1, C2 and C3 are the three different plants grown for 56 days with the NPK sulfur polymer composite. All of these plants with the controlled release fertiliser bore fruit and blossoms (fruit shown in the inset). Reproduced with permission from *Org. Biomol. Chem.*, 2019,17, 1929–1936. Copyright 2025, Royal Society of Chemistry.

concept in car tyres under accelerated ageing conditions, using EDX analysis to determine a decrease in the sulfur content of the rubber materials with ageing.[184] With inverse vulcanised materials, this could result in the recrystallisation of elemental sulfur also known as sulfur blooming. When the depolymerised sulfur within the polymer network is sufficiently abundant and mobile, it can crystallise inside the network, causing sulfur bloom. This is related to a visual effect where the polymer becomes more opaque, its colour shifts towards yellow and sulfur crystals may even form on the surface (Fig. 9).[5,55]

As can be seen in Fig. 7, 9 and 12 inverse vulcanised polymers are mostly dark brown and black in colour due to their high level of light absorption and direct exposure to sunlight and UV irradiation, and photochemical ageing processes might only affect outer layers of the material down to 1–2 mm. Cracks in the material surface further accelerate their degradation when they are exposed to warm and humid environments. In some reports it was observed that with time, inverse vulcanised polymers turn from soft and flexible to hard and brittle, which could be attributed to curing under ambient conditions.[138] Over time, atmospheric moisture can penetrate the polymer network, which can be monitored by the development of a water peak DSC. This adsorbed water can facilitate depolymerisation and the release of hydrogen sulfide gas. The susceptibility to ageing by water penetration varies with the cross-linking density as well as the sulfur content, with polymers with higher amounts of sulfur being more prone to depolymerisation. Additionally, certain comonomers could increase a polymer's tendency to undergo depolymerisation due to water if the monomer exhibits hydrophilic character, although further research is needed to better understand the structure–property relationships that govern ageing in these materials.

It has been observed that sulfur may exist within the polymer matrix in an amorphous form.[55] When crystalline sulfur is not observed in PXRD or in the melting transition of the DSC, amorphous sulfur can be extracted and observed by means of HPLC or UV-vis spectroscopy. This unreacted sulfur can then be quantified against a standard of elemental sulfur. The presence

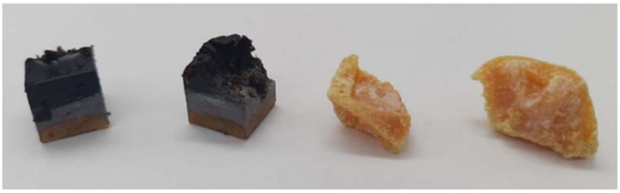


Fig. 9 Inverse vulcanised polymers showing visual evidence of the sulfur bloom effect. The polymers on the right show severe sulfur bloom all over the pieces due to being made with excessively high sulfur contents and not being cured. The polymers on the left show moderate sulfur bloom. Note how the sulfur bloom occurs toward the bottom of these polymer cubes because they were poured into a 1 cm^3 mould too early in their reaction, resulting in the denser sulfur sinking to the bottom of the cube in the absence of stirring. This led to excessively high sulfur concentrations in the bottom of the cube in comparison to the top, which could not be stabilised, resulting in sulfur bloom. Reproduced with permission from *RSC Appl. Polym.*, 2025, 3, 10–42. Under the Creative Commons Attribution 3.0 Unported Licence, Royal Society of Chemistry.

of this unreacted sulfur may lead to accelerated sulfur bloom and hydrogen sulfide evolution. Adjusting the reaction conditions allowed for control over the quantity of unreacted sulfur generated during the reaction. The quantification of this unreacted sulfur has been reported in multiple instances *e.g.* in lignin–sulfur polymer composite materials assessed for their mechanical properties.[185,186]

Next to water and moisture, amines can also catalyse the ring opening of elemental sulfur as well as sulfide bonds in these materials and therefore promote their depolymerisation and degradation.[187,188] It can be suggested that naturally occurring amines, such as amino acids and ammonia could also catalyse their degradation and oxidation, yet it was shown that not all inverse vulcanised polymers are affected by the presence of amines.[53]

Degradation and ageing through moisture and water is also often accompanied by biological attacks such as biofouling and molding, which is the most common cause of microbiological damage to sealants and coatings.[180,189,190] Beyond biological impacts, pH variations in soils are a major influence on the ageing of polymer materials. Yet acids, bases and organic solvents have minor effects on the S–S bonds; however, depending on the used comonomer, swelling behaviour can change, as well as the acid/base catalysed degradation of the organic components, especially with ester bearing monomers. Since there are only limited studies on their ageing behaviour, we can draw comparisons with well-studied materials such as organic polysulfides that are widely applied as sealants, *etc.* and can act as model materials on how weathering end environmental exposure could affect S–S and C–S. Hence in the following section parallels will be drawn between commercial polysulfide materials and inverse vulcanised polymers.

In civil engineering, the resistance of sealants and building materials to biodegradation is crucial, particularly for applications in tunnels, sewers, sewage treatment plants, concrete, asphalt, pipelines or coatings where the materials are exposed to aerobic and anaerobic bacteria.[191] In several studies on sulfur-based sealant biodegradation resistance, various natural and synthetic rubber seals and cured-in-place sealants were tested in soil samples and the sludge tank of a sewage treatment plant. Polyurethane sealants and synthetic rubber seals demonstrated the highest resistance to microbiological attack, while foamed rubber seals made from natural and synthetic rubber blends showed the least resistance.[180] A possible explanation could be that inorganic polysulfides are intermediates of sulfide oxidation that occur in a range of environmentally relevant processes including pyrite formation, organic matter sulfidisation, isotope exchange among reduced sulfur species, and metal chelation.[15] The biological oxidation of C–S and S–S bonds may lead to bond scission and the formation of sulfates that can be consumed by plants and microorganisms. This has been shown in laboratory experiments with microbial cultures and enzymes and indicates both indirect and direct roles of microorganisms in affecting polysulfide chemistry in natural environments through production and consumption.[192,193] As polysulfides have been detected in a wide array of natural systems ranging from microbial mats to hydrothermal vents, it is possible that sulfur metabolising bacteria and fungi might indeed attack polysulfide moieties in sulfur polymers. Ribeiro *et al.* showed that the sulfur species in inverse vulcanised polymers slowly oxidise in soil in the presence of microorganisms.[176]

The findings underline the necessity of long term (bio) degradation studies and the impact of degradation products on the environment, especially in fields where degradation is advantageous, such as fertiliser release. The aforementioned study by Chalker *et al.* exploring the potential of sulfur polymer composites as slow-release fertilisers, suggests that the sulfur polymer may slowly degrade in soil, with potential impacts on the soil structure and plant health. Since the polymer is based on plant oils, the ester groups might hydrolyse under the basic conditions of the soil, releasing glycerol. The smaller degradation products could then also be better metabolised or oxidised by microbes and plants as sulfur rich nutrients.[87]

System sustainability

The real-life applications show great potential to contribute to a circular economy. They can replace current IR lens technology, separation methods or new smart fertilisers. Reparability is one of the main concepts to increase circularity and longevity of these materials, especially for the building industry. The only technology mentioned, where the concept for circular economy (in this case recycling) is not fully developed yet, is sulfur batteries. Nevertheless, high capacity, lower weight and long-term stability can also decrease environmental impact, showing that circular economy is popular but not the only solution. To introduce recycling the end-of-life process itself must be compatible with current technology and further be economical as well. Well-founded recommendations based on environmental and social credentials of inverse vulcanisation-based products are only possible through a detailed comparison with the established life cycle of products. Certain factors can indicate which process is less harmful, such as extended lifespan, higher efficiency, reduced waste generation, or the use of environmentally safer materials that prevent leaching of toxic substances to the environment.

The characteristics of ageing of inverse vulcanised polymers need to be studied further, because as emergent technology, their ageing is less studied; quality degradation over time may lead to land or water pollution due to leeching or degradation which can also lead to lower quality products in end-of-life treatments. The identification of triggers for degradation can also help define the most appropriate use-case examples for scale-up as well as recommendations for efficient end-of-life treatment. Even though degradation during the use phase might lead to environmental harm, we think the most significant environmental impact will occur during the production and end-of-life.

From a social standpoint, introducing inverse vulcanisation-based products, every measure that reduced health and safety risks, making technology more accessible and the handling easier improve social sustainability during the use phase and are not less important than environmental impact. Introducing technologies which are repairable such as IR lenses or cement could create new job opportunities, which influences employees and the general society positively. Using products which are built with less harmful materials and therefore are safer and easier to handle, *e.g.* sulfur batteries, increase the value for customers. Separation technologies increase the community and overall social value simply due to its use to bind heavy metals and oils. Keeping or increasing the value of the product without having to make major adjustments to one's own behaviour could promise an easier switch of the society towards the environmentally friendly alternative. The overall social value needs to be assessed when the products are on the market and it is recommended to pay as much attention to social responsibility as to ecological assessment.

End-of-life

From a technical standpoint there are many ways inverse vulcanised polymers can be reprocessed to restore the original properties of the material or to create new materials. Both the dynamic nature of the S–S bonds, and the properties of the comonomers, mean that the intermingling of different sulfur-based polymers could impact end product quality. This suggests that, just as in traditional plastic waste recycling, proper sorting of the waste streams is essential. Considering commercial waste stream compatibility and sorting, due to the dark colour and/or high IR refraction of the polymers, it can be difficult to identify sulfur polymers and separate them from other commodity plastics. The vast range of different comonomers further complicates the separation of individual materials, as does the suggested applications where deployment will most likely be in multi-material products such as batteries, filtration cartridges or built environment infrastructure. Regardless, high accuracy sorting will be necessary to guarantee homogeneous material properties even after reprocessing through, *e.g.*, melting and reshaping.

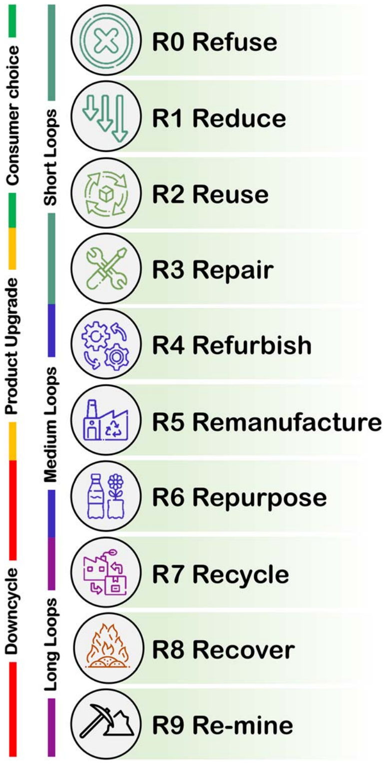


Fig. 10 The 10 Rs for the end-of-life treatment of plastics.

Since inverse vulcanised polymers should contribute to a circular economy, we are not considering scenarios like landfills – especially due to their unclear environmental fate – or thermal energy recovery since the incineration of sulfur generated toxic gases. The most common end-of-life scenario mentioned in the literature concerning inverse vulcanised materials is "recycling", but recycling is only one of many considerations to improve the lifecycle of a product for a circular economy: The 10 Rs (refuse, reduce, reuse, repair, refurbish, remanufacture, repurpose, recycling, recover, and re-mine), as shown in Fig. 10, provide a comprehensive framework for designing and managing products and services to reduce waste, conserve resources, and minimise environmental impact.[69] In the following section we discuss opportunities for inverse vulcanised materials for selected Rs from short, medium and long loop circularity that are most promising.

Repair

The meaning of 'repair' is often misinterpreted: The purpose of repairing is to extend the lifetime of the product and is described as 'making it as good as new' or 'replacing broken parts'.[69] Even though this concept is quite clear, it is often subject to misuse in a different context such as 'refurbishment'. The important difference is that repairing can be done by the users themselves or a third-party repair company, without return to the original manufacturer.

It was shown that infrared lenses made from inverse vulcanised DIB can be repaired to gain the original mechanical and optical properties, offering a huge advantage over traditional inorganic infrared lenses made from germanium or chalcogenide glasses. In particular, the poly(S-*r*-DIB) lenses

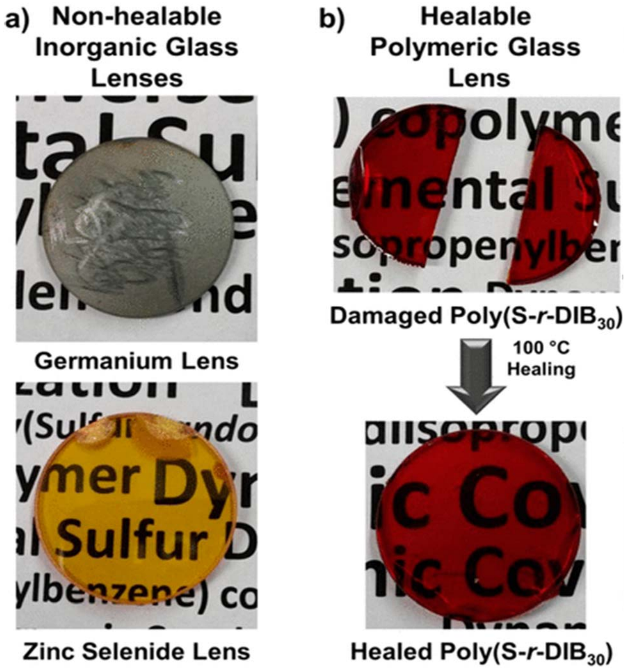


Fig. 11 (a) Damaged inorganic lenses (germanium lens (top) and zinc selenide lens (bottom)) that cannot be repaired for IR imaging. (b) Poly(S-*r*-DIB30) copolymer lens which is drastically damaged but repaired and functional by thermal annealing at 100 °C. Reproduced with permission from *ACS Macro Lett.* 2015, 4, 862–866. Under the Creative Commons public use license, CC-BY or CC-BY-NC-ND, American Chemical Society.

maintained their dimensional integrity during the healing process, with minimal deformation (Fig. 11).[194]

In the chemical repair process of sulfur materials, nucleophiles such as amines or phosphines are used to catalyse S–S bond metathesis at room temperature, enabling adhesion, repair, and recycling without the need for high-energy inputs, compared to thermal repair. Specifically, pyridine and tributylphosphine are effective catalysts for S–S bond exchange. Tributylphosphine is consumed in the reaction, providing rapid metathesis, while pyridine (even though toxic) acts as a catalyst that can be regenerated and removed. The repair effectiveness mainly depends on the sulfur rank, where higher ranks (>2) enable more efficient S–S metathesis, meaning that higher sulfur content also contributes to better repairability. However, compared to thermal treatment, the tensile strength cannot be fully recovered. It was shown that under optimal conditions a maximum of up to 74% recovery of tensile strength was achieved.[188]

Remanufacture

'Remanufacture' applies where a multi-component product is disassembled, checked, cleaned and when necessary replaced or repaired in an industrial process to restore the original state. The final product can partly consist of new and/or recycled materials, or fully consist of recycled components. Even though the original properties are restored, the lifespan of remanufactured products is expected to be shorter due to the use of recycled components.[195] Besides remanufacturing of materials that are damaged beyond repair, remanufacturing processes would come into play also with IV-based composite materials, where filler particles, glass- or carbon fibers are used to improve mechanical properties. It was shown that composites can be healed by thermal treatment such as hot pressing; even though these materials retain good mechanical stability over multiple healing cycles, the incorporated fibers wear and tear with mechanical stress. As a potential solution to this problem, in a remanufacturing process, the sulfur-polymer based matrix could be melted so that the fillers or fibers can be removed and replaced by a virgin material. Similar to the repair process, melting and reshaping is highly dependent on the used monomers and the arising cross-linking density (Fig. 12).[98]

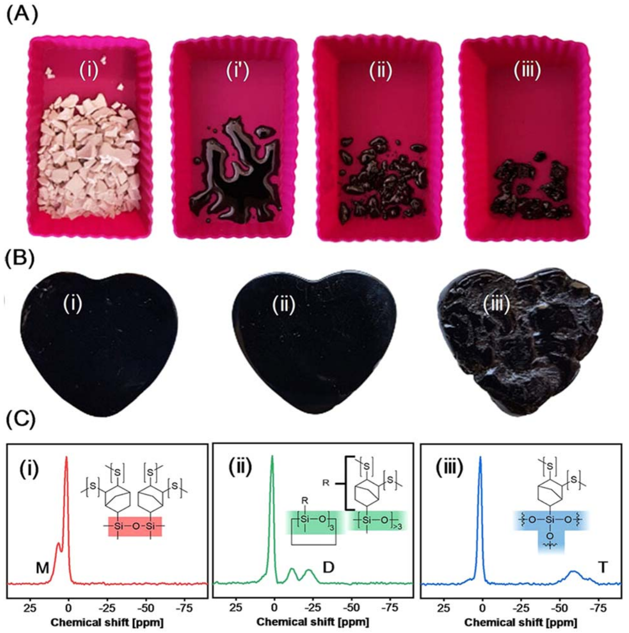


Fig. 12 (A) Melting behaviour of branch-poly(S-*r*-NBS20) with different degrees of siloxane branching. Granules of branch-poly(S-*r*-MENBS20) before (i) and after 2 h (i′) at 80 °C. Granules of (ii) branch-poly(S-*r*-DCNBS20) and (iii) branch-poly(S-*r*-TCNBS20) after 2 h at 80 °C. (B) Moulded objects made from 2 g of branch-poly(S-*r*-NBS20) at 80 °C overnight. While (i) branch-poly(S-*r*-MENBS20) and (ii) branch-poly(S-*r*-DCNBS20) adopted the shape of the mould, branch-poly(S-*r*-TCNBS20) was still rubbery at 80 °C and did not fully adopt the shape of the mould. (C) 29Si CP/MAS NMR spectra of (i) branch-poly(S-*r*-MENBS20), (ii) branch-poly(S-*r*-DENBS20), and (iii) branch-poly(S-*r*-TENBS20), showing characteristic peaks for M, D, and T siloxane bonds, respectively. The peak at 1.4 ppm present in each of the spectra corresponds to the trimethyl-substituted silicon atom stemming from the TMNBS comonomer. Reproduced with permission from *Angew. Chem. Int. Ed.* 2022, 61, e202114896. Copyright 2025, John Wiley and Sons.

Repurpose

The concept of 'repurpose' is rarely used in the literature.[69] By reusing discarded high and low value goods or components adapted for another function, the material gets a distinct new life cycle. This is of special interest for materials with a range of

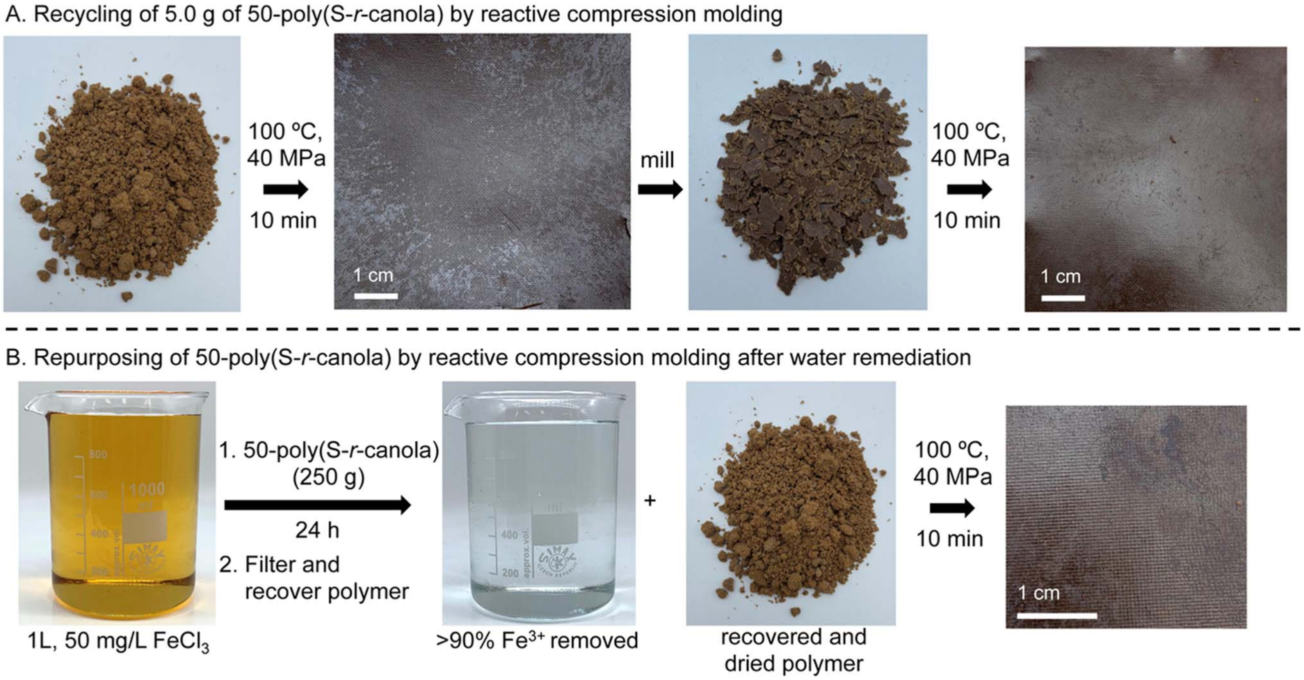


Fig. 13 (A) Reactive compression molding can be used to recycle the 50-poly(S-*r*-canola) material. (B) 50-poly(S-*r*-canola) can be used to remove Fe^{3+} from water and then repurposed to a new architecture *via* reactive compression molding. At these levels, the bound iron did not affect the reactive compression molding. Reproduced with permission from *Chem. Eur. J.* 2020, 26, 10035. Copyright 2025, John Wiley and Sons.

useful properties and promising applications such as inverse vulcanised polymers.

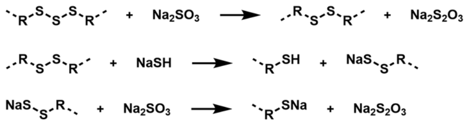
One example for the repurposing of inverse vulcanised materials is by compression molding of spent heavy metal adsorbers (or other materials that cannot be returned to their original purpose) by heating the material to moderate temperatures (approximately 100 °C) while applying mechanical compression (Fig. 13). This allows the material to be reformed into new shapes or configurations under solvent-free conditions while maintaining the material's mechanical and chemical integrity. By combining the sulfur polymer with fillers like sand, coconut coir, or carbon fiber, high performance composites can be produced with tuneable mechanical properties. These composites demonstrate enhanced flexibility, stiffness, or other desirable characteristics depending on the filler used. Further applications include bitumen binders for concrete or asphalt to confine toxic materials instead of landfilling with potential leeching of toxic substances.[196]

Recycling

While 'recycling' is the most frequently discussed end-of-life treatment for plastics and polymers, for value retention options it is nearer to the bottom. Especially for low-value, high-turnover products, recycling can limit the extraction of virgin materials. Here it is crucial to state that recycling only works if the input streams are very pure and consist of the same composition such as monomers and additives. The tedious separation and selection of recyclable materials through numerous methods leads to different quality levels. This makes it difficult to compete especially with cheap virgin materials such as polyethylene, polypropylene, or polystyrene, even though high value polymers such as HDPE could be recycled nearly 100 times.[197] This is an example of only a few polymers that can be recycled with minimum quality loss, but when collected and separated in sufficient purity, even inverse vulcanised polymers might be potential candidates for efficient recycling.

A first attempt to recover the carbon-based components could be achieved by the reduction of the S_x species to thiols by the addition of Na_2SO_3, which reduces polysulfide linkages to disulfide groups. Subsequent treatment with NaSH splits the disulfide linkages forming –SH and –SSH end groups. This cleavage occurs at both the internal and terminal groups (Scheme 1).

This approach is commercially used to produce Thiokol sealants and high performance disulfide-based resins.[85] The residual thiols produced this way could then be separated and purified and potentially be reused in IV processes or as a base chemical for higher value materials.[198,199] An advantage of this approach could be the input of more inhomogeneous waste streams, as the recovered organic compounds can be purified by



Scheme 1 Reaction scheme of a possible chemical degradation pathway of organic polysulfides.

standard chemical separation methods. This would facilitate the collection and sorting process, as well as the feedback loop of raw materials to the IV manufacturing process.

Recent studies also showed promising results in the environmentally friendly chemical devulcanisation of tyre rubber using choline chloride–urea deep eutectic solvents.[200] With efficiencies of around 50% devulcanisation, this holds great potential not only for vulcanised rubbers, but this could also be transferred to inverse vulcanised materials to depolymerise them and recover the initial organic compounds.

Recently it has been shown that polytrisulfides can be efficiently depolymerised by S–S metathesis reactions with small molecule trisulfides.[56] In this work, Chalker *et al.* introduced a HDPE analogue with trisulfides as breaking points, with the potential for this platform technology to make a wide range of polymers chemically recyclable, including inverse vulcanised polymers. The general approach to incorporate breaking points in polymers, such as ester groups that can be hydrolysed under specific conditions is a widely investigated technology. This could also help to make sulfur polymers easily recyclable and potentially biodegradable, as they break down inverse vulcanised polymers into smaller molecules that can be reused in inverse vulcanisation, as the base material for other sulfur containing materials. Smaller fractions could also improve their metabolisation by sulfur bacteria in the environment. As previously mentioned, initial findings by Chalker *et al.* suggest that polymers based on plant oils can break down by hydrolysis, releasing glyceride fragments and smaller sulfur containing oligomers.[87] This opens up the potential for biological recycling of inverse vulcanised polymers and recovery of valuable materials, such as thiols and glycerides, that could be reintroduced in the IV process or used as lower value base chemicals. However, an in-depth investigation of the behaviour of sulfur polymers under biological conditions is still pending. Lastly, it needs to be noted that not all bio-based cross-linkers are biodegradable when incorporated in a polymeric structure.

Further chemical recycling methods include catalytic pyrolysis, but due to the development of toxic gases upon incineration and sulfur acting as catalyst poison, sulfur containing polymers are not suitable for conventional pyrolysis plants. Selective catalytic oxidation of sulfur components at elevated temperatures, however, generates SO_2 that may ultimately contribute to the production of sulfuric acid. SO_2 can also be used together with H_2S from the IV process for the recovery of elemental sulfur *via* the Claus process, which is a well-established technology and the main source for elemental sulfur in industrial processes, thus contributing to the starting material for sulfur polymers.

Mechanical recycling methods that are commercially applied to grind and reprocess polymer materials that cannot be separated or chemically recycled into lower value products, could also be applied to these materials. Here, mixed waste fractions of different comonomers could be combined and serve as, *i.e.*, bitumen binders, where no specific chemical functionality is required. As a fine granulate with large surfaces, possible downcycling applications can be as adsorber materials for waste water treatment and environmental remediation. It is important to highlight that with an increasing lifespan of products through reusability, repairability or refurbishment, their end-of-life get pushed further down the timeline. Nevertheless, in every product's life cycle there will be a point, where it will be disposed, because the product cannot be used for its purpose anymore. Depending on its properties it might still be considered for repurposing. In order to recover the materials themselves, especially if they consist of limited resources, recycling as closed or open loop recycling should definitely be the aim.

Despite its ecological importance, success often depends on its competitiveness to common waste streams such as landfills and thermal treatment in the context of environmental impact but also economical. Given that its value retention is near the bottom, circular economy concepts such as reduction of materials, design for repairability and the choice of materials should be considered first. Closed loop recycling describes the retention of the material quality, allowing it to be used for the same product or other products with the same material quality. Open loop describes the decrease of material quality, and therefore introducing the material in a different product stream with lower material requirements.[201] Long life spans of products raise a question regarding material availability, as the product is used for several years, its materials can only be reintroduced into the material stream as recyclate after that. If this takes a long time, then a lot of goods are produced while others are still in use, which requires further primary or secondary raw materials from other product streams. This does not mean designing a product with the properties to be recyclable, but that for certain types of products, especially with long life spans, other properties, such as made bio-based materials, easy design, repairability, *etc.* are even more important.

System sustainability

Examining the end-of-life for inverse vulcanised materials is very important as circular economy involves much more than recycling. The most sustainable path – ranging from repair to waste incineration – depends on the specific use case scenario and the ease of recovery of the materials. Our goal should be to keep these materials in their highest value condition for as long as possible. Yet, to enable a concept of circular economy, the infrastructure and technology to collect and sort needs to be implemented. Support from product manufacturers to design objects enabling repair and remanufacturing, as well as recognition from recycling companies and waste management policymakers is crucial if these materials are to be scaled up. Regardless of which type of end-of-life treatment is chosen, it must be guaranteed that the materials do not simply end up in the environment, especially when the products are not biodegradable. An important question that arises when evaluating end-of-life scenarios is the quality and purity of materials that result from any measures except incineration. If the purity is high, a closed-loop recycling could be considered, although in reality an open-loop recycling is more likely.

As for all other phases the details of the products and processes are necessary to make a comparison between different scenarios. Complex, elaborate recycling methods – as necessitated in chemical recycling strategies – require inputs such as chemicals, electricity, heat for the process, and additional waste occurs. Combined with potentially long transportation routes, there is the possibility that the disposal in landfills or through energy recovery could have less environmental impact. While recycling is important to avoid the production of more primary materials, from a life cycle perspective, the amount of materials that need to be recycled and the necessary effort can favour incineration, especially when only the end-of-life phase is considered and not the entire life cycle. While the LCA might deliver results in favour of incineration or landfills, making the end-of-life more environmentally friendly still needs to be discussed, as technologies for recycling could become cheaper, more efficient or available in the future. Also, as highlighted several times, it is very important to mention that GHG emissions are just one part of the environmental impact products and processes generate. Therefore, other impacts, such as water and land use, potential toxicity due to chemical reaction and usage of solvents during recycling, as well as pollution, *etc.* need to be assessed and potential trade-offs need to be discussed.

When introducing different end-of-life scenarios for inverse vulcanisation-based products, it is important that from a social standpoint, the health and safety of the workers and labour rights at the recycling plants or waste incineration plants are guaranteed. Similar to the production phase, preventing pollution to protect workers and local communities needs to be assured. To minimise the pollution, new infrastructure must be created, or established infrastructure has to be adjusted. To implement the necessary infrastructure, communication with the responsible supply chain is crucial to ensure correct handling of the materials. Although it is the customer's responsibility to dispose of the product in the correct waste stream, designers, researchers and everyone involved in the product development should consider how to make it recyclable at the end of its life. Considering the habits of customers in the use phase, communicating and educating the general public about the correct handling and disposal, especially in regards to circular economy is vital to successfully introduce new products such as inverse vulcanisation-based materials.[202] The prevention of uncontrollable spills into the environment, as well as striving to decrease environmental impact should be a concern to everyone in our society.[123] If these materials live up to their claim of sustainability, it should be the highest priority to communicate that in contrast to their substitutes, the use of inverse vulcanisation processes and the resulting products could reduce the environmental impact, thereby promoting the ability of this and future generations to fulfil their needs.[203]

Measuring sustainability

The intertwined climate change and pollution challenges we face cannot be overcome without proper data, collective effort, and transparency. Putting numbers to the problem is the first step to understand its range and develop possible solutions. Sustainability assessment is a multidisciplinary technique to monitor and evaluate sustainable characteristics of products, projects, processes and policies in social, environmental and economic aspects. There are many methods to evaluate sustainability, where each one has its own advantages and disadvantages based on the level of detail provided, the accuracy and precision of the results and the considerations of society, environment and economy, as indicated in Fig. 14. Importantly, they must comprise scope and objectives of assessment, appropriate sustainability indicators, the assessment technique, and finally the interpretation and application of the assessment. In the following section we describe methods that can be used to evaluate inverse vulcanisation on the lab-scale and on an industrial level.

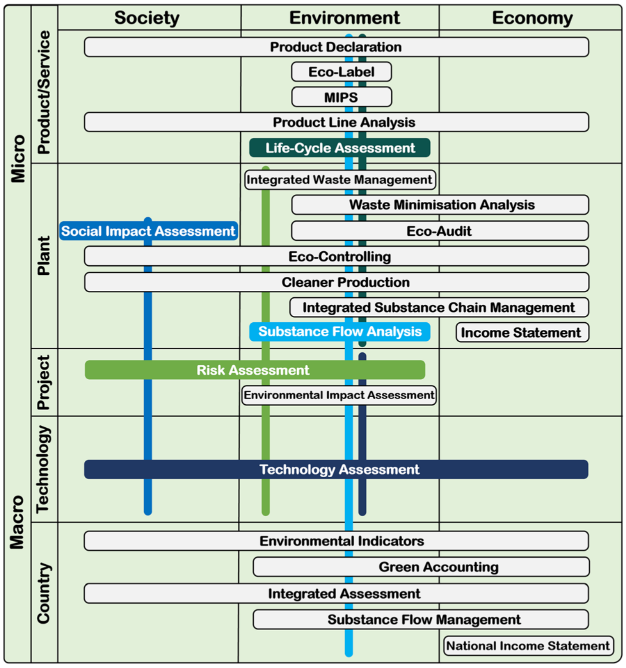


Fig. 14 A structure for important environmental analysis tools arranged by two criteria: the scale of the analysis object—ranging from micro (small) to macro (large)—and the dimension of sustainability (society, environment, and economy).

The E-factor

On an everyday level the conduction of LCAs for simple lab experiments is highly impractical, therefore we want to introduce the Environmental Factor (E-factor) – first established by Roger Sheldon in 1992 – as an efficient and quick tool to evaluate lab-scale synthesis in terms of their environmental footprint.[204] It describes the mass of waste generated per mass of the desired product, meaning less waste equals a lower E-factor with an optimum at 0: $E = m_{\text{waste}} + m_{\text{byproducts}}/m_{\text{product}}$. It is also not limited to simple lab reactions it can also be used to assess whole industrial production lines and factories. Even though it does not include factors such as energy input, which would require other tools such as LCA, it provides good comparison between different manufacturing routes. Furthermore, similar to all environmental considerations, they are highly dependent on the boundaries set for the process. Initially, E-factors were calculated on a gate-to-gate basis – from raw materials entering to products leaving a manufacturing site – focusing only on processes conducted at that site. However, raw materials used in the synthesis, can already be advanced intermediates produced through multi-step processes. Purchasing intermediates rather than producing them on site can already lower the E-factor drastically, but creates inconsistencies in assessing process sustainability. To address this, E-factors should ideally account for the environmental impact of procured raw materials, possibly starting from basic, commercially available raw materials.

If we look at the E-factor of the inverse vulcanisation process, it is mainly dependent on the used comonomers. Since inverse vulcanisation can be conducted in bulk and has an extremely high atom economy of close to 100%, with minor losses to the evolution of by-products such as H_2S, the E-factor can be considered to be close to 0 (Table 3).[205] This factor will change when the reaction is conducted with additional solvents or catalysts. Furthermore, since sulfur itself is a waste product from oil refining and most of the used comonomers are also cheap chemicals from oil refining, the overall E-factor of inverse vulcanisations can be assumed to be very low.

However, since the E-factor does not account for the energy input, additional tools such as life-cycle assessments have to be employed to understand a more detailed and in-depth environmental impact of inverse vulcanised polymers. So, what the E-factor accounts for regarding sustainability, is a simple calculation of the waste generated by polymer production and processing but does not account for other inputs and outputs. It is a tool that gives scientists in the lab the chance to quickly choose a synthetic route that reduces waste, and therefore environmental impacts related to chemical waste. Yet this perspective should have shown that waste is only one small part of a very complex system when it comes to sustainability. As for many other tools, data availability and data quality are crucial and still very limited. However, the biggest point of criticism is that it does not account for an environmental impact. Because waste is reduced it can be assumed that the environmental impact decreases, but it does not provide measurable evidence to connect waste reduction and environmental impacts. At the same time waste reduction can also simply mean a reduction of costs, which is rather an economical point of view. So, the E-factor can act as an incentive to integrate measures regarding sustainability through an easy way, yet to fully incorporate sustainability, the measurement and understanding must go further using tools that measure environmental impacts, one of which is discussed in the following section.

Table 3 E-factors in the chemical industry and an estimated E-factor for inverse vulcanisation

Sector	tonnes per year	E-factor
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–>100
Inverse vulcanisation	<1	<0.1–5 (ref. 205)

A guideline for future life-cycle assessments

Although inverse vulcanised polymers are increasingly discussed in the context of sustainable materials, their environmental performance has not yet been quantitatively assessed. Existing literature often refers to presumed ecological advantages, but these are typically not supported by comprehensive data.[6,33,99,196,206,207] So far, no comprehensive, publicly accessible LCA has been conducted for inverse vulcanised polymers. In the following section, the methodology of LCA is introduced, and important aspects to consider in the environmental evaluation of polymers – particularly in the case of high sulfur polymers – are discussed.

Methodology

The LCA is an instrument for estimating the environmental impact of products or systems over their entire life cycle, from the extraction of raw materials through production and use to disposal.[88] In addition to economic and technical aspects, the ecological impact can be a decisive indicator for making well-founded decisions or evaluating measures. Sustainable development – meeting present needs without compromising the ability of future generations to meet their own needs[203] – requires compliance with planetary boundaries[207] such as climate change, biosphere integrity or changes in terrestrial, freshwater, and oceanic systems. As a quantitative method, the LCA offers valuable guidance as part of the sustainability concept. It enables industry and policymakers to comprehensively record the actual ecological footprint of a product, as it not only considers individual factors such as CO_2 emissions but also includes various impact categories.

The International Organisation for Standardisation has standardised the process with two standards: DIN EN ISO 14040 sets out the principles and framework conditions for life cycle assessments, while DIN EN ISO 14044 defines the requirements for their implementation.[208,209]

The process of an LCA is defined and comprises four phases (Fig. 15). The first phase consists of the definition of objectives and the scope of the study, which determines the framework and content of the study.[209] The second phase is the life cycle inventory, in which all data on the system's relevant input and output flows defined in the first phase are collected and

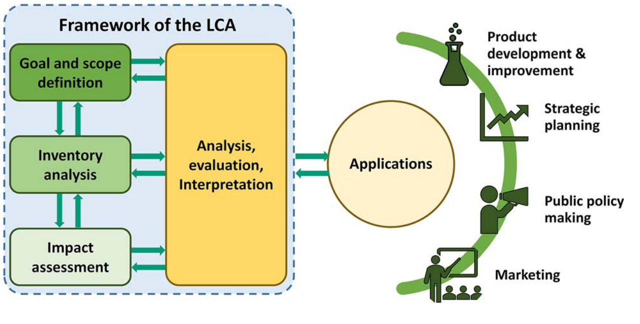


Fig. 15 The four phases of a LCA include goal and scope definition, life cycle inventory, impact assessment, and interpretation. It is an iterative process that supports application in decision making.

calculated.[210] These flows include categories such as energy, raw material and operating material inputs, products, co-products, waste and emissions to air, water and soil.[209]

For better comparability, all recorded flows are related to the functional unit that describes the quantified benefit of the system.[88] The third phase is the impact assessment, which uses the life cycle inventory to determine the potential environmental impacts of the system. It comprises the selection of impact categories, the classification of the life cycle inventory results, and the characterisation of the impact indicators. Optionally, standardisation and weighting of the indicators can follow.[209] In the final phase, the results are analysed and interpreted in the scope of the objective in order to derive conclusions and recommendations for action.[209]

Key issues in ecological assessments of polymers

To address the environmental and human health impacts of plastics, it is essential to conduct an LCA that evaluates the entire lifecycle of plastics, from production to disposal. LCA methodologies provide a comprehensive understanding of the environmental issues associated with plastics, such as greenhouse gas emissions, land use, eutrophication, and toxicity. For example, an LCA methodology used by Ghent University's Sustainable Systems Engineering Group highlights the diverse environmental impacts linked to each stage of the plastic lifecycle.[211] When assessing novel materials such as inverse vulcanised polymers, it is critical to evaluate their environmental performance in replacement scenarios, where they are intended to substitute less sustainable polymers. Moreover, LCA plays a crucial role in assessing the environmental sustainability of polymers not only in cradle-to-gate and recycling scenarios, but also in use-phase contexts, such as extended product lifetimes and avoided impacts through functional replacement. A review of 43 LCA studies reveals that fossil-based, petrochemical polymers are responsible for significant environmental impacts, especially during production and end-of-life management. Recycling of these polymers is effective in reducing energy consumption and mitigating some of the environmental impacts compared to the production of virgin polymers. However, bio-based polymers, although considered more sustainable in certain aspects, tend to require more agricultural land as indicated by LCA results.[212]

Conducting an LCA of inverse vulcanised polymers involves addressing several critical factors to ensure accurate, robust results. Sulfur polymers can offer potential environmental benefits compared to conventional plastics. However, due to their novelty and unique synthesis processes, there are specific challenges in data quality, methodological approaches, and managing uncertainties. This section discusses these key considerations and proposes approaches for a scientifically rigorous LCA of such polymers.

Data quality

Data quality depends on accuracy, completeness, representativeness, and consistency. High-quality LCAs rely on reliable primary data, comprehensive process coverage (geographical, temporal, and technological), and consistent modelling to ensure comparability and reproducibility.[88,209] For inverse vulcanised polymers, accurate environmental impact calculations require comprehensive data on monomer and sulfur inputs, including their origin and quantity. Energy consumption in their synthesis also demands attention. Production often involves high temperatures or the use of catalysts.

Another key challenge is life-cycle inventory data availability. As inverse vulcanised polymers are relatively new, obtaining reliable data specific to their production processes is often difficult. Since they have not yet reached the industrial scale, it is crucial to collaborate with manufacturers to collect valuable primary data. If there is no primary data, using proxies from similar polymer production processes can serve as a temporary solution.

Framework and methodological decisions

Comparing inverse vulcanised polymers to conventional plastics or other specialised polymers enables a clear assessment of their relative environmental impacts, particularly in terms of resource consumption, waste generation, and emissions. This approach helps to contextualise their potential advantages and disadvantages compared to those of existing materials.

End-of-life scenarios are crucial in LCA. Frischknecht highlights two main approaches: the cut-off method assigns recycling impacts to the product using secondary materials, while the avoided burden approach credits the recycling product system for displacing primary production, promoting forward-looking material use and design for recycling.[88,210]

Understanding the end-of-life characteristics of polymers is essential, as their degradation pathways can differ significantly from those of conventional polymers. These pathways may produce unique by-products with varying environmental impacts, which need careful assessment in both natural and industrial waste-processing contexts. Additionally, the recyclability of inverse vulcanised polymers—whether they can be mechanically or chemically recycled, or if they require specialised handling—must be analysed to determine their contribution to a sustainable lifecycle. Potential repurposing or reuse can further enhance sustainability.

LCA is also essential for evaluating strategies that extend product lifetimes. These approaches can significantly reduce environmental impacts by delaying end-of-life processes and avoiding the production of new goods. LCAs can quantify these benefits by accounting for avoided resource extraction, energy use, and emissions. A consistent LCA framework enables fair comparisons between extended-use strategies and conventional linear models.

When quantifying the environmental impact, it is important to use the appropriate impact categories and impact analysis models. For this purpose, various midpoint and endpoint indicators were developed to describe environmental impacts.[210] The impact categories most widely analysed in the literature for plastics recycling are global warming potential, ozone depletion, acidification potential and eutrophication potential. Furthermore, established categories such as land use, ecotoxicity and human toxicity follow.[213]

Uncertainty

The relative novelty of high sulfur polymers introduces significant data uncertainty. Key uncertainty types in LCA include parameter, scenario, and model uncertainty, with methods such as sensitivity analysis and Monte Carlo sampling commonly applied to address these. Basic approaches involve defining minimum and maximum values for parameter uncertainty and exploring alternative scenarios to capture context or model structure uncertainty, supported by qualitative discussions. Intermediate methods refine uncertainty characterisation with probability distributions and expert-reviewed scenarios, often analysed using Monte Carlo simulations. Advanced techniques include screening uncertainty sources exhaustively, incorporating correlations, validating models, and applying global sensitivity analysis for a more comprehensive assessment.[214,215]

In conclusion a comprehensive LCA of inverse vulcanised polymers should carefully address data quality, establish clear comparative baselines, assess end-of-life treatments, evaluate a broad range of environmental impact categories, and explore potential for circularity. Accounting for uncertainty through sensitivity analysis and considering the effects of scale-up can further strengthen the assessment. By following these key issues, researchers can achieve a robust, scientifically valid LCA that accurately reflects the environmental profile of inverse vulcanised polymers.

Life-cycle costing

At the end of the day, sustainability must be affordable. To develop an industrially feasible, full-scale process, a thorough techno-economic assessment is essential. Several process simulation tools are available for such studies; among them, Aspen Plus is one of the most widely used commercial options, while DWSIM offers a reliable free and open-source alternative. A basic flow sheet that includes the essential components of a production plant provides a strong foundation for a meaningful analysis. Both capital expenditures (CAPEX)—the initial investment—and operational expenditures (OPEX) must be considered. In the context of inverse vulcanisation, several key factors are expected to significantly influence OPEX:

- Raw material costs: the primary reactants—sulfur (typically $\sim$£224/t from bulk sources) and comonomers (£787/t)—directly affect production costs. While sulfur is inexpensive, comonomers represent the most significant and often prohibitive cost, making their affordability critical for market competitiveness. Transportation costs may also contribute to the total raw material expense.
- Energy requirements: IV processes require substantial heat input, making energy costs a major operational consideration. Implementing heat integration strategies, such as reusing process heat, can help reduce external energy demand, cut costs, and improve sustainability.
- Emission control: sulfur compound emissions, particularly hydrogen sulfide and sulfur dioxide, necessitate an efficient exhaust after-treatment system to capture and neutralise harmful gases.

By addressing these factors early in the design process, a more cost-effective and sustainable industrial IV process can be achieved.

Outlook

There is no doubt that inverse vulcanised polymers are a highly promising class of materials that can emerge to contribute to global challenges in the fields of environmental pollution, energy storage, construction or even agriculture. After discussing all aspects of the potential lifecycle of inverse vulcanised polymers, the only question remaining is: can it really be sustainable? The short answer is: it depends. The long answer can be separated into the three pillars of sustainability.

Environmental

One of the most direct environmental benefits of inverse vulcanisation is the valorisation of elemental sulfur, which is otherwise stockpiled and poses environmental harm. While the long-term environmental fate and degradation pathways of inverse vulcanised polymers themselves remain under investigation, initial studies suggest a low risk profile. Nonetheless, further research is needed to fully understand their lifecycle and ecological impact to ensure that they are a more environmentally friendly alternative to their commodity counterparts in certain applications. Additionally, the integration of renewable and waste-derived comonomers—such as used cooking oils and upcycled plastic waste—marks a promising step toward a circular economy and especially lower carbon footprints compared to their fossil derived comonomers. However, it is important to note that "renewable" does not automatically equate to "sustainable," as some bio-based monomers fail to demonstrate an improved carbon footprint compared to petrochemical alternatives. Factors such as water and land use for crops also play a crucial role in terms of sustainability. A holistic evaluation of feedstock sourcing and processing is therefore essential.

Economic

Affordability and scalability are probably the most critical aspects for the broader adoption of more sustainable technologies in general and therefore inverse vulcanised polymers as well. Fortunately, the economic case is strong: elemental sulfur, as well as most of the comonomers used so far, is an abundant and inexpensive feedstock, and many polymerisation processes can be carried out without solvents or expensive catalysts. However, to maximise both economic and environmental benefits, synthesis must be efficient, and supply chains must be optimised. Controlling the highly exothermic reaction and making use of the generated energy is crucial to minimise energy input and therefore GHG emissions. This also highly depends on the comonomers used and therefore the respective application. In many cases however, the location of production facilities and the associated transportation requirements are among the most significant contributors to production costs as well as environmental impact. Especially for bulk materials, the production should be as close to the sulfur source as possible. A truly circular process will also require investment in end-of-life treatment strategies tailored to these materials, starting with collections and sorting, which is the most critical part to achieve high value secondary products, and ending with appropriate technologies to maximise the value of the outcoming products, such as mechanical or chemical recycling, repair or remanufacture as well as repurposing of existing materials. Biodegradation should only be considered as a worst-case scenario when a material is released uncontrolled to the environment.

Social

The implementation of inverse vulcanisation technologies at an industrial scale has the potential to create new employment opportunities, particularly in regions where sulfur and compatible feedstocks are readily available. Additionally, the development of cost-effective and high-performance materials from waste streams could enable more equitable access to advanced materials, particularly in applications such as construction, energy storage, or environmental remediation. By converting industrial by-products into valuable resources, we can not only reduce environmental burdens but also drive innovation in socially impactful ways. Yet, negative impacts such as highly exothermic reactions that can undergo thermal runaway and toxic emissions like hydrogen sulfide have to be taken into account. Again, these factors can be controlled by choice of comonomers as well as respective plant design, but still pose reasonable risks for work safety.

Future directions

To fully unlock the huge potential of inverse vulcanised materials as a more sustainable alternative for many applications, future progress will depend on the integration of fundamental chemistry, process engineering and environmental science.

A critical scientific priority lies in advancing our understanding of the reaction mechanisms and resulting polymer network structures. The inherent complexity and diversity of sulfur-rich cross-linked systems call for detailed mechanistic studies, which will enable precision design of polymer architectures tailored to specific applications. Another way to introduce better control and safety is the development of sulfur containing monomers that are then polymerised in a controlled manner. This has been proven to be a complementary concept to conventional inverse vulcanisation by Pyun *et al.* by the reaction of sulfenyl chloride with various allylic monomers to develop linear polymers and segmented block-copolymers.[216] Chalker *et al.* demonstrated that trisulfides are an effective alternative feedstock for the synthesis of IV-like polymers in electrochemical and S–S metathesis polymerisations.[56,62] In this context, computational chemistry—supported by machine learning and artificial intelligence—has the potential to accelerate materials discovery by predicting structure–property relationships, reaction pathways, and performance under targeted conditions. This deeper chemical insight will then help the design of scalable and safe industrial processes. The development of continuous or bulk-scale reactor systems for effective heat management strategies will be a major success factor. Additionally, catalytic systems could help in lowering the energy threshold for inverse vulcanisation, reducing thermal risk and enabling milder reaction conditions. Catalysis may also expand the monomer scope, leading to greater versatility in polymer design.

From a technological and societal perspective, it is essential to improve communication and visibility of inverse vulcanised polymers within the broader scientific community. Increased awareness can foster interdisciplinary collaboration, draw new talent into the field, and catalyse further research. At the same time, small-scale field trials in real-world applications will be vital to demonstrate practical utility and build confidence among industry stakeholders and end users.

On the environmental front, comprehensive investigation into the environmental impact of sulfur-based polymers remains a pressing need. This includes studies on biodegradability, bioaccumulation, toxicity to microorganisms and ecosystems, and potential human health effects. Understanding these aspects is crucial not only for regulatory approval and risk assessment but also for gaining public trust and broadening societal acceptance.

As inverse vulcanised materials approach commercialisation, their integration into existing waste management systems becomes increasingly important. Future work should address strategies for effective end-of-life treatment, including cleaning, sorting, and recycling of high sulfur polymer products from mixed waste streams. The development of such systems must be considered early in the design phase of both materials and products.

Ultimately, the sustainability of these polymers can only be fully understood through methods such as life cycle assessment (LCA), encompassing resource extraction, polymer synthesis, product use, and end-of-life scenarios. These studies must be grounded in real-world data and consider environmental, economic, and social dimensions to determine whether inverse vulcanised polymers can truly offer a lower-impact alternative to conventional materials.

Author contributions

Christian W. Schmitt: conceptualization, writing – original draft, review & editing, visualization. Liam J. Dodd: writing – original draft, review & editing. Julia K. Walz: conceptualization, writing – original draft, review & editing. Leon Deterding: writing – original draft, review & editing. Patrick Lott: writing – original draft, review & editing. Alexander P. Grimm: writing – original draft, review & editing. Michael P. Shaver: review & editing. Tom Hasell: review & editing. Patrick Théato: review & editing, supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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Notes and references

1 T. E. Commission, *The European Green Deal*, The European Council, Brussels, 2019.
2 T. E. Commission, *Chemical Strategy for Sustainability towards a Toxic-free Environment*, The European Council, Brussels, 2020.
3 G. C. I. Association, *VCI Position on Chemicals Strategy for Sustainability*, German Chemical Industry Association, (VCI.de), 2020.
4 C. Goodyear, *US Pat.*, US3633, 1844.
5 L. J. Dodd, *RSC Appl. Polym.*, 2025, **3**, 10–42.
6 A. Abbasi, M. M. Nasef and W. Z. N. Yahya, *Green Mater.*, 2020, **8**, 172–180.
7 M. J. H. Worthington, R. L. Kucera and J. M. Chalker, *Green Chem.*, 2017, **19**, 2748–2761.
8 K. Winnacker, *Chemische Technik*, Wiley-VCH, 2003, vol. 3.
9 U. S. G. Survey, *Mineral Commodity Summaries 2025*, Reston, VA, 2025.
10 M. Maslin, L. Van Heerde and S. Day, *Geogr. J.*, 2022, **188**, 498–505.
11 A.-M. O. Mohamed and M. E. Gamal, *Sulfur Concrete for the Construction Industry*, J. Ross Publishing, 1966.
12 C. M. Griffith, J. E. Woodrow and J. N. Seiber, *Pest Manage. Sci.*, 2015, **71**, 1486–1496.
13 J. G. Wagenfeld, K. Al-Ali, S. Almheiri, A. F. Slavens and N. Calvet, *Waste Manage.*, 2019, **95**, 78–89.
14 K. Kuklińska, L. Wolska, J. Namieśnik, M. Cieszynska and L. Wolska, *TrAC, Trends Anal. Chem.*, 2013, **48**, 14–21.
15 J. J. Germida and H. H. Janzen, *Fert. Res.*, 1993, **35**, 101–114.
16 K. T. Osman, *Management of Soil Problems*, Springer Cham, 2018.
17 A. E. Robinson, J. V. Marra and L. O. Amberg, *I&EC Product Research and Development*, 1961, vol. 1, pp. 78–82.
18 A. R. Kemp and F. S. Malm, *Ind. Eng. Chem.*, 1934, **27**, 141–146.
19 S. Penczek, R. Slazak and A. Duda, *Nature*, 1978, **273**, 738.
20 C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, Pearson Education Limited (Verlag), 5th edn, 2018.
21 F. Fairbrother, G. Gee and G. T. Merrall, *J. Polym. Sci.*, 2003, **16**, 459–469.
22 Q. Lian, Y. Li, K. Li, J. Cheng and J. Zhang, *Macromolecules*, 2017, **50**, 803–810.
23 Y. Lyu and Q. Su, *Polym. Polym. Compos.*, 2023, **31**, DOI: 10.1177/09673911231181255.
24 M. M. Coleman, J. R. Shelton and J. L. Koenig, *Product R&D*, 1974, **13**, 154.
25 S. Mostoni, P. Milana, B. Di Credico, M. D'Arienzo and R. Scotti, *Catalysts*, 2019, **9**, 664.
26 B. Meyer, *Chem. Rev.*, 1975, **76**, 367–388.
27 W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, A. Somogyi, P. Theato, M. E. Mackay, Y. E. Sung, K. Char and J. Pyun, *Nat. Chem.*, 2013, **5**, 518–524.
28 A. Medhat, W. Shehata, F. Gad and A. Bhran, *J. Eng. Appl. Sci.*, 2024, **71**, 109.
29 A. Frye, J. Liu, L. Neal and F. Li, *ACS Sustain. Chem. Eng.*, 2024, **12**, 14059–14069.
30 J. M. Chalker, M. J. H. Worthington, N. A. Lundquist and L. J. Esdaile, *Top. Curr. Chem.*, 2019, **377**, 16.
31 S. J. Tonkin, L. N. Pham, J. R. Gascooke, M. R. Johnston, M. L. Coote, C. T. Gibson and J. M. Chalker, *Adv. Opt. Mater.*, 2023, **11**, 2300058.
32 D. H. Kim, W. Jang, K. Choi, J. S. Choi, J. Pyun, J. Lim, K. Char and S. G. Im, *Sci. Adv.*, 2020, **6**, eabb5320.
33 H. Shen, B. Zheng and H. Zhang, *Polym. Rev.*, 2024, **64**, 1211–1266.
34 X. Wu, J. A. Smith, S. Petcher, B. Zhang, D. J. Parker, J. M. Griffin and T. Hasell, *Nat. Commun.*, 2019, **10**, 647.
35 A. P. Grimm, J. M. Scheiger, P. W. Roesky and P. Théato, *Polym. Chem.*, 2022, **13**, 5852–5860.
36 J. Jia, J. Liu, Z. Q. Wang, T. Liu, P. Yan, X. Q. Gong, C. Zhao, L. Chen, C. Miao, W. Zhao, S. D. Cai, X. C. Wang, A. I. Cooper, X. Wu, T. Hasell and Z. J. Quan, *Nat. Chem.*, 2022, **14**, 1249–1257.
37 P. Yan, W. Zhao, F. McBride, D. Cai, J. Dale, V. Hanna and T. Hasell, *Nat. Commun.*, 2022, **13**, 4824.
38 L. He, J. Yang, H. Jiang, H. Zhao and H. Xia, *Ind. Eng. Chem. Res.*, 2023, **62**, 9587–9594.
39 R. Tedjini, R. Viveiros, T. Casimiro and V. D. B. Bonifácio, *RSC Mechanochem.*, 2024, **1**, 176–180.
40 B. H. Stuart, *Polymer Analysis*, John Wiley & Sons, New York, 2002.
41 V. K. Shankarayya Wadi, K. K. Jena, S. Z. Khawaja, K. Yannakopoulou, M. Fardis, G. Mitrikas, M. Karagianni, G. Papavassiliou and S. M. Alhassan, *ACS Omega*, 2018, **3**, 3330–3339.
42 B. Zheng, L. Zhong, X. Wang, P. Lin, Z. Yang, T. Bai, H. Shen and H. Zhang, *Nat. Commun.*, 2024, **15**, 5507.
43 Z. Sun, M. Xiao, S. Wang, D. Han, S. Song, G. Chen and Y. Meng, *J. Mater. Chem. A*, 2014, **2**, 9280.
44 L. J. Dodd, W. Sandy, R. A. Dop, B. Zhang, A. Lunt, D. R. Neill and T. Hasell, *Polym. Chem.*, 2023, **14**, 4064–4078.
45 H. K. Lin and Y. L. Liu, *Macromol. Rapid Commun.*, 2018, **39**, e1700832.
46 S. Sahu and B. Lochab, *ACS Sustain. Chem. Eng.*, 2024, **12**, 7126–7135.
47 M. Arslan, B. Kiskan and Y. Yagci, *Sci. Rep.*, 2017, **7**, 5207.
48 S. Park, M. Chung, A. Lamprou, K. Seidel, S. Song, C. Schade, J. Lim and K. Char, *Chem. Sci.*, 2022, **13**, 566–572.
49 Y.-S. Lai and Y.-L. Liu, *Polym. Chem.*, 2024, **15**, 1748–1757.
50 A. Abbasi, W. Z. N. Yahya, M. M. Nasef, M. Moniruzzaman and A. S. M. Ghumman, *Polym. Polym. Compos.*, 2021, **29**, S1446–S1456.
51 J. M. Scheiger, M. Hoffmann, P. Falkenstein, Z. Wang, M. Rutschmann, V. W. Scheiger, A. Grimm, K. Urbschat,

T. Sengpiel, J. Matysik, M. Wilhelm, P. A. Levkin and P. Theato, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114896.

52 A. Abbasi, M. M. Nasef, W. Z. N. Yahya, M. Moniruzzaman and A. S. M. Ghumman, *Eur. Polym. J.*, 2021, **143**, 110202.

53 A. P. Grimm, M. Plank, A. Stihl, C. W. Schmitt, D. Voll, F. H. Schacher, J. Lahann and P. Theato, *Angew. Chem., Int. Ed.*, 2024, **63**, e202411010.

54 I. Gomez, D. Mecerreyes, J. A. Blazquez, O. Leonet, H. Ben Youcef, C. Li, J. L. Gómez-Cámer, O. Bondarchuk and L. Rodriguez-Martinez, *J. Power Sources*, 2016, **329**, 72–78.

55 J. J. Dale, S. Petcher and T. Hasell, *ACS Appl. Polym. Mater.*, 2022, **4**, 3169–3173.

56 H. Patel, A. Tikoalu, J. Smith, Z. Pei, R. Shapter, S. Tonkin, P. Yan, W. Bloch, M. Johnston, J. Harmer, C. Gibson, M. Perkins, T. Hasell, M. Coote, Z. Jia and J. Chalker, *ChemRxiv* 2025.

57 M. Mann, T. P. Nicholls, H. D. Patel, L. S. Lisboa, J. M. M. Pople, L. N. Pham, M. J. H. Worthington, M. R. Smith, Y. Yin, G. G. Andersson, C. T. Gibson, L. J. Esdaile, C. E. Lenehan, M. L. Coote, Z. Jia and J. M. Chalker, *Nat Sustainability*, 2025.

58 I. P. Gerothanassis and L. B. Kridvin, *Molecules*, 2024, **29**, 3301.

59 J. Pyun, C. F. Carrozza, S. Silvano, L. Boggioni, S. Losio, A. R. de Angelis and W. O'Neil Parker Jr, *J. Polym. Sci.*, 2022, **60**, 3471–3477.

60 J. Bao, K. P. Martin, E. Cho, K. S. Kang, R. S. Glass, V. Coropceanu, J. L. Bredas, W. O. Parker, Jr., J. T. Njardarson and J. Pyun, *J. Am. Chem. Soc.*, 2023, **145**, 12386–12397.

61 S. Penczek, M. Cypryk, J. Pretula, K. Kaluzynski and P. Lewinski, *Prog. Polym. Sci.*, 2024, **152**, 101818.

62 J. M. M. Pople, T. P. Nicholls, L. N. Pham, W. M. Bloch, L. S. Lisboa, M. V. Perkins, C. T. Gibson, M. L. Coote, Z. Jia and J. M. Chalker, *J. Am. Chem. Soc.*, 2023, **145**, 11798–11810.

63 T. S. Kleine, T. Lee, K. J. Carothers, M. O. Hamilton, L. E. Anderson, L. Ruiz Diaz, N. P. Lyons, K. R. Coasey, W. O. Parker, Jr., L. Borghi, M. E. Mackay, K. Char, R. S. Glass, D. L. Lichtenberger, R. A. Norwood and J. Pyun, *Angew. Chem., Int. Ed.*, 2019, **58**, 17656–17660.

64 L. J. Dodd, C. Lima, D. Costa-Milan, A. R. Neale, B. Saunders, B. Zhang, A. Sarua, R. Goodacre, L. J. Hardwick, M. Kuball and T. Hasell, *Polym. Chem.*, 2023, **14**, 1369–1386.

65 J. A. Smith, X. Wu, N. G. Berry and T. Hasell, *J. Polym. Sci., Part A: Polym. Chem.*, 2018, **56**, 1777–1781.

66 M. Mann, T. Nicholls, H. Patel, L. Lisboa, J. Pople, L. N. Pham, M. Worthington, M. Smith, Y. Yin, G. Andersson, C. Gibson, L. Esdaile, C. Lenehan, M. Coote, Z. Jia and J. Chalker, *ChemRxiv*, 2024.

67 J. Jumper, R. Evans, A. Pritzel, T. Green, M. Figurnov, O. Ronneberger, K. Tunyasuvunakool, R. Bates, A. Zidek, A. Potapenko, A. Bridgland, C. Meyer, S. A. A. Kohl, A. J. Ballard, A. Cowie, B. Romera-Paredes, S. Nikolov, R. Jain, J. Adler, T. Back, S. Petersen, D. Reiman, E. Clancy, M. Zielinski, M. Steinegger, M. Pacholska, T. Berghammer, S. Bodenstein, D. Silver, O. Vinyals, A. W. Senior, K. Kavukcuoglu, P. Kohli and D. Hassabis, *Nature*, 2021, **596**, 583–589.

68 H. Tran, R. Gurnani, C. Kim, G. Pilania, H.-K. Kwon, R. P. Lively and R. Ramprasad, *Nat. Rev. Mater.*, 2024, **9**, 866–886.

69 D. Reike, W. J. V. Vermeulen and S. Witjes, *Resour., Conserv. Recycl.*, 2018, **135**, 246–264.

70 T. Keijer, V. Bakker and J. C. Slootweg, *Nat. Chem.*, 2019, **11**, 190–195.

71 J. H. C. K. Kümmerer and V. G. Zuin, *Science*, 2020, **367**, 369–370.

72 C. Silvestri, L. Silvestri, A. Forcina, G. Di Bona and D. Falcone, *J. Cleaner Prod.*, 2021, **294**, 126137.

73 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.

74 M. P. Crockett, A. M. Evans, M. J. Worthington, I. S. Albuquerque, A. D. Slattery, C. T. Gibson, J. A. Campbell, D. A. Lewis, G. J. Bernardes and J. M. Chalker, *Angew. Chem., Int. Ed.*, 2016, **55**, 1714–1718.

75 K. S. Kang, A. Phan, C. Olikagu, T. Lee, D. A. Loy, M. Kwon, H. J. Paik, S. J. Hong, J. Bang, W. O. Parker, Jr., M. Sciarra, A. R. de Angelis and J. Pyun, *Angew. Chem., Int. Ed.*, 2021, **60**, 22900–22907.

76 M. J. H. Worthington, R. L. Kucera, I. S. Albuquerque, C. T. Gibson, A. Sibley, A. D. Slattery, J. A. Campbell, S. F. K. Alboaiji, K. A. Muller, J. Young, N. Adamson, J. R. Gascooke, D. Jampaiah, Y. M. Sabri, S. K. Bhargava, S. J. Ippolito, D. A. Lewis, J. S. Quinton, A. V. Ellis, A. Johs, G. J. L. Bernardes and J. M. Chalker, *Chemistry*, 2017, **23**, 16219–16230.

77 A. Nayeem, M. F. Ali and J. H. Shariffuddin, *Chem. Eng. Technol.*, 2022, **45**, 971–978.

78 A. Nayeem, M. F. Ali and J. H. Shariffuddin, *J. Environ. Chem. Eng.*, 2024, **12**, 111853.

79 M. K. Lauer, M. S. Karunarathna, A. G. Tennyson and R. C. Smith, *Mater. Adv.*, 2020, **1**, 590–594.

80 M. K. Lauer, A. G. Tennyson and R. C. Smith, *ACS Appl. Polym. Mater.*, 2020, **2**, 3761–3765.

81 T. Sehn, J. Fanelli, L. Wahl and M. A. R. Meier, *RSC Sustain.*, 2025, **3**, 291–299.

82 S. Afonso and H. Mutlu, *Eur. J. Lipid Sci. Technol.*, 2025, e70018.

83 I. Gomez, A. F. De Anastro, O. Leonet, J. A. Blazquez, H. J. Grande, J. Pyun and D. Mecerreyes, *Macromol. Rapid Commun.*, 2018, **39**, e1800529.

84 D. Wang, J. Chen, Z. Tang, R. Huang, Y. Xiao, J. Chen, P. Yin, B. Guo and L. Zhang, *Macromolecules*, 2024, **57**, 470–480.

85 A. Mahon, *PhD Thesis*, University of Warwick, UK, 1996.

86 S. F. Valle, A. S. Giroto, R. Klaic, G. G. F. Guimarães and C. Ribeiro, *Polym. Degrad. Stab.*, 2019, **162**, 102–105.

87 M. Mann, J. E. Kruger, F. Andari, J. McErlean, J. R. Gascooke, J. A. Smith, M. J. H. Worthington, C. C. C. McKinley, J. A. Campbell, D. A. Lewis, T. Hasell, M. V. Perkins and J. M. Chalker, *Org. Biomol. Chem.*, 2019, **17**, 1929–1936.

88 R. Frischknecht, *Lehrbuch für Ökobilanzierung*, Springer-Verlag GmbH, Deutschland, 2020.
89 N. Loste, E. Roldan and B. Giner, *Environ. Sci. Pollut. Res. Int.*, 2020, **27**, 6215–6227.
90 J. J. Griebel, G. Li, R. S. Glass, K. Char and J. Pyun, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **53**, 173–177.
91 M. J. H. Worthington, C. J. Shearer, L. J. Esdaile, J. A. Campbell, C. T. Gibson, S. K. Legg, Y. Yin, N. A. Lundquist, J. R. Gascooke, I. S. Albuquerque, J. G. Shapter, G. G. Andersson, D. A. Lewis, G. J. L. Bernardes and J. M. Chalker, *Adv. Sustainable Syst.*, 2018, **2**, 1800024.
92 J. M. Chalker, M. Mann, M. J. H. Worthington and L. J. Esdaile, *Org. Mater.*, 2021, **03**, 362–373.
93 J. W. Gooch, in *Encyclopedic Dictionary of Polymers*, Springer, New York, 2011.
94 J. J. Dale, J. Stanley, R. A. Dop, G. Chronowska-Bojczuk, A. J. Fielding, D. R. Neill and T. Hasell, *Eur. Polym. J.*, 2023, **195**.
95 J. Dale, *Dissertation Thesis*, University of Liverpool, United Kingdom, 2024.
96 K. Y. -seok, K. D. -gyun, Ji Mok, Y. Y. -jae, P. S. -min and B. Hwa, KR1020210050818A, 2021.
97 Y. Ren, H. Shui, C. Peng, H. Liu and Y. Hu, *Fluid Phase Equilib.*, 2011, **312**, 31–36.
98 Y. A. Wickramasingha, F. Stojcevski, D. J. Eyckens, D. J. Hayne, J. M. Chalker and L. C. Henderson, *Macromol. Mater. Eng.*, 2023, **309**, 2300298.
99 A. S. M. Ghumman, M. M. Nasef, M. R. Shamsuddin and A. Abbasi, *Polym. Polym. Compos.*, 2020, **29**, 1333–1352.
100 Z. Abo-Shanab, A. Altalhi, M. Noh, A. farag, A. Mansour, M. Elshafie, U. Kandil and E. Azmy, *Egypt. J. Chem.*, 2023.
101 C. M. Marshall, J. Molineux, K. S. Kang, V. Kumirov, K. J. Kim, R. A. Norwood, J. T. Njardarson and J. Pyun, *J. Am. Chem. Soc.*, 2024, **146**, 24061–24074.
102 https://www.cost.eu/, 27.05.2025.
103 A method for preparing sulfur-containing polymer by photocatalytic reverse vulcanization at room temperature, *Chinese Pat.*, CN112831047A, Northwest Normal University, 2021.
104 B. Zhang, L. J. Dodd, P. Yan and T. Hasell, *React. Funct. Polym.*, 2021, **161**, 104865.
105 Q. Pan, Q. Hong, Y. Fan, X. Sun, W. Huang, N. Yan, Z. Qu and H. Xu, *Sep. Purif. Technol.*, 2024, **333**, 125917.
106 L. J. Dodd, Ö. Omar, X. Wu and T. Hasell, *ACS Catal.*, 2021, **11**, 4441–4455.
107 H. Zhou and V. DeFlorio, Catalysts for making polymeric materials from elemental sulfur and the method of using the same, *US Pat.*, US20200346196A1, ExxonMobil Technology and Engineering Co, 2020.
108 M. Mousavi, T. Zhou, R. Liu, Z. Dong and E. H. Fini, *J. Environ. Chem. Eng.*, 2024, **12**, 111687.
109 V. Diniz, J. C. Bear, S. Rath and C. R. Crick, *Surf. Interfaces*, 2024, **51**, 104691.
110 M. Z. Hauschild, R. K. Rosenbaum and S. I. Olsen, *Life Cycle Assessment - Theory and Practice*, Springer International Publishing AG, 2018.
111 https://apps.carboncloud.com/climatehub/product-reports/id/4135729823377, 08.05.2025.
112 P. Fobl, *Carbon Footprint Statement DCPD*, ORLEN Unipetrol, Czech Republic, 2023.
113 Styrene production, *From Ethyl Benzene Dehydrogenation – RER Styrene*, 2024,.
114 https://apps.carboncloud.com/climatehub/product-reports/id/3298965659284, 08.05.2025.
115 T. D. Alcock, D. E. Salt, P. Wilson and S. J. Ramsden, *Sci. Total Environ.*, 2022, **829**, 154539.
116 N. Jungbluth, M. F. Emmenegger, F. Dinkel, C. Stettler, G. Doka, M. Chudacoff, A. Dauriat, E. Gnansounou, M. Spielmann, J. Sutter, N. Kljun, M. Keller and K. Schleiss, *Life Cycle Inventories of Bioenergy*, Swiss Centre for Life Cycle Inventories, Dübendorf, 2007.
117 K. Patel and S. K. Singh, *Environ. Dev. Sustain.*, 2024.
118 S. Nizamuddin, A. J. Baloch, C. Chen, M. Arif and N. M. Mubarak, *Int. Biodeterior. Biodegrad.*, 2024, **195**.
119 E. A. R. Zuiderveen, K. J. J. Kuipers, C. Caldeira, S. V. Hanssen, M. K. van der Hulst, M. M. J. de Jonge, A. Vlysidis, R. van Zelm, S. Sala and M. A. J. Huijbregts, *Nat. Commun.*, 2023, **14**, 8521.
120 R. T. Mathers, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **50**, 1–15.
121 N. Winterton, *Clean Technol. Environ. Policy*, 2021, **23**, 2499–2522.
122 N. Thonemann, A. Schulte and D. Maga, *Sustainability*, 2020, **12**, 1192.
123 C. B. N. M. Traverso, S. Neugebauer, E. Ekener, T. Schaubroeck, S. R. Garrido, M. Berger, S. Valdivia, A. Lehmann, M. Finkbeiner and G. Arcese, *Guidelines for Social Life Cycle Assessment of Products and Organizations 2020*, United Nations Environment Programme (UNEP), 2020.
124 S. W. K. Lowig, *Ann. Phys.*, 1839, **46**, 84–91.
125 D. A. Boyd, *Angew. Chem., Int. Ed.*, 2016, **55**, 15486–15502.
126 H. Mutlu, E. B. Ceper, X. Li, J. Yang, W. Dong, M. M. Ozmen and P. Theato, *Macromol. Rapid Commun.*, 2019, **40**, e1800650.
127 Y. Teng, Q. Zhou and P. Gao, *Crit. Rev. Environ. Sci. Technol.*, 2019, **49**, 2314–2358.
128 K. W. Park and E. M. Leitao, *Chem. Commun.*, 2021, **57**, 3190–3202.
129 C. King-Poole and H. Thérien-Aubin, *Adv. Funct. Mater.*, 2024, **34**.
130 T. Lee, P. T. Dirlam, J. T. Njardarson, R. S. Glass and J. Pyun, *J. Am. Chem. Soc.*, 2022, **144**, 5–22.
131 H. Berk, M. Kaya, M. Topcuoglu, N. Turkten, Y. Karatas and A. Cihaner, *React. Funct. Polym.*, 2023, **187**, 105581.
132 S. Cherumukkil, S. Agrawal and R. V. Jasra, *ChemistrySelect*, 2023, **8**, e202204428.
133 H. Yu, S. Lin, D. Sun and Q. Pan, *High Perform. Polym.*, 2020, **32**, 729–737.
134 J. Pyun and R. A. Norwood, *Prog. Polym. Sci.*, 2024, **156**, 101865.

135 T. S. Kleine, R. S. Glass, D. L. Lichtenberger, M. E. Mackay, K. Char, R. A. Norwood and J. Pyun, *ACS Macro Lett.*, 2020, **9**, 245–259.

136 P. W. Atkins and J. D. Paula, *Atkins' Physical Chemistry, 10th Edition*, Oxford University Press, Oxford, 2014.

137 J. Molineux, T. Lee, K. J. Kim, K. S. Kang, N. P. Lyons, A. Nishant, T. S. Kleine, S. W. Durfee, J. Pyun and R. A. Norwood, *Adv. Opt. Mater.*, 2023.

138 D. A. Boyd, V. Q. Nguyen, C. C. McClain, F. H. Kung, C. C. Baker, J. D. Myers, M. P. Hunt, W. Kim and J. S. Sanghera, *ACS Macro Lett.*, 2019, **8**, 113–116.

139 D.-C. Pyun and R. Liang, 3D-printing of ultra-high refractive index polymers, *US Pat.*, US10920020B2, University of Arizona, 2017.

140 Z. W. Seh, Y. Sun, Q. Zhang and Y. Cui, *Chem. Soc. Rev.*, 2016, **45**, 5605–5634.

141 Q. Zhang, Q. Huang, S. M. Hao, S. Deng, Q. He, Z. Lin and Y. Yang, *Adv. Sci.*, 2022, **9**, e2103798.

142 G. Gao, X. Sun and L.-W. Wang, *J. Mater. Chem. A*, 2020, **8**, 21711–21720.

143 J. Neumann, M. Petranikova, M. Meeus, J. D. Gamarra, R. Younesi, M. Winter and S. Nowak, *Adv. Energy Mater.*, 2022, **12**, 2102917.

144 L. Schwich, P. Sabarny and B. Friedrich, *Metals*, 2020, **10**, 1513.

145 J. Yan, X. Liu and B. Li, *Adv. Sci.*, 2016, **3**, 1600101.

146 H. Song, K. Munch, X. Liu, K. Shen, R. Zhang, T. Weintraut, Y. Yusim, D. Jiang, X. Hong, J. Meng, Y. Liu, M. He, Y. Li, P. Henkel, T. Brezesinski, J. Janek and Q. Pang, *Nature*, 2025, **637**, 846–853.

147 D. S. Thomas, *Cost-Effective Environmental Sustainability - A Focus on the Circular Economy*, National Institute of Standards and Technology, Gaithersburg, 2023.

148 K. Jomova, S. Y. Alomar, E. Nepovimova, K. Kuca and M. Valko, *Arch. Toxicol.*, 2025, **99**, 153–209.

149 R. Shrestha, S. Ban, S. Devkota, S. Sharma, R. Joshi, A. P. Tiwari, H. Y. Kim and M. K. Joshi, *J. Environ. Chem. Eng.*, 2021, **9**, 105688.

150 H.-C. Hsi, M. J. Rood, M. ASCE, M. Rostam-Abadi, S. Chen and R. Chang, *J. Environ. Eng.*, 2002, **128**, 1080–1089.

151 J. J. Dale, M. W. Smith and T. Hasell, *Adv. Funct. Mater.*, 2024, **34**.

152 X. Deng, R. A. Dop, D. Cai, D. R. Neill and T. Hasell, *Adv. Funct. Mater.*, 2024.

153 X. Zhou, Y. Cui, X. Xun, J. Jia, X.-C. Wang and Z.-J. Quan, *Sep. Purif. Technol.*, 2025, **365**.

154 M. L. Eder, C. B. Call and C. L. Jenkins, *ACS Appl. Polym. Mater.*, 2022, **4**, 1110–1116.

155 T. Hasell, D. J. Parker, H. A. Jones, T. McAllister and S. M. Howdle, *Chem. Commun.*, 2016, **52**, 5383–5386.

156 S. Petcher, D. J. Parker and T. Hasell, *Environ. Sci.:Water Res. Technol.*, 2019, **5**, 2142–2149.

157 https://www.spiegel.de/geschichte/deepwater-horizon-explosion-2010-das-hoellen-bohrloch-a-1ba2a13e-6774-4fff-ba1e-9acc3c0b590e, 14.05.2025.

158 M. W. Thielke, L. A. Bultema, D. D. Brauer, B. Richter, M. Fischer and P. Theato, *Polymers*, 2016, **8**, 266.

159 J. M. Scheiger, C. Direksilp, P. Falkenstein, A. Welle, M. Koenig, S. Heissler, J. Matysik, P. A. Levkin and P. Theato, *Angew. Chem., Int. Ed.*, 2020, **59**, 18639–18645.

160 N. A. Lundquist and J. M. Chalker, *Sustainable Mater. Technol.*, 2020, **26**, e00222.

161 D. B. Paul, P. J. Hanhela and R. H. E. Huang, in *Adhesives, Sealants, and Coatings for Space and Harsh Environments*, ed. L.-H. Lee, Plenum Press, New York, 1988, pp. 269–280.

162 M. Shin, K. Kim, S.-W. Gwon and S. Cha, *Constr. Build. Mater.*, 2014, **69**, 167–176.

163 M. J. Graham, C. V. Lopez, C. P. Maladeniya, A. G. Tennyson and R. C. Smith, *J. Appl. Polym. Sci.*, 2023, **140**.

164 http://www.sulphuric-acid.com/techmanual/storage/trans_sulphur.htm, 23.06.2025.

165 https://debontegroup.com/en/innovations/thiocrete/, 14.05.2025.

166 J. Wreczycki, Y. Demchuk, D. M. Bielinski, M. Bratychak, V. Gunka, R. Anyszka and T. Gozdek, *Materials*, 2022, **15**, 1774.

167 K. A. Tisdale, C. P. Maladeniya, C. V. Lopez, A. G. Tennyson and R. C. Smith, *J. Compos. Sci.*, 2023, **7**, 35.

168 M. Zakertabrizi, E. Hosseini, S. Sukumaran, A. H. Korayem and E. H. Fini, *Resour., Conserv. Recycl.*, 2021, **174**, 105778.

169 I. Bu Najmah, N. A. Lundquist, M. K. Stanfield, F. Stojcevski, J. A. Campbell, L. J. Esdaile, C. T. Gibson, D. A. Lewis, L. C. Henderson, T. Hasell and J. M. Chalker, *ChemSusChem*, 2021, **14**, 2352–2359.

170 D. Gilfillan, G. Marland, R. A. T. Boden, *Global, Regional, and National Fossil-Fuel CO2 Emissions: 1751-2017, ESS-DIVE repository*, 2020, doi:DOI: 10.15485/1712447,.

171 J. Farfan, M. Fasihi and C. Breyer, *J. Cleaner Prod.*, 2019, **217**, 821–835.

172 L. O. Fuentes-Lara, J. Medrano-Macias, F. Perez-Labrada, E. N. Rivas-Martinez, E. L. Garcia-Enciso, S. Gonzalez-Morales, A. Juarez-Maldonado, F. Rincon-Sanchez and A. Benavides-Mendoza, *Molecules*, 2019, **24**.

173 A. S. M. Ghumman, R. Shamsuddin, M. M. Nasef, E. G. Krivoborodov, S. Ahmad, A. A. Zanin, Y. O. Mezhuev and A. Abbasi, *Polymers*, 2021, **13**.

174 A. S. M. Ghumman, R. Shamsuddin, M. M. Nasef, C. Maucieri, O. U. Rehman, A. A. Rosman, M. I. Haziq and A. Abbasi, *Agronomy*, 2021, **12**.

175 A. S. M. Ghumman, R. Shamsuddin, M. M. Nasef, W. Z. N. Yahya, A. Abbasi and H. Almohamadi, *Sci. Total Environ.*, 2022, **846**, 157417.

176 S. F. do Valle, A. S. Giroto, H. P. G. Reis, G. G. F. Guimaraes and C. Ribeiro, *J. Agric. Food Chem.*, 2021, **69**, 2392–2402.

177 S. F. Valle, A. S. Giroto and C. Ribeiro, *ACS Appl. Polym. Mater.*, 2023, **5**, 6941–6949.

178 V. Pimolsiriphol, P. Saeoui and C. Sirisinha, *Polym.-Plast. Technol. Eng.*, 2007, **46**, 113–121.

179 https://www.theaa.com/driving-advice/safety/tyre-life-and-age, 08.05.2025.

180 A. T. Wolf, *Environmental Effects on Sealants*, 1991.

181 H. E. Ashton, Division of Building Research, *Weathering of Organic Building Materials*, 1969.

182 A. T. Wolf, *Polym. Degrad. Stab.*, 1989, **23**, 135–163.

183 J. Qiu, Z. Huang, B. Huang, G. Wang and L. Zhou, *Macromol. Mater. Eng.*, 2022, **307**.

184 M. F. van Os, M. G. A. Nooijens, A. van Renesse van Duivenbode, P. C. Tromp, E. M. Hoppener, K. Grigoriadi, A. Boersma and L. A. Parker, *Chemosphere*, 2025, **372**, 144121.

185 M. S. Karunarathna, A. G. Tennyson and R. C. Smith, *J. Mater. Chem. A*, 2020, **8**, 548–553.

186 M. S. Karunarathna, C. P. Maladeniya, M. K. Lauer, A. G. Tennyson and R. C. Smith, *RSC Adv.*, 2023, **13**, 3234–3240.

187 J. H. Hwang, J. M. Lee, J. H. Seo, G. Y. Noh, W. Byun, S. Kim, W. Lee, S. Park, D.-G. Kim and Y. S. Kim, *Green Chem.*, 2023, **25**, 4641–4646.

188 S. J. Tonkin, C. T. Gibson, J. A. Campbell, D. A. Lewis, A. Karton, T. Hasell and J. M. Chalker, *Chem. Sci.*, 2020, **11**, 5537–5546.

189 S. Church, S. J. Harris, A. Rattana and J. F. Watts, *Surf. Interface Anal.*, 2002, **34**, 19–24.

190 A. M. Usmani, *Polym.-Plast. Technol. Eng.*, 2006, **19**, 165–199.

191 K. Scrivener and N. De Belie, in *Performance of Cement-Based Materials in Aggressive Aqueous Environments*, 2013, pp. 305–318.

192 D. E. Canfield, B. Thamdrup and S. Fleischer, *Limnol. Oceanogr.*, 2003, **43**, 253–264.

193 H. Satoh, M. Odagiri, T. Ito and S. Okabe, *Water Res.*, 2009, **43**, 4729–4739.

194 J. J. Griebel, N. A. Nguyen, S. Namnabat, L. E. Anderson, R. S. Glass, R. A. Norwood, M. E. Mackay, K. Char and J. Pyun, *ACS Macro Lett.*, 2015, **4**, 862–866.

195 A. Gehin, P. Zwolinski and D. Brissaud, *J. Cleaner Prod.*, 2008, **16**, 566–576.

196 N. A. Lundquist, A. D. Tikoalu, M. J. H. Worthington, R. Shapter, S. J. Tonkin, F. Stojcevski, M. Mann, C. T. Gibson, J. R. Gascooke, A. Karton, L. C. Henderson, L. J. Esdaile and J. M. Chalker, *Chemistry*, 2020, **26**, 10035–10044.

197 Z. O. G. Schyns and M. P. Shaver, *Macromol. Rapid Commun.*, 2021, **42**, e2000415.

198 S. Zhang, L. Pan, L. Xia, Y. Sun and X. Liu, *React. Funct. Polym.*, 2017, **121**, 8–14.

199 H. Kim, J. Lee, H. Ahn, O. Kim and M. J. Park, *Nat. Commun.*, 2015, **6**, 7278.

200 H. Ramezani, F. Scarpa, Q. Zhang, W. Ji, A. Khorramshokouh, S. Rochat, J.-C. Eloi, R. L. Harniman and V. K. Thakur, *RSC Sustain.*, 2024, **2**, 2295–2311.

201 S. Huysman, S. Debaveye, T. Schaubroeck, S. D. Meester, F. Ardente, F. Mathieux and J. Dewulf, *Resour., Conserv. Recycl.*, 2015, **101**, 53–60.

202 H. Holmes, M. Shaver, T. Holmes and K. Kortsen, *Tackling Household Plastic Waste: Best Practice for a Circular Plastics Economy*, 2023.

203 G. H. Brundtland, *Our Common Future: Report of the* World Commission on Environment and Development, Geneva, 1987.

204 R. A. Sheldon, *Green Chem.*, 2023, **25**, 1704–1728.

205 B. G. S. Guinati, P. Y. Sauceda Oloño, N. L. Kapuge Dona, K. M. Derr, S. K. Wijeyatunga, A. G. Tennyson and R. C. Smith, *RSC Sustain.*, 2024, **2**, 1819–1827.

206 A. Abbasi, S. F. Taghinezhad, M. Mansourieh, H. Xu, M. M. Nasef and I. Major, *Polym. Test.*, 2024, **140**, 108625.

207 J. Rockström, W. Steffen, K. Noone, Å. Persson, F. S. Chapin, E. F. Lambin, T. M. Lenton, M. Scheffer, C. Folke, H. J. Schellnhuber, B. Nykvist, C. A. d. Wit, T. Hughes, S. v. d. Leeuw, H. Rodhe, S. Sörlin, P. K. Snyder, R. Costanza, U. Svedin, M. Falkenmark, L. Karlberg, R. W. Corell, V. J. Fabry, J. Hansen, B. Walker, D. Liverman, K. Richardson, P. Crutzen and J. A. Foley, *Nature*, 2009, 461.

208 *Environmental management – Life cycle assessment – Requirements and guidelines, DIN EN ISO 14040:2021-02*, 2021, doi: DOI: 10.31030/3179655.

209 *Environmental management – Life cycle assessment – Principles and framework, DIN EN ISO 14044*, 2021-02, 2021, doi: DOI: 10.31030/3179656.

210 M. Z. Hauschild and M. A. Huijbregts, *LCA Compendium - the Complete World of Life Cycle Assessment. Life Cycle Impact Assessment*, Springer Dordrecht, 2015.

211 OECD, Paris, *Global Plastics Outlook: Policy Scenarios to 2060*, 2022.

212 P. Ramesh and S. Vinodh, *Int. J. Sustain. Eng.*, 2020, **13**, 411–422.

213 K. Sabate and A. Kendall, *Clean. Environ. Syst.*, 2024, **14**, 100205.

214 E. Igos, E. Benetto, R. Meyer, P. Baustert and B. Othoniel, *Int. J. Life Cycle Assess.*, 2018, **24**, 794–807.

215 N. Bamber, I. Turner, V. Arulnathan, Y. Li, S. Zargar Ershadi, A. Smart and N. Pelletier, *Int. J. Life Cycle Assess.*, 2019, **25**, 168–180.

216 K. S. Kang, C. Olikagu, T. Lee, J. Bao, J. Molineux, L. N. Holmen, K. P. Martin, K. J. Kim, K. H. Kim, J. Bang, V. K. Kumirov, R. S. Glass, R. A. Norwood, J. T. Njardarson and J. Pyun, *J. Am. Chem. Soc.*, 2022, **144**, 23044–23052.