doi:10.1038/nature21002

Polymers with autonomous life-cycle control

Jason F. Patrick[1], Maxwell J. Robb[1,2], Nancy R. Sottos[1,3], Jeffrey S. Moore[1,2] & Scott R. White[1,4]

The lifetime of man-made materials is controlled largely by the wear and tear of everyday use, environmental stress and unexpected damage, which ultimately lead to failure and disposal. Smart materials that mimic the ability of living systems to autonomously protect, report, heal and even regenerate in response to damage could increase the lifetime, safety and sustainability of many manufactured items. There are several approaches to achieving these functions using polymer-based materials, but making them work in highly variable, real-world situations is proving challenging.

The life cycle of plastics and other materials used for engineering begins with the extraction of raw materials, followed by the synthesis and processing of the polymer building blocks, which are manufactured into a product that has a particular use or function. The product is eventually degraded or damaged during use, and is ultimately disposed of or recycled[1,2]. Polymers and polymer-based composites are designed and manufactured to be as robust as possible for a given application, but failure is eventually inevitable. In the case of high-volume and simple, low-cost products, such as the ubiquitous plastic bag, the materials will ideally be recycled after use. But in many instances, the life cycle of polymeric materials could be expanded by programming them with biologically inspired, autonomous functions to protect them from, and to limit, damage, or even to reverse damage and regenerate in response to environmental stress. The attraction of this approach is not only waste reduction, but also the ability to create products with increased safety and superior reliability — a particularly appealing feature for applications such as medical implants, undersea pipelines or structures in space, where damage is difficult to detect, and repair is costly or even impossible.

Research that encompasses chemistry, polymer science, processing and engineering has delivered polymeric materials that have remarkable self-healing, sensing and reporting properties. In this Review we sketch our vision of how such functions could extend the life cycle of functional polymeric materials, and outline the basic performance criteria and material-design principles that should guide the development of practically useful systems. We then examine in more detail the different biologically inspired functions that have been realized, and explore how they can endow materials and devices with improved performance. Finally, we discuss the problems that need to be overcome for this class of polymeric materials to fulfil its promise and find commercial uses.

Polymers with autonomous functions

Nature provides many inspiring examples of materials that perform well in difficult environments, and that can self-heal to regain function when they are damaged. Figure 1 shows the autonomous functions that would enable a polymeric system to similarly maintain and recover its performance throughout its functional life: self-protection guards against potentially damaging environmental factors, such as mechanical stress, chemical corrosion or extreme temperatures; self-reporting capabilities ensure that loss of performance caused by a detrimental event is registered, communicated and ideally initiates action to recover performance; and when a system has been damaged, self-healing recovers the performance and thereby promotes longevity. However, every polymeric material will inevitably reach an irrecoverable state where self-healing is no longer viable. If such a state is reached because of damage that has physically displaced mass (such as chips, punctures or impacts), it is in principle possible to restore performance by regenerating the lost material. When this is not an option, a desirable final life-cycle step is controlled degradation — achieved by adjusting the rate of degradation or by actively triggering it — to enable active management of the end-of-life removal of the material. For medical implants, this is known as transience[3] and ensures that devices function over the required time frame before being resorbed by the body. In other consumer products, controlled degradation can help to recycle material building blocks for use in regeneration or manufacture.

The design of autonomous polymers for life-cycle control is a complex interplay of both intrinsic and extrinsic factors that correlate with the length scale of the damage suffered by a material. The damage length scale (see Fig. 2) is extrinsically influenced by the type of damage event (ballistic impact or fatigue loading), and intrinsically by the inherent nature of the material (the failure and extent of damage of a soft rubber will differ from that of a stiff and brittle polymer). The damage length scale also affects the response function that can be used for repair. For example, dealing with damage that has resulted in the physical removal of mass requires the transport of new material to the damage site for regeneration. This can be achieved by capillary flow on the micrometre scale, but is not practical on the macro scale.

The design of autonomous polymers must also be framed by the property or function that is to be restored. The specifications will be quite different if the target function is mechanical load-carrying capability as opposed to electrical conductivity, for example. Irrespective of function and performance requirements, attempts to put polymers with autonomous functions to practical use also face the considerable challenge of having to do so with a simple, scalable and cost-effective design that meets increasingly stringent regulations.

Figure 2 depicts the three primary approaches to imparting polymers with autonomous function, and gives an indication of the length scales on which they operate. Damage caused by bond scission can be repaired by reversible chemical interactions if the fracture interfaces remain in intimate contact. Success requires rapid bond reorganization at the molecular level, and this can be achieved with supramolecular interactions such as ion pairing. The changes that bring about restoration in

---

[1]Beckman Institute for Advanced Science and Technology, [2]Department of Chemistry, [3]Department of Materials Science and Engineering, and [4]Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA.

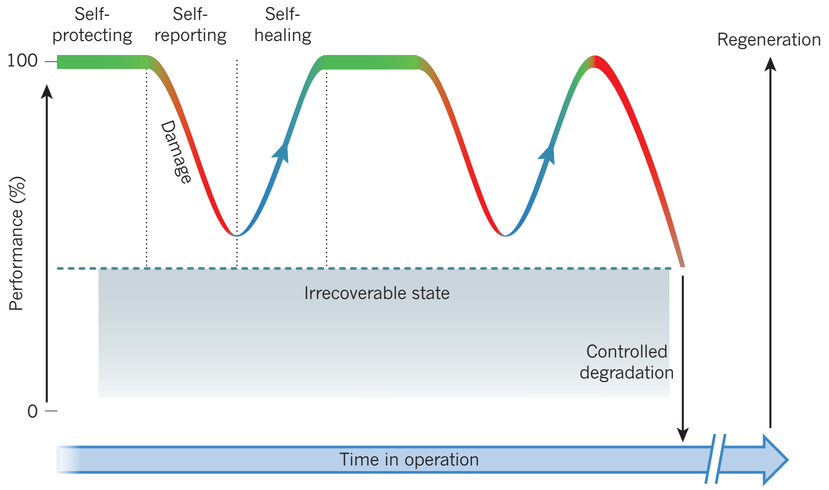

Figure 1 | The life cycle of polymers with autonomous healing functions. Self-protection maintains the structural integrity of a material and minimizes environmental degradation. Self-reporting communicates a loss of performance induced by damage or degradation. Self-healing enables recovery from damage. Controlled degradation brings about the disintegration of a material after irrecoverable damage has occurred or after a predetermined time in operation. Regeneration effectively restarts the polymer life cycle by rebuilding the material.

this case take place internally and require molecular engineering of the polymer to equip it with the intrinsic characteristics of reconfigurable or dynamic bonds. When the damage grows to the microscale, healing by dynamic bonding is usually no longer viable, and an extrinsic source of repair agents is needed. In such instances, two basic strategies are available: the incorporation in the polymeric material of mesoscale additives (such as microcapsules or fibres) with a functional fluid payload that is discharged and initiates healing once damage occurs; or the incorporation of a larger-scale, vascular fluid-delivery network. Healing is initiated either when repair agents are mixed, or when a repair agent interacts with an additional component present in the matrix (such as a catalyst). Both of these trigger chemical reactions that transform the fluid into a structural adhesive that bonds the microcrack interfaces together. In cases where damage has resulted in the physical displacement of mass (for example, puncture), and a substantial volume of repair agents is needed, healing is only feasible using delivery from a vascular network.

The three approaches to autonomous polymers sketched in Fig. 2 address the spectrum of damage from ångström-scale bond scission to microcracking and millimetre-scale puncture damage. They have enabled the development of systems that exhibit self-protection, self-reporting, self-healing, regeneration and controlled degradation (see Fig. 1), mainly in proof-of-principle demonstrations, although some are nearing commercialization.

Self-protection

The best way of ensuring the longevity of materials and systems is to prevent damage before it occurs, and coatings have long been used for that purpose. Coatings passively protect substrates against mechanical and chemical degradation by forming a physical barrier that increases resistance to corrosion or wear. Augmenting this passive protection with self-repairing capabilities improves the overall performance of coatings[4] (Fig. 3a). This additional protection is typically achieved by incorporating mesoscale additives that deliver active payloads consisting of corrosion inhibitors[5] or compounds that react with water to form a physical[6] or hydrophobic[7] protective barrier (Fig. 3b) in response to surface cracking, ablation or corrosion[8–10]. Purely inorganic sol–gel coatings, for example, have been shown to achieve enhanced corrosion protection of an aluminium alloy[11] by incorporating mesoporous silica nanoparticles loaded with a corrosion inhibitor. Protection strategies that aim to create repellent surface layers rely on tailored surface chemistry. Although it is a departure from our theme of polymers with autonomous functions, another approach to creating self-protecting functional surfaces relies on liquid-repellent surfaces comprising porous substrates infused with a lubricating liquid. The porous substrate locks the lubricant in place, giving a smooth, defect-free and stable liquid surface that can be tailored to repel a wide range of different liquids and that readily self-repairs after mechanical damage[12,13].

As well as mechanical damage and corrosion, materials and devices also frequently face the threat of thermal degradation. Consider, for example, lightweight, fibre-reinforced, thermoset polymer composites, which are inherently resistant to many forms of environmental deterioration (such as corrosion). They are increasingly replacing traditional structural materials in advanced engineering applications, but their mechanical performance rapidly diminishes at temperatures near the glass transition temperature of the polymer matrix (typically at or below 200 °C). At temperatures above the glass transition, the matrix can no longer carry structural loads. The development of matrix materials with enhanced thermal stability is one potential solution for expanding the scope of polymer fibre composites.

Alternatively, circulating fluids through vascular networks embedded within the composite, which occupy a small fraction of the overall material volume[14,15], can protect against thermal degradation while retaining structural performance[16–18] — an approach well known in the aerospace industry and long used to cool high-performance ceramic turbine blades[19]. Indeed, a recent study[20] showed that an actively cooled vascular polymer matrix composite, with a matrix glass transition temperature of 150 °C and a channel volume comprising only a few per cent, retains its flexural stiffness upon continuous exposure to 325 °C. When endowed with such active cooling functionality, it should in principle be possible to use conventional thermoset, polymer matrix composites in applications subject to high thermomechanical loading, such as aerospace structures, microelectronics packaging, or battery packaging for electric vehicles. Putting self-cooling materials to practical use, however, will require efficient and inexpensive means of manufacture, and innovative approaches for accommodating the coolant and pumping equipment they require.

Self-protection implemented at the device level is exemplified by high-energy-density lithium-ion batteries that manage thermal runaway, which poses a significant safety hazard after batteries have been damaged or discharged too quickly. One strategy is to incorporate thermally responsive polymer microspheres that melt above a critical temperature and disrupt conduction pathways within the battery to irreversibly shut down the cell[21]. Reversible shutdown, in which normal battery operation is restored once the thermal perturbation is removed, can be achieved using conductive particles within a temperature-responsive polymer binder[22]. Thermal degradation, however, is not the only operational challenge for high-energy-density batteries. Mechanical damage resulting from dramatic volumetric expansion and contraction in next-generation silicon electrodes leads to rapid capacity fade and diminished cyclability. This problem can be mitigated by using silicon particles in combination with a flexible polymer binder that accommodates large volume change through reversible hydrogen bonding, significantly improving the cell's lifetime and retention of capacity[23].

The examples so far illustrate protection of functional performance at a system or device level, but molecular-scale protection can also be achieved by using mechanochemically active polymers[24]. These materials incorporate force-sensitive molecules, known as mechanophores, that directly harness mechanical energy to promote productive chemical transformations[25]. Mechanical stress usually breaks covalent bonds, and thereby degrades a material's properties and performance, but mechanophores give materials the ability to survive otherwise degrading conditions. This ability could be useful when operating conditions are unpredictable and the use of alternative materials with overengineered properties would be wasteful and inefficient. A recent example of mechanochemical self-protection used polymers containing dibromocyclopropane mechanophores, which transform under shear stress into reactive functional groups that can be crosslinked *in situ* to bring about autonomic strengthening[26] and enhance stiffness. Mechanophores with a wide range of chemical functionalities are becoming available[27,28]. Noteworthy in this context is the mechanical activation of catalysts[29], which makes it possible to initiate a variety of protective chemistries (such as polymerization or crosslinking reactions) while also achieving chemical amplification. However, these materials are difficult to synthesize and are expensive, which could limit their practical application, but there may be opportunities, particularly when coupling mechanochemically active polymers with mesoscale additives to generate materials with hierarchical function. For example, polymers that produce acid in response to mechanical stress[30] could be combined with a pH-responsive delivery vehicle to give a system that will release its payload under mechanical force.

Self-reporting

Many systems and devices benefit from the ability to autonomously signal the occurrence of stress or damage (Fig. 3c). A powerful strategy for creating such a warning system uses mechanophores to monitor molecular force and convey visual information about the condition and mechanical history of a polymer. As with the mechanophores that bring about molecular self-protection, the mechanical forces that lead to damage induce a chemical transformation in the mechanophore, but to enable self-reporting, this chemical transformation should be accompanied by changes in optical properties. For example, the mechanically activated ring-opening reaction of spiropyran[31] in bulk polymeric materials results in changes in both the visible colour (from yellow to red) and fluorescence. In many cases, mechanochemical transformations are achieved at the expense of permanent plastic deformation of the material, which exemplifies the difficulty of achieving efficient transduction of mechanical energy to a specific mechanophore molecule. Integrating a spiropyran mechanophore into a silicone elastomer[32], in contrast, provides a visually discernible indication of stress or strain in combination with complete shape recovery (Fig. 3d). Three-dimensional (3D) printing of mechanochromic polymers is also possible, and has been used to produce a prototype force sensor that can be used to evaluate loads simply by observation of the mechanically induced colour change[33]. These examples all require a light source for visualization, but mechanophores such as bis(adamantyl)-1,2-dioxetane can also use mechanical energy to generate light that is visualized directly[34]. An earlier approach to molecular strain sensors used dye aggregates in polymer blends, in which macroscopic deformation affects the aggregation and thereby produces changes in the photoluminescence emission colour[35].

Self-reporting of mechanical damage is also possible using mesoscale additives and vascular networks[36] that, when ruptured, release indicators for visual detection through a change in colour or fluorescence[37]. Most systems rely on a chemical reaction between an indicator molecule and a secondary reagent or catalyst incorporated into the polymeric material, or through the use of dual-capsule systems containing the two reactive precursors[38]. For example, a visual colour change is generated in regions of mechanical damage using microcapsules containing a colourless conjugated cyclic monomer that when released and allowed to react with an embedded catalyst transforms into a deeply coloured polymer[39]. Microcapsules containing a pH-sensitive dye[40] that reacts with residual amine groups in an epoxy polymer matrix have led to particularly robust and clear visual indications of damage even on the micrometre scale, but this approach shares the limitation of other systems of requiring

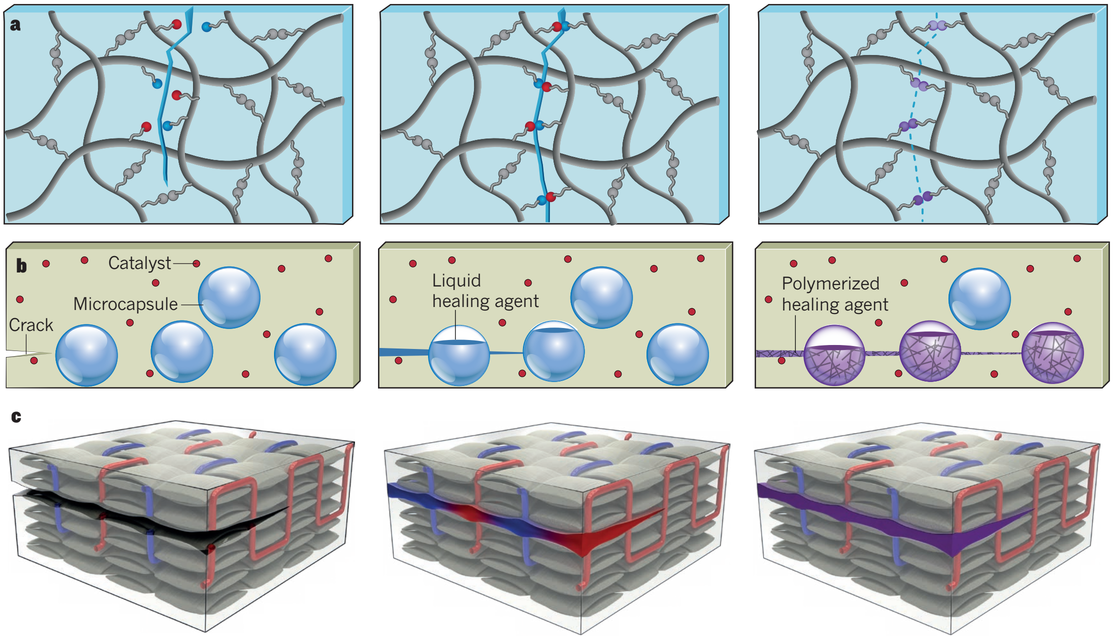

Figure 2 | Multiscale strategies for autonomous repair functions in polymeric materials. Three primary strategies enable autonomous repair functions in polymeric materials. They are exemplified here by self-healing over a range of damage length scales. **a**, At the smallest scale (ångströms), molecular engineering brings about the repair of damage by dynamic or reversible bonding of fractured interfaces that are in intimate contact. Bond scission occurs (left) followed by dynamic rebonding (middle), and the fracture is mended (right). **b**, Mesoscale additives that are dispersed in a polymeric material can store and release healing agents to recover damage at the microscale (<100 μm). A microcrack occurs (left), the microcapsules release a healing agent (middle) that polymerizes on contact with an embedded catalyst, and the crack is healed (right). **c**, Vascular networks capable of fluid circulation and repeated delivery of healing agents can repair material from the micrometre to the millimetre scale. Delamination occurs (left), the ruptured vascular network releases reactive, liquid healing agents (middle), and the delamination is repaired (right).

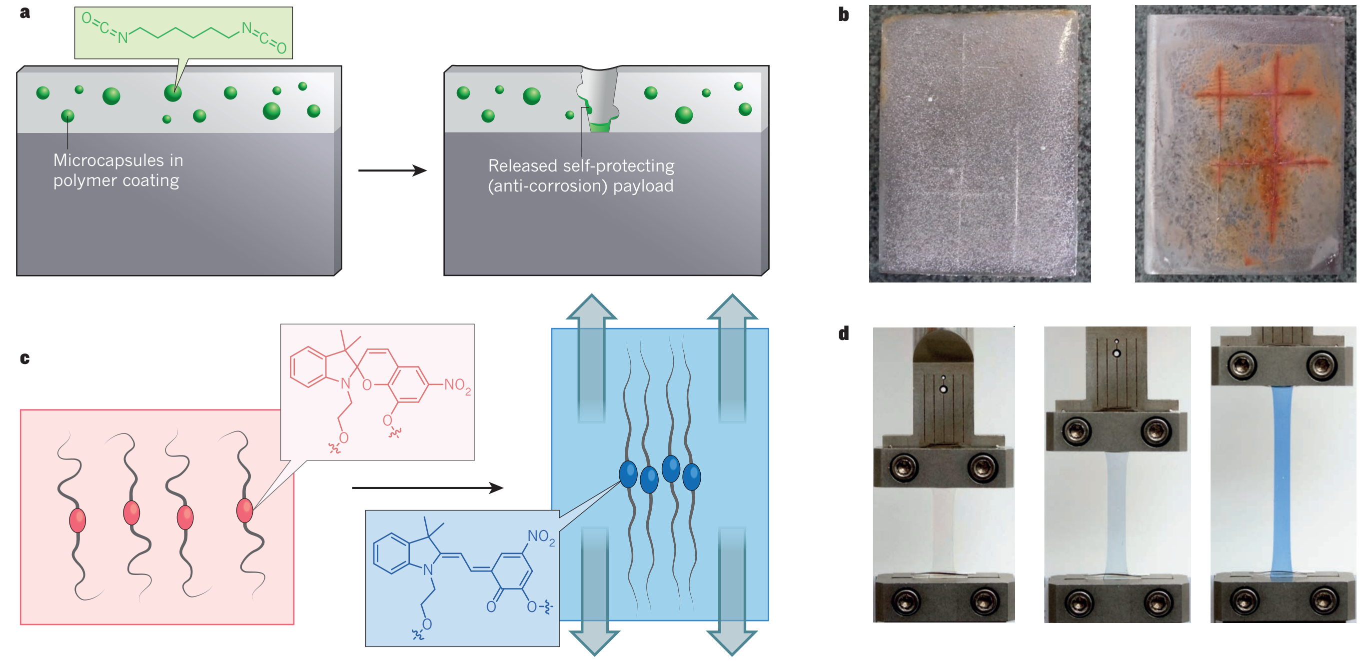

Figure 3 | Autonomous prevention and communication of material degradation. **a**, A self-protecting material incorporating mesoscale additives. Damage to a coating causes microcapsules to rupture and release an anti-corrosion payload that protects the underlying substrate. **b**, Examples of coated steel substrates subjected to corrosive environments. Left, an autonomous self-protecting epoxy coating incorporating microcapsules with a reactive isocyanate payload. Scratch damage to the coating releases the capsule payload and protects the underlying steel substrate from active corrosion. Right, a conventional epoxy coating (with no microcapsules) in which scratch damage initiates widespread corrosion of the substrate (red). Images reprinted with permission from ref. 6. **c**, A self-reporting material incorporating a molecular force probe (mechanophore). Mechanical activation causes the material to change colour, providing a visual indication of critical stress or strain. **d**, A polydimethylsiloxane elastomer containing a spiropyran mechanophore that turns blue during tensile loading, providing a visual indication of mechanical stress or strain. Images reprinted with permission from ref. 32.

specific chemical interactions. This highlights the need for more general visualization strategies that are applicable to a wider range of materials, irrespective of chemical composition. With this objective in mind, a recently developed approach uses microcapsules containing molecules that exhibit aggregation-induced emission, which become fluorescent after rupture and release by a physical change of state[41]. Another example of a general, autonomous approach for damage detection is the entropy-driven migration of fluorescent nanoparticles to cracks in layered composite structures[42]. Compared with mechanophore activation, which typically requires large and often irreversible polymer deformation, microcapsules produce a more permanent response with enhanced sensitivity to microscale damage.

Self-healing

An ideal self-healing polymer system would repair any damage it suffers in a site-specific and fully autonomous fashion to regain functional performance. Of the three approaches outlined in Fig. 2, self-healing based on molecular engineering of the polymer comes closest to this ideal because repair can occur wherever it is needed without the use of additives[43,44]. However, many early examples of this sort required external energy input to drive the reorganization of bonds and polymer chains necessary for the repair process. One such system comprising a covalently crosslinked thermoset polymer based on Diels–Alder chemistry is shown in Fig. 4a,b. The thermally reversible nature of the covalent bonds in this system enables dynamic exchange when heated to mend cracks[45]. Such thermal re-mending has also been accomplished with thermoplastic phases that are incorporated into a crosslinked polymer matrix to enable repair of cracks through local entanglement when heated[46]. Vitrimers[47] are a similar class of polymer that become malleable and mendable at high temperatures but retain their covalently crosslinked network throughout[48], so the system's viscosity changes gradually, allowing local mending and reshaping. Light has also been used to induce the mobility[49] needed for healing, and to allow localized heating and self-healing in metallo-supramolecular polymers[50]. When embedding super-paramagnetic nanoparticles, even an oscillating magnetic field can induce amorphous flow and re-mending in a thermoplastic polymer[51] by means of the rapidly vibrating particles.

But for self-healing to be fully autonomous, it needs to proceed without the input of external energy. The molecular-engineering approach using dynamic bonding accomplishes this relatively readily in soft, rubbery polymers or gels. A striking example, based on hydrogen-bonding interactions between small molecules, is a highly extensible rubber that is capable of autonomously, repeatedly and fully healing fractured surfaces at room temperature[52]. Similar design principles have also produced self-healing thermoplastic elastomers[53] with a mechanical performance approaching that of conventional, structural polymeric materials. The interaction of charged ionic species is an alternative bonding motif that can yield self-repairing rubbers[54] and hydrogels. When implemented using polymer-modified clay nanosheets and a dendritic binder[55], the resulting hydrogels retain their shape and completely recover their mechanical integrity after cleavage and reassembly. Although such supramolecular interactions are an obvious bonding platform, dynamic covalent chemistry has also been used in adaptive[56] and self-healing polymers[57,58]. The ease with which self-healing proceeds, and the ability to heal repeatedly, are attractive features of the molecular-engineering approach, but it is largely restricted to elastomeric polymers and can usually deal with only small damage length scales, as there needs to be intimate contact between damaged surfaces.

As early, inspirational work showed[59], some limitations on materials and damage length scales can be overcome by using extrinsic healing agents embedded in encapsulated form in the material, ready to be released when damage occurs. An important proof-of-principle demonstration of such autonomous self-healing in a structural polymer introduced the basic and now widely used microcapsule design[60]. Crack propagation ruptured the microcapsules contained within the material and released the encapsulated monomer fluid. When this

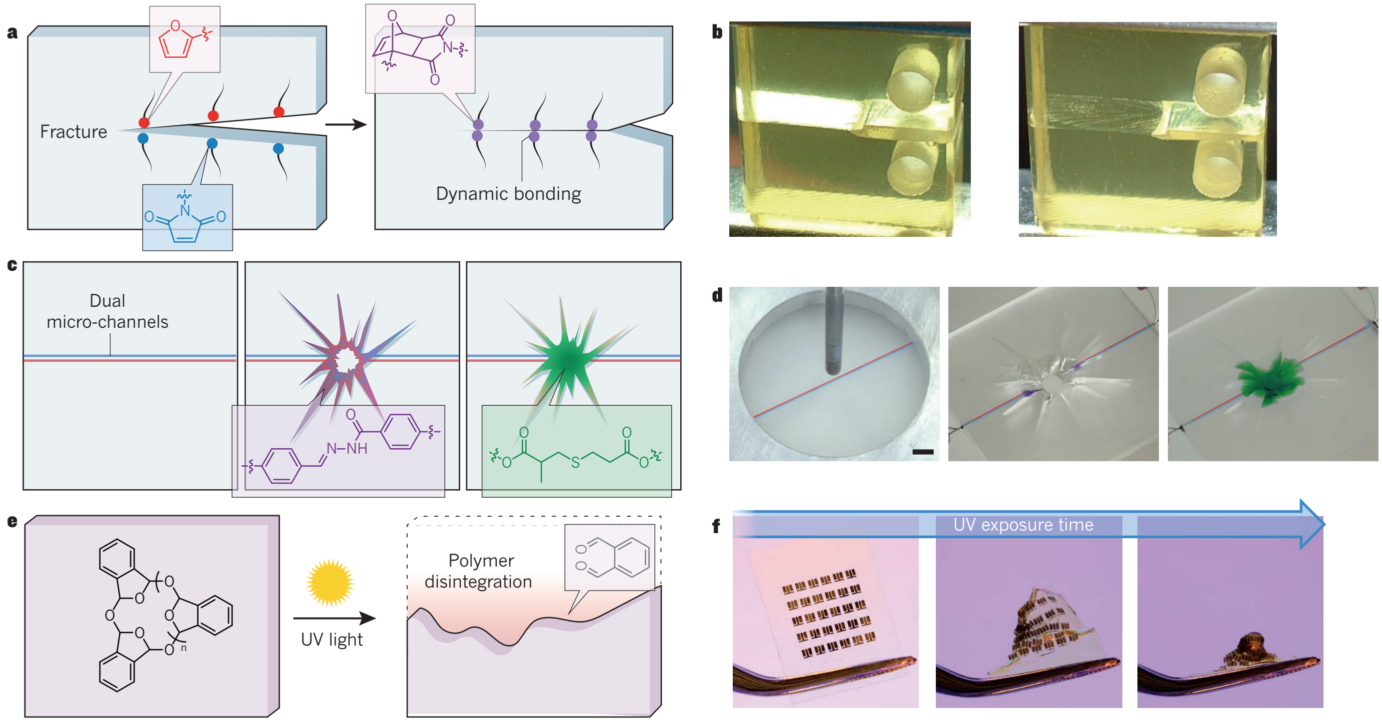

Figure 4 | Autonomous healing, regeneration and degradation. **a**, A self-healing material using a molecular-engineering strategy. Reversible bonding between the two crack surfaces enables repair after they are brought into intimate contact. **b**, Repair of fracture damage in a re-mendable, covalently crosslinked polymeric material after heating. Left, the fracture plane can be clearly seen because of light reflection. Right, after clamping the fracture and heating to promote repair, the crack is no longer visible. Images reprinted with permission from ref. 45. **c**, Regeneration of a polymeric material. Micro-channels embedded in the polymer (left) deliver liquid healing agents to the site of large-scale damage (middle) to restore lost material (right). **d**, Dual microvascular networks (blue and red; left) deliver a two-part healing system to restore puncture damage in an epoxy substrate[86]. The puncture (~10 mm; middle) is completely filled with the healing agents and closed after pressurized delivery (right). **e**, A material programmed for controlled degradation (left). An environmental stimulus (such as sunlight) triggers the degradation of the material (right). **f**, Packaging of an electronic device with a transient polymer enables the controlled disintegration of the device (left to right) when exposed to UV light. Reprinted with permission from ref. 89.

fluid made contact with catalyst particles contained in the crosslinked epoxy matrix, it polymerized to bond the fractured surfaces and restore mechanical performance. This example motivated the development of many capsule-based self-healing systems, implemented in both hard and soft polymers and using a multitude of different healing chemistries (for in-depth reviews, see refs 43 and 61). Importantly, microcapsules can be incorporated into polymers without sacrificing the inherent fracture toughness and related mechanical properties[62,63].

Critical to the further success and translation of these systems is the need for robust capsules and healing chemistries that remain stable and functional, despite being exposed to a variety of mechanical, thermal and chemical environments, until damage occurs. Protective capsule coatings can enhance the stability of microcapsules that are exposed to challenging processing and environmental conditions[64]. However, this still leaves one major limitation: capsules can be used only once in a particular location to release their liquid payload and initiate healing. One possible way of overcoming this issue is to use capsules with semi-permeable shells[65] for tunable and controlled payload release.

Although microcapsules can be made to be stable and functional, and incorporated using standard material-processing techniques, a fundamental limitation is the total amount of healing agent that can be delivered to damaged areas. Vascular networks overcome these shortcomings and also allow repeated healing by replenishing the supply of healing agent to sites of repeated damage. Precursors of this basic strategy (the use of one-dimensional tubular structures for delivering healing agent) involved isolated hollow, glass fibres[36] or microchannels[66,67]. Multiple cycles of self-healing have been achieved in both coatings[68] and neat polymers[69] by using interconnected, three-dimensional microvascular networks. More-complex, interpenetrating 3D microvascular networks containing two-part healing agents have been shown to sustain more than 30 cycles of repeated healing[70], and adding a third independent network enabled regulation of the healing temperature and time[71], which could, in principle, enable healing under otherwise prohibitive environmental conditions.

The development of vascular-based healing has relied on the efficient integration of complex networks into high-performance, fibre-reinforced composites. Early fabrication techniques[72,73] either produced only one-dimensional isolated channels with limited fluid pathways, or used direct-write processes[74] that are incompatible with most industrial manufacturing techniques. The more recent approach of using a robust, sacrificial template of polylactic acid polymer can be seamlessly integrated into existing manufacturing processes for polymer-based composites[14,15]. This so-called vaporization of sacrificial components technique has enabled more complex vascular architectures to be seamlessly integrated into fibre-reinforced composites with no decrease in mechanical strength and stiffness[17], while increasing delamination resistance and enabling multiple cycles of healing at high efficiencies[75]. Many significant hurdles remain to be overcome before such self-healing, high-performance composites can be put to practical use, however. Not only are costs potentially prohibitive, but the delivery of healing agents needs to become fully autonomous, network design must be made redundant to damage and/or blockage, and *in situ* repair of ruptured vasculature must be realized to achieve sustained delivery of agents and prolonged healing cycles.

The biological world has inspired many of the concepts that guide the development of materials and systems capable of autonomously repairing damage, but self-healing remains relatively unexplored by the biomaterials research community. Toxicity and biocompatibility impose important constraints that have so far restricted progress to proof-of-concept studies[76–78] demonstrating the feasibility of microcapsule-based self-healing of bone cement (a polymeric material used to anchor implants including artificial joints, which can lose function through wear and microcracking). Further development of these and other synthetic polymer-based biomaterials with the ability to autonomously repair damage holds considerable promise for future biomedical applications[79].

The examples of self-healing discussed above all relate to the restoration of mechanical performance, but the approach based on mesoscale additives in particular is well suited for targeting other functions as well. Efforts so far have focused on electrical properties (either on their own[80–83] or in conjunction with the restoration of mechanical properties[84] that might be useful for electronic skin applications), but we envisage that materials with the ability to repair other functional properties will also be developed.

Regeneration

The ultimate challenge in the development of self-healing materials is regeneration — the ability to replace severely damaged or lost materials (analogous to the biological regeneration of tissues). Damage that involves a loss of mass on this scale (Fig. 4c) requires a delivery system to supply sufficient amounts of healing agents. As with biological growth and regeneration[85], this requires a rich interplay of transport, kinetics and dynamically changing material properties. This concept is illustrated by the restoration and healing of millimetre-scale puncture damage in an epoxy polymer[86], which used the vascular delivery of two-stage healing chemistry to combat the constraints of gravity and surface tension on the amount of healing fluid that can be retained in a large void. The first healing stage involved the gelation of a monomer to form a permeable scaffold that allowed the accumulation of material to completely fill the damaged region. The second healing stage involved the polymerization of a secondary orthogonal monomer to generate a robust structural polymer (Fig. 4d). This strategy proved effective at filling the central puncture, but it was unable to ensure complete infiltration and repair of the smaller radial cracks that resulted from the impact. This shortcoming aptly illustrates the problems posed by repairing damage that spans multiple size scales simultaneously.

Controlled degradation

Even the most robust self-healing materials will eventually reach the end of their life. Ideally, there will be controlled degradation of the material to recover useful products for recycling (Fig. 4e). Controlled degradation is not only desirable when damage has led to an irrecoverable state in which self-healing and regeneration are no longer viable, but also when a material or device is needed for only a limited time period, so its transience, rather than its stability, is desirable. Of course, degradability (or transience) has been pursued for some time, not least to deal with the millions of tonnes of plastic waste that is discarded every year. But although materials such as biodegradable bags and other personal products are becoming widespread, attempts to make advanced polymer-based materials and devices degradable are still at an early stage.

One approach to the paradoxical materials-design challenge of obtaining readily degradable materials that are robust and stable while they are being used is to design materials that will disintegrate when exposed to a particular triggering event. One promising example uses poly(benzyl ether) as a basic platform that can easily be modified to produce traditional polymeric materials, leading to chemically induced depolymerization for selective end-of-life recycling[87,88]. In the case of derivatives of poly(phthalaldehyde), which are used as packaging material for electronic devices, degradation has been triggered by ultraviolet light[89] and heat[90]. But there remains a need for broader classes of materials that can readily degrade upon exposure to suitable stimuli.

Transience also arises naturally in cases where materials continuously disintegrate during use. This feature can be controlled to ensure that the degradation rate is such that adequate functional performance is maintained over the intended period of use. The resorbable sutures often used by surgeons illustrate the benefits and elegance of this approach. A more recent example[91] (involving both organic and inorganic materials) is the use of multifunctional silicon nanomembrane sensors for the brain that are implanted in rats, as these can be resorbed naturally to avoid surgical removal (Fig. 4f). Especially in the case of medical implants that have active functions, accelerated degradation when exposed to a suitable stimulus — so-called triggered transience — could further expand the opportunities for use.

Although some strategies make it possible to achieve controlled degradation, a more demanding objective is the recapture and reuse of the resulting products. Proof-of-principle experiments have demonstrated the mechanically triggered depolymerization of poly(phthalaldehyde) into monomer that was subsequently repolymerized[92]. But major challenges remain before a fully integrated materials system can be created that approaches the ideal of a closed, autonomous, polymer life cycle.

Outlook

Materials have traditionally been developed to be robust enough to withstand the wear and tear of normal use. This approach has worked well, but moving towards active damage and life-cycle management using autonomous functions promises materials with enhanced, safer and more efficient performance, while minimizing resource use and waste production. There are several major obstacles to using autonomous polymers in real-world applications, not least the fact that they have so far largely been developed and tested in highly controlled and optimized laboratory settings. In stark contrast, materials in service will need to perform in highly variable environmental conditions and remain stable throughout their operational life. The chemistry that enables healing in particular is often sensitive to temperature, humidity, pressure, pH and atmospheric oxygen, which all make it difficult to maintain robust healing performance. If autonomous technologies are to enter the commercial sector, it is essential that stability is established over periods much longer than the six months explored in one study[93]. We also note that many healing agents are not only expensive but also toxic, which largely precludes their commercial use. In addition, the need for self-reporting and self-healing to occur quickly enough to deal with damage — particularly if it rapidly worsens or propagates — poses significant challenges. Most of the systems we have discussed require lengthy healing periods that often cannot be readily accommodated, especially if healing under continuous loading is not effective.

The commercialization of self-healing polymer-based materials faces significant practical challenges, and developments in the field so far have been largely empirically driven owing to the relative lack of suitable computational tools and models. We envisage that efforts to redress this situation will deliver considerable benefits. For example, computer modelling can provide deeper insight into the current behaviour of autonomous polymers, and thereby aid the formulation of effective guidelines for optimizing both the synthesis of these polymers and the design of the system. Multi-scale models are needed that effectively connect chemical transformations on the molecular scale with relatively local material responses on the mesoscale, and with the macroscale behaviour of the system overall. Modelling will also need to deal with a wide range of processes and phases, given that structural and other damage gives rise to a healing response in which the flow of repair agents and chemical reactions involving fluid and solid phases has a critical role. Steps towards modelling materials and systems with autonomous functions have been taken[94–99], but it is difficult to capture sufficient detail about the underlying mechanisms to enable meaningful predictions, while still ensuring that model calculations can be performed on reasonable timescales.

Even when an effectively functioning, self-healing material or system is available, practical implementation in the commercial sector will require the product to be manufactured in commercially relevant quantities and deliver value in the marketplace. This remains a largely unsolved problem for autonomous polymers. Some soft, rubbery polymers with fully autonomous self-repairing properties can be produced using simple processes and inexpensive, renewable materials[52]. When aiming for structural applications, however, materials usually require extrinsic healing agents. Systems that rely on microcapsules for this purpose face the problem that although emulsion processes can produce reasonable quantities of capsule material, they are restrictive in terms of the chemistry that can be used. For example, hydrophilic healing agents cannot be encapsulated in an oil-in-water emulsion process (which is by far the most common commercial encapsulation method), and reactive core materials are chemically incompatible with many polymer shell-forming chemistries. Microfluid-based processes[100] can overcome some of these problems but are unlikely to be cost-effective on a commercial scale owing to difficulties of scalability and the slow rate of capsule production. Another obstacle for systems that use mesoscale additives, especially those carrying sensitive payloads, is their incompatibility with the processing methods used to manufacture high-performance fibre-composite materials. Autonomous systems that use vascular networks have largely overcome these problems, but the complexity of their design, and the need to introduce and pump reactive agents within the network, pose further manufacturing and implementation challenges. Advances in additive manufacturing for the rapid production of 3D scaffolds[101] or even 4D-printing concepts[102] may overcome some of these hurdles, but commercial viability is unlikely in the near future except in specialized applications in which the additional costs are warranted.

The ultimate goal for autonomous polymers is to perform the desired function for as long as necessary without being replaced or requiring external maintenance. The end of life should be designed in such a way that the building blocks of the polymer can be recaptured and recycled efficiently, reducing the amount that is discarded in landfill. Imagine a car tyre that lasts the entire lifetime of the vehicle, before being recycled and regenerated with 100% efficiency. Alternatively, a bridge that is painted once and is protected from corrosion for its entire lifetime will greatly reduce maintenance costs while improving the safety of our civil infrastructure. Beyond simply replacing existing materials, self-healing polymers might also enable product designers to explore new concepts that incorporate healing as an integral part of the design. Irrespective of whether and how the futuristic goal of autonomous control of the entire polymer life cycle can be achieved, the first exciting steps have been taken, and the challenge for the field now is to deliver on the promise of improved sustainability by providing smarter, safer, better-performing and longer-lasting materials.

Received 11 March; accepted 12 October 2016.

1. Rebitzer, G. *et al.* Life cycle assessment: part 1: framework, goal and scope definition, inventory analysis, and applications. *Environ. Int.* **30,** 701–720 (2004).
2. Hopewell, J., Dvorak, R. & Kosior, E. Plastics recycling: challenges and opportunities. *Phil. Trans. R. Soc. B* **364,** 2115–2126 (2009).
3. Hwang, S.-W. *et al.* A physically transient form of silicon electronics. *Science* **337,** 1640–1644 (2012).
   This paper describes the first physically transient electronics and application in an implantable biomedical device.
4. García, S. J., Fischer, H. R. & van der Zwaag, S. A critical appraisal of the potential of self healing polymeric coatings. *Prog. Org. Coatings* **72,** 211–221 (2011).
5. Selvakumar, N., Jeyasubramanian, K. & Sharmila, R. Smart coating for corrosion protection by adopting nano particles. *Prog. Org. Coatings* **74,** 461–469 (2012).
6. Huang, M. & Yang, J. Facile microencapsulation of HDI for self-healing anticorrosion coatings. *J. Mater. Chem.* **21,** 11123–11130 (2011).
7. Latnikova, A., Grigoriev, D. O., Hartmann, J., Möhwald, H. & Shchukin, D. G. Polyfunctional active coatings with damage-triggered water-repelling effect. *Soft Matter* **7,** 369–372 (2011).
8. Shchukin, D. & Möhwald, H. A coat of many functions. *Science* **341,** 1458–1459 (2013).
9. Shchukin, D. G. Container-based multifunctional self-healing polymer coatings. *Polym. Chem.* **4,** 4871–4877 (2013).
10. Esser-Kahn, A. P., Sottos, N. R., White, S. R. & Moore, J. S. Programmable microcapsules from self-immolative polymers. *J. Am. Chem. Soc.* **132,** 10266–10268 (2010).
11. Borisova, D., Möhwald, H. & Shchukin, D. G. Mesoporous silica nanoparticles for active corrosion protection. *ACS Nano* **5,** 1939–1946 (2011).
12. Wong, T.-S. *et al.* Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. *Nature* **477,** 443–447 (2011).
13. Cui, J., Daniel, D., Grinthal, A., Lin, K. & Aizenberg, J. Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing. *Nature Mater.* **14,** 790–795 (2015).
14. Esser-Kahn, A. P. *et al.* Three-dimensional microvascular fiber-reinforced composites. *Adv. Mater.* **23,** 3654–3658 (2011).
15. Gergely, R. C. R. *et al.* Multidimensional vascularized polymers using degradable sacrificial templates. *Adv. Funct. Mater.* **25,** 1043–1052 (2015).
16. Kousourakis, A., Mouritz, A. P. & Bannister, M. K. Interlaminar properties of polymer laminates containing internal sensor cavities. *Compos. Struct.* **75,** 610–618 (2006).
17. Coppola, A. M., Thakre, P. R., Sottos, N. R. & White, S. R. Tensile properties and damage evolution in vascular 3D woven glass/epoxy composites. *Composites A* **59,** 9–17 (2014).
18. Hartl, D. J., Frank, G. J. & Baur, J. W. Effects of microchannels on the mechanical performance of multifunctional composite laminates with unidirectional laminae. *Compos. Struct.* **143,** 242–254 (2016).
19. Han, J.-C., Dutta, S. & Ekkad, S. *Gas Turbine Heat Transfer and Cooling Technology*, 2nd edn (CRC Press, 2012).
20. Coppola, A. M., Griffin, A. S., Sottos, N. R. & White, S. R. Retention of mechanical performance of polymer matrix composites above the glass transition temperature by vascular cooling. *Composites A* **78,** 412–423 (2015).
21. Baginska, M. *et al.* Autonomic shutdown of lithium-ion batteries using thermoresponsive microspheres. *Adv. Energy Mater.* **2,** 583–590 (2012).
22. Chen, Z. *et al.* Fast and reversible thermoresponsive polymer switching materials for safer batteries. *Nature Energy* **1,** 15009 (2016).
23. Wang, C. *et al.* Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. *Nature Chem.* **5,** 1042–1048 (2013).
24. Berkowski, K. L., Potisek, S. L., Hickenboth, C. R. & Moore, J. S. Ultrasound-induced site-specific cleavage of azo-functionalized poly(ethylene glycol). *Macromolecules* **38,** 8975–8978 (2005).
25. Hickenboth, C. R. *et al.* Biasing reaction pathways with mechanical force. *Nature* **446,** 423–427 (2007).
26. Ramirez, A. L. B. *et al.* Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces. *Nature Chem.* **5,** 757–761 (2013).
    This paper describes *in situ* strengthening of polymers in response to shear forces by mechanically induced covalent crosslinking.
27. Li, J., Nagamani, C. & Moore, J. S. Polymer mechanochemistry: from destructive to productive. *Acc. Chem. Res.* **48,** 2181–2190 (2015).
28. Simon, Y. C. & Craig, S. L. (eds). *Mechanochemistry in Materials* (Royal Society of Chemistry, in the press).
29. Piermattei, A., Karthikeyan, S. & Sijbesma, R. P. Activating catalysts with mechanical force. *Nature Chem.* **1,** 133–137 (2009).
30. Diesendruck, C. E. *et al.* Proton-coupled mechanochemical transduction: A mechanogenerated acid. *J. Am. Chem. Soc.* **134,** 12446–12449 (2012).
31. Davis, D. A. *et al.* Force-induced activation of covalent bonds in mechanoresponsive polymeric materials. *Nature* **459,** 68–72 (2009).
    This paper describes the first demonstration of a mechanically activated covalent reaction in bulk polymeric materials.
32. Gossweiler, G. R. *et al.* Mechanochemical activation of covalent bonds in polymers with full and repeatable macroscopic shape recovery. *ACS Macro Lett.* **3,** 216–219 (2014).
33. Peterson, G. I., Larsen, M. B., Ganter, M. A., Storti, D. W. & Boydston, A. J. 3D-printed mechanochromic materials. *ACS Appl. Mater. Interf.* **7,** 577–583 (2015).
34. Chen, Y. *et al.* Mechanically induced chemiluminescence from polymers incorporating a 1,2-dioxetane unit in the main chain. *Nature Chem.* **4,** 559–562 (2012).
35. Löwe, C. & Weder, C. Oligo(p-phenylene vinylene) excimers as molecular probes: Deformation-induced color changes in photoluminescent polymer blends. *Adv. Mater.* **14,** 1625–1629 (2002).
36. Pang, J. W. C. & Bond, I. P. A hollow fibre reinforced polymer composite encompassing self-healing and enhanced damage visibility. *Compos. Sci. Technol.* **65,** 1791–1799 (2005).
    This paper describes damage indication and healing of a fibre-reinforced polymer composite by the incorporation of hollow glass fibres that rupture and release reactive liquids.
37. van den Dungen, E. T. A., Loos, B. & Klumperman, B. Use of a profluorophore for visualization of the rupture of capsules in self-healing coatings. *Macromol. Rapid Commun.* **31,** 625–628 (2010).
38. Lavrenova, A., Farkas, J., Weder, C. & Simon, Y. C. Visualization of polymer deformation using microcapsules filled with charge-transfer complex precursors. *ACS Appl. Mater. Interf.* **7,** 21828–21834 (2015).
39. Odom, S. A. *et al.* Visual indication of mechanical damage using core–shell microcapsules. *ACS Appl. Mater. Interf.* **3,** 4547–4551 (2011).
40. Li, W. *et al.* Autonomous indication of mechanical damage in polymeric coatings. *Adv. Mater.* **28,** 2189–2194 (2016).
41. Robb, M. J. *et al.* A robust damage-reporting strategy for polymeric materials enabled by aggregation-induced emission. *ACS Central Sci.* **2,** 598–603 (2016).
42. Gupta, S., Zhang, Q., Emrick, T., Balazs, A. C. & Russell, T. P. Entropy-driven segregation of nanoparticles to cracks in multilayered composite polymer structures. *Nature Mater.* **5,** 229–233 (2006).
43. Blaiszik, B. J. *et al.* Self-healing polymers and composites. *Annu. Rev. Mater. Res.* **40,** 179–211 (2010).
44. Murphy, E. B. & Wudl, F. The world of smart healable materials. *Prog. Polym. Sci.* **35,** 223–251 (2010).

45. Chen, X. *et al.* A thermally re-mendable cross-linked polymeric material. *Science* **295,** 1698–1702 (2002).
This paper describes multiple cycles of healing in a crosslinked polymer network by thermally reversible covalent bonding.
46. Hayes, S. A., Jones, F. R., Marshiya, K. & Zhang, W. A self-healing thermosetting composite material. *Composites A* **38,** 1116–1120 (2007).
47. Denissen, W., Winne, J. M. & Du Prez, F. E. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **7,** 30–38 (2016).
48. Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **334,** 965–968 (2011).
49. Scott, T. F., Schneider, A. D., Cook, W. D. & Bowman, C. N. Photoinduced plasticity in cross-linked polymers. *Science* **308,** 1615–1617 (2005).
50. Burnworth, M. *et al.* Optically healable supramolecular polymers. *Nature* **472,** 334–337 (2011).
51. Corten, C. C. & Urban, M. W. Repairing polymers using oscillating magnetic field. *Adv. Mater.* **21,** 5011–5015 (2009).
52. Cordier, P., Tournilhac, F., Soulié-Ziakovic, C. & Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* **451,** 977–980 (2008).
This paper describes the first thermoreversible self-healing rubber made by supramolecular assembly.
53. Hentschel, J., Kushner, A. M., Ziller, J. & Guan, Z. Self-healing supramolecular block copolymers. *Angew. Chem. Int. Edn Engl.* **51,** 10561–10565 (2012).
54. Das, A. *et al.* Ionic modification turns commercial rubber into a self-healing material. *ACS Appl. Mater. Interf.* **7,** 20623–20630 (2015).
55. Wang, Q. *et al.* High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder. *Nature* **463,** 339–343 (2010).
56. Lu, Y.-X., Tournilhac, F., Leibler, L. & Guan, Z. Making insoluble polymer networks malleable via olefin metathesis. *J. Am. Chem. Soc.* **134,** 8424–8427 (2012).
57. Imato, K. *et al.* Self-healing of chemical gels cross-linked by diarylbibenzofuranone-based trigger-free dynamic covalent bonds at room temperature. *Angew. Chem. Int. Edn Engl.* **51,** 1138–1142 (2012).
58. Yoon, J. A. *et al.* Self-healing polymer films based on thiol–disulfide exchange reactions and self-healing kinetics measured using atomic force microscopy. *Macromolecules* **45,** 142–149 (2012).
59. Dry, C. M. Procedures developed for repair of polymer matrix composite materials. *Compos. Struct.* **35,** 263–269 (1996).
60. White, S. R. *et al.* Autonomic healing of polymer composites. *Nature* **409,** 794–797 (2001).
This paper demonstrates the first autonomic self-healing of a fracture in a structural polymer by dispersed liquid-monomer-filled microcapsules and reactive catalyst particles.
61. Diesendruck, C. E., Sottos, N. R., Moore, J. S. & White, S. R. Biomimetic self-healing. *Angew. Chem. Int. Edn Engl.* **54,** 10428–10447 (2015).
62. Brown, E. N., White, S. R. & Sottos, N. R., Microcapsule induced toughening in a self-healing polymer composite. *J. Mater. Sci.* **39,** 1703–1710 (2004).
63. Jones, A. S., Rule, J. D., Moore, J. S., Sottos, N. R. & White, S. R., Life extension of self-healing polymers with rapidly growing fatigue cracks. *J. R. Soc. Interf.* **4,** 395–403 (2007).
64. Kang, S., Baginska, M., White, S. R. & Sottos, N. R. Core–shell polymeric microcapsules with superior thermal and solvent stability. *ACS Appl. Mater. Interf.* **7,** 10952–10956 (2015).
65. Kim, B., Jeon, T. Y., Oh, Y.-K. & Kim, S.-H. Microfluidic production of semipermeable microcapsules by polymerization-induced phase separation. *Langmuir* **31,** 6027–6034 (2015).
66. Norris, C. J. *et al.* Autonomous stimulus triggered self-healing in smart structural composites. *Smart Mater. Struct.* **21,** 094027 (2012).
67. Norris, C. J., Meadway, G. J., O'Sullivan, M. J., Bond, I. P. & Trask, R. S. Self-healing fibre reinforced composites via a bioinspired vasculature. *Adv. Funct. Mater.* **21,** 3624–3633 (2011).
68. Toohey, K. S., Sottos, N. R., Lewis, J. A., Moore, J. S. & White, S. R. Self-healing materials with microvascular networks. *Nature Mater.* **6,** 581–585 (2007).
This paper describes the self-healing of a polymer coating by monomer-filled, interconnected microvascular channels made by direct-write assembly of a sacrificial scaffold.
69. Hamilton, A. R., Sottos, N. R. & White, S. R. Self-healing of internal damage in synthetic vascular materials. *Adv. Mater.* **22,** 5159–5163 (2010).
70. Hansen, C. J. *et al.* Self-healing materials with interpenetrating microvascular networks. *Adv. Mater.* **21,** 4143–4147 (2009).
71. Hansen, C. J. *et al.* Accelerated self-healing via ternary interpenetrating microvascular networks. *Adv. Mater.* **21,** 4320–4326 (2011).
72. Huang, C.-Y., Trask, R. S. & Bond, I. P. Characterization and analysis of carbon fibre-reinforced polymer composite laminates with embedded circular vasculature. *J. R. Soc. Interf.* **7,** 1229–1241 (2010).
73. Trask, R. S. & Bond, I. P. Bioinspired engineering study of Plantae vascules for self-healing composite structures. *J. R. Soc. Interf.* **7,** 921–931 (2010).
74. Therriault, D., White, S. R. & Lewis, J. A. Chaotic mixing in three-dimensional microvascular networks fabricated by direct-write assembly. *Nature Mater.* **2,** 265–271 (2003).
75. Patrick, J. F. *et al.* Continuous self-healing life cycle in vascularized structural composites. *Adv. Mater.* **26,** 4302–4308 (2014).
This paper describes the first repeated self-healing of a fibre-reinforced composite by two-part, reactive liquid delivery through 3D, interpenetrating microvascular networks.
76. Brochu, A. B. W., Chyan, W. J. & Reichert, W. M. Microencapsulation of 2-octylcyanoacrylate tissue adhesive for self-healing acrylic bone cement. *J. Biomed. Mater. Res. B* **100,** 1764–1772 (2012).
77. Brochu, A. B. W., Evans, G. A. & Reichert, W. M. Mechanical and cytotoxicity testing of acrylic bone cement embedded with microencapsulated 2-octyl cyanoacrylate. *J. Biomed. Mater. Res. B* **102,** 181–189 (2014).
78. Gladman, A. S., Celestine, A.-D. N., Sottos, N. R. & White, S. R. Autonomic healing of acrylic bone cement. *Adv. Healthcare Mater.* **4,** 202–207 (2015).
79. Brochu, A. B. W., Craig, S. L. & Reichert, W. M. Self-healing biomaterials. *J. Biomed. Mater. Res. A* **96,** 492–506 (2011).
80. Odom, S. A. *et al.* Restoration of conductivity with TTF-TCNQ charge-transfer salts. *Adv. Funct. Mater.* **20,** 1721–1727 (2010).
81. Odom, S. A. *et al.* A Self-healing conductive ink. *Adv. Mater.* **24,** 2578–2581 (2012).
82. Odom, S. A. *et al.* Autonomic restoration of electrical conductivity using polymer-stabilized carbon nanotube and graphene microcapsules. *Appl. Phys. Lett.* **101,** 043106 (2012).
83. Blaiszik, B. J. *et al.* Autonomic restoration of electrical conductivity. *Adv. Mater.* **24,** 398–401 (2012).
84. Tee, B. C.-K., Wang, C., Allen, R. & Bao, Z. An electrically and mechanically self-healing composite with pressure- and flexion-sensitive properties for electronic skin applications. *Nature Nanotechnol.* **7,** 825–832 (2012).
85. Birnbaum, K. D. & Alvarado, A. S. Slicing across kingdoms: regeneration in plants and animals. *Cell* **132,** 697–710 (2008).
86. White, S. R. *et al.* Restoration of large damage volumes in polymers. *Science* **344,** 620–623 (2014).
This paper describes the self-healing of large-scale damage by vascular delivery of two-stage chemistry that first forms a dynamic gel scaffold and then polymerizes.
87. Kim, H., Mohapatra, H. & Phillips, S. T. Rapid, on-command debonding of stimuli-responsive crosslinked adhesives by continuous, sequential quinone methide elimination reactions. *Angew. Chem. Int. Edn Engl.* **54,** 13063–13067 (2015).
88. Baker, M. S., Kim, H., Olah, M. G., Lewis, G. G. & Phillips, S. T. Depolymerizable poly(benzyl ether)-based materials for selective room temperature recycling. *Green Chem.* **17,** 4541–4545 (2015).
89. Hernandez, H. L. *et al.* Triggered transience of metastable poly(phthalaldehyde) for transient electronics. *Adv. Mater.* **26,** 7637–7642 (2014).
90. Park, C. W. *et al.* Thermally triggered degradation of transient electronic devices. *Adv. Mater.* **27,** 3783–3788 (2015).
91. Kang, S.-K. *et al.* Bioresorbable silicon electronic sensors for the brain. *Nature* **530,** 71–76 (2016).
92. Diesendruck, C. E. *et al.* Mechanically triggered heterolytic unzipping of a low-ceiling-temperature polymer. *Nature Chem.* **6,** 623–628 (2014).
93. Jin, H. *et al.* Thermally stable autonomic healing in epoxy using a dual-microcapsule system. *Adv. Mater.* **26,** 282–287 (2014).
94. Maiti, S., Shankar, C., Geubelle, P. H. & Kieffer, J. Continuum and molecular-level modeling of fatigue crack retardation in self-healing polymers. *J. Eng. Mater. Technol* **128,** 595–602 (2006).
95. Balazs, A. C. Modeling self-healing materials. *Mater. Today* **10,** 18–23 (2007).
96. Jones, A. S. & Dutta, H. Fatigue life modeling of self-healing polymer systems. *Mech. Mater.* **42,** 481–490 (2010).
97. Zhang, M. Q. & Rong, M. Z. Theoretical consideration and modeling of self-healing polymers. *J. Polym. Sci. B* **50,** 229–241 (2012).
98. Soghrati, S. *et al.* Computational analysis of actively-cooled 3D woven microvascular composites using a stabilized interface-enriched generalized finite element method. *Int. J. Heat Mass Transfer* **65,** 153–164 (2013).
99. Bluhm, J., Specht, S. & Schröder, J. Modeling of self-healing effects in polymeric composites. *Arch. Appl. Mech.* **85,** 1469–1481 (2015).
100. Nie, Z., Xu, S., Seo, M., Lewis, P. C. & Kumacheva, E. Polymer particles with various shapes and morphologies produced in continuous microfluidic reactors. *J. Am. Chem. Soc.* **127,** 8058–8063 (2005).
101. Tumbleston, J. R. *et al.* Continuous liquid interface production of 3D objects. *Science* **347,** 1349–1352 (2015).
102. Gladman, A. S., Matsumoto, E. A., Nuzzo, R. G., Mahadevan, L. & Lewis, J. A. Biomimetic 4D printing. *Nature Mater.* **15,** 413–418 (2016).

Acknowledgements J.F.P. and M.J.R. are grateful to the Arnold and Mabel Beckman Foundation for financial support through the Beckman Institute Postdoctoral Fellowship Program. The authors thank the Air Force Office of Scientific Research for support through the Center of Excellence in Self-Healing, Regeneration, and Structural Remodeling, the National Science Foundation (DMR 1307354), the Defense Advanced Research Project Agency (FA8650-13-C-7347) and the BP International Center for Advanced Materials (ICAM). We are grateful to D. Loudermilk, C. Klinger, A. Jerez and I. Patrick for assistance with graphics, and G. Wilson and M. Andersson for insightful discussions.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare competing financial interests, see go.nature.com/2gnh9ma. Readers are welcome to comment on the online version of this paper at go.nature.com/2gnh9ma. Correspondence should be addressed to S.R.W. (swhite@illinois.edu).