



Understanding Functional Polymers

How Smart Materials Are Impacting The Plastics Industry



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by Andy Pye

Functional Polymers

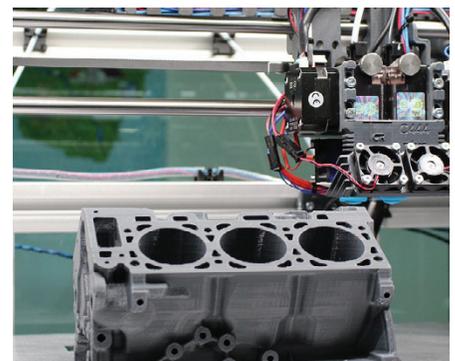
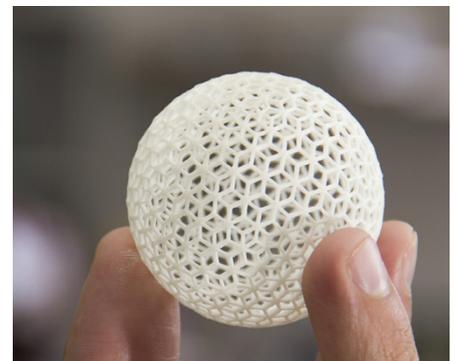
Smart materials, otherwise known as functional materials, are materials or structures that can sense and then respond according to a change in their local environment. The stimulus might be a change in temperature, stress, moisture content, pH, or electric/magnetic field. The response might be as simple as providing a visual or audible alarm if a threshold is reached, or as complex as activating a damping system.

Temperature indicators that check the temperature of a baby's bath water are examples of a simple system. Other examples include:

- surfaces for self-cleaning glass
- thermochromic materials for temperature measurement
- materials for packaging, lingerie, fashion and sports goods
- electro-rheological fluids for active auto suspensions
- systems for automatic ventilation
- optical fibre sensors for structural health monitoring
- morphing structures to reduce drag
- time-temperature indicators on food packaging
- stress sensors on tyres
- triboluminescent crystals used for impact detection

Smart materials use a range of materials or combinations of materials right across the spectrum, including metals, ceramics, coatings, gels and fluids - and of course polymers. The polymers may be used on their own, or in combination with other materials. Although some smart materials have emerged onto the market, many only exist at the concept stage and are some way from commercial production.

This white paper looks at a selection of smart, or functional, materials which are predominantly polymeric and which are commercialised or close to it. Table 1 shows a range of smart materials, highlighting the ones which are discussed here. They may exhibit advanced mechanical, optical and/or electronic properties. And because the properties are in many cases unique or highly unusual, and not always commercialised, they do not appear in materials selection systems.



Functional materials highlighting those which are significantly polymeric in nature		
4D Printing	Ferroelectric	Photorefractive
Antimicrobial	Hall effect	Photorestrictive
Auxetics	Hydrophillic Polymers	Photovoltaic
Biomimetic	Intumescent	Piezoelectric
Chemi-resisting	Magenticsma	Piezoresistive
Chemchromic	Magetocaloric	Pyroelectric
Chemi-luminescent	Magnetolectric	Self-Healing
Conductive Adhesives	Magnetoopic	Shape Memory
Electroactive	Magnetostrictive	Shear thickening
Electrocalorific	Mechanochromic	Superhydrophobic
Electrochromic	Microencapsulatedchemicals	Thermochromic
Electroluminescent	Paramagnetic	Thermocouples
Electrooptic	Photocatalytic	Thermoelectric
Electrophoretic	Photochromic	Thermoluminescent
Electrorheological	Photoelastic	Thixotropic
Electrostrictive (with electroactive)	Photoluminescent	Thiboluminescent

Table 1

4D Printing

This is a subject which has been well reported by UL Prospector in recent years.

4D printing is an emerging technology similar to 3D printing (additive manufacturing), but with the fourth dimension of time added. Some industry commentators are now preferring to use the term "3D printing and self-assembly".

Using this technology, the manufactured products grow into their original form after exposing them in a particular environment. Shape memory alloys using temperature fluctuations to cause changes in material shapes have been around for many decades and are being exploited in 4D printing.

Electro-active Polymers, on the other hand, use an approach that is more chemically geared with catalysts that activate polymers with pressurised fluids, gases or even with light. Other 4D printed structures are catalysed using moisture.

While companies are still in the development phase and investing huge revenue amounts for applications of this technology, major end uses are already seen in healthcare, manufacturing, and construction. North America is the leading region in the 4D Printing Market with many situated there.

Researchers at Lawrence Livermore National Laboratory have 3D printed shape-shifting structures that can fold and unfold themselves, or expand and contract in size, when prompted by changes in electricity or heat.¹ The primary shapes they created were printed with shape-memory polymer inks the team developed using a direct-ink writing 3D printing process. The ink is made from soybean oil and additional co-polymers, plus carbon nanofibers.

Other functional materials include:

- Membrane Materials
- Biomimetic Materials
- Self-healing polymers
- 4D printing materials
- Semiconducting Conjugated Polymers

Stimuli-Responsive Polymers - which allow for responsive "controlled release" drug delivery systems - also fall under the umbrella, as do smart surfaces for cell culture and regenerative medicine.

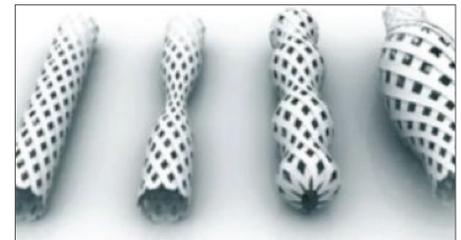


Figure 1 – Early 4D printed structures

Read more about 4D printing:
<https://knowledge.ulprospector.com/tag/4d-printing/>

The team claims to be the first to combine conductive shape-memory materials with 3D printing and origami-like materials, although a couple of years ago, using an Objet Connex multi-material 3D printer, a University of Colorado-Boulder team combined shape-changing materials that respond to heat and printed objects in one shape that changed their shape later, including a self-assembling cube.²

Researchers say the technology could have applications in aerospace, such as solar arrays or antennae that can unfold; flexible circuits; robotics devices; and medical uses, such as stents that expand after being exposed to heat. The work derives from a project to develop high-performance 3D-printed carbon fibre composites.

UK sports car maker Briggs Automotive Company, together with Autodesk and Carbitex, has designed a car aerofoil that changes shape and operates in response to different environmental changes in temperature or air pressure. Airbus is interested in similar programmable carbon fibre composites. Components can be designed which could replace hinges, or even motors and hydraulic actuators.^{3,4}

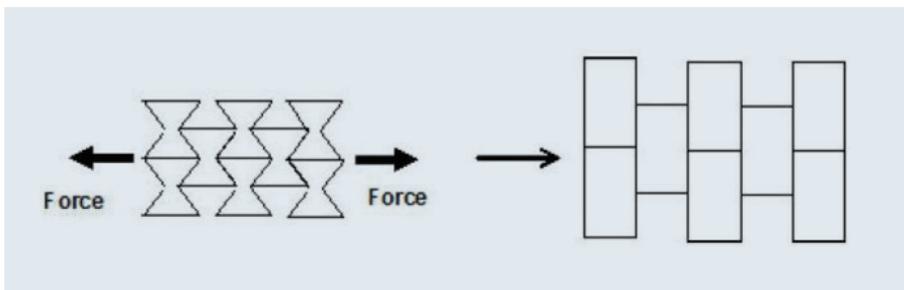
Carbitex is a manufacturer of 3D printable carbon composites that remain flexible after curing. The degree of flexibility is controllable in response to heat, light, or water.

Auxetic Materials

The majority of materials become thinner when stretched, but **auxetic materials** show the opposite effect - when they are stretched in one direction, they become thicker in the directions perpendicular to the applied force. The opposite is also true – when they are compressed in one direction, they also become thinner in the other directions. The initial materials developed were foams, while honeycomb structures and fibres now exist. In all cases, the counter-intuitive mechanical behaviour is due to a ‘hinged’ cellular structure, which allowed the cells to open out when stretched.

Auxetic materials have yet to be produced on a commercial basis but there are several markets where their unusual property could be an advantage. Examples include:

- Energy absorption and fracture resistance applications – body armour, packaging
- Biomedical – implants, anchors, dilators for blood vessels
- Filters – self-cleaning





Chemi-Resisting Materials

Chemi-resisting materials react to organic compounds by changing their electrical conductivity. How they do this depends on the nature of the material used.

In composite polymer chemi-resistors, a combination of an insulating, chemically-sensitive polymer film (such as polyvinyl acetate, polyethylene oxide or polyvinyl butyral) and an inactive conductive agent (such as carbon black) which swell in the presence of certain chemicals, causing an increase in resistance. Reaction times are in the order of a few seconds.

Applications are for gas sensors, such as the 'lab on a chip', detecting volatile organic compounds - the so-called electronic nose – as well as in environmental or emissions monitoring, engine management systems, vehicle health monitoring, toxin detection and flammable gas detection.

Pulsed laser deposition and polymer film growth techniques are used to fabricate polymer/carbon nanocomposite thin films for use in chemi-resistors.

Conductive Adhesives

Around the world, interest in lead-free solder alternatives have increased dramatically, primarily because of initiatives to rapidly eliminate the presence of leaded solders in electronic assemblies.

For years, many manufacturers used lead-free alloys in niche applications to provide a higher melting point or to satisfy particular material requirements. However, the goal of today's lead-free solder research is to determine which alloys should be used to best replace the

estimated 50,000 metric tons of tin-lead solder which was used at its peak.

[Conductive adhesives](#) traditionally have been used as die-attach materials that bond integrated circuits to lead frames. They are also used to make laminates for printed circuits, to attach copper foil to boards or flexible substrates, and to bond circuits to heat sinks. As a result of lead-free initiatives, conductive adhesives have become an attractive alternative to solder for attaching surface mount components.

Curing at room temperature or processing quickly with minimal exposure to temperatures between 100 and 150°C, these adhesives are excellent for bonding temperature-sensitive components and for providing electrical connections on non-solderable substrates like plastic and glass.

Conductive adhesives combine thermosetting epoxy adhesive resin and conductive metal particles. They are used for the assembly and repair of flexible circuits or bonding flexible substrates and connectors.

Both lead-free solders and conductive adhesives are strong candidates for providing electrical interconnection and thermal transfer in electronic devices; however, each technology has its own strengths and weaknesses. Solders form metallurgical bonds between metal substrates, whereas conductive adhesives form mechanical and chemical bonds at the substrate surface.⁵ Metallurgical bonds are more thermally and electrically conductive and generally stronger.

But solders are often prone to stress cracking on flexible substrates, whereas

conductive adhesives also better resist cracking from vibration and shock.

Both lead-free solders and conductive adhesives are more expensive than traditional tin-lead solders for a variety of reasons. Whereas lead is among the least expensive metals available (\$0.40 per pound), alternative alloys can be substantially costlier.⁵

Electro-Active Ionic Polymers

[Electro-active Polymers](#) (EAPs) are able to change their shape when a voltage is applied. They are primarily used as either an actuator or sensor. Often called “artificial muscle” due to their ability to induce large strains, they are regularly considered for robotic applications.⁶ Other applications include hinges, grab/hold mechanisms and contract/expand mechanisms.

EAPs are available in many different material forms including polymers and polymer composites, and tend to be made in research laboratories, though certain types can be bought commercially.

Although they can induce strains much greater than Electro-Active Ceramics (EACs), they are not so robust and reach their elastic limit at low stress levels.

There are two main types of EAP material; electronic and ionic. **Electronic EAPs** have a rapid response, can induce relatively large actuation forces, and DC activation can be used to hold a strained position. However, large voltages (~150MV/m) are required to activate electronic EAPs, and the glass transition temperature limits their use at low temperatures, so one must compromise between actuation strain and actuation stress.



Ionic EAPs require an electrolyte and encapsulation and are consequently sometimes referred to as ‘wet’ EAPs as compared to ‘dry’ electronic EAPs. They operate mainly with bending actuation with large displacements, where low voltages are required to actuate them. Ionic EAPs are unable to hold strain under DC voltage (except conductive polymers), and have a slower response time. Consistency of material fabrication can be a problem and electrolysis occurs in aqueous systems at >1.23 V.\

Hydrophilic Polymers For Ultra-Capacity Polymer Supercapacitors

Up to now, we have generally assumed that electric cars would be battery operated and hybrid vehicles will form a major part of the market. But what about the potential for an alternative technology - supercapacitors?

Both batteries and supercapacitors are electrochemical energy storage media, but they are as different as night and day. Both are capable of energy storage and targeted energy release – and yet there are major differences between the two. Batteries store very large amounts of energy that is released slowly but constantly.

By contrast, supercapacitors can only store small amounts of energy (they have poor energy density per kilogramme) but they release this energy much faster and more powerfully with large short-term peak currents. Nevertheless, they have, until now, been unable to compete with conventional battery energy storage in many applications.

Now, a major scientific breakthrough based on ground-breaking research from the University of Surrey claims to have discovered new materials offering an alternative to battery power and between 1000 and 10,000 times more powerful than existing supercapacitors.⁷ Patents on the new materials have been filed by a company called Augmented Optics and its wholly owned subsidiary Supercapacitor Materials, registered specifically for the purpose of commercialising them.

Supercapacitors with these properties would allow electric cars to travel similar distances as petrol cars, but without the need to stop for lengthy recharging breaks of typically six to eight hours. Instead, they would recharge fully in the time it takes to fill a regular car with petrol. Very high energy density supercapacitors would also make it possible to recharge a mobile phone or laptop in just a few seconds.

The Chemistry

The technology has been adapted from the principles used to make soft contact lenses, which Dr Donald Highgate (of Augmented Optics, and an alumnus of the University of Surrey) developed following his postgraduate studies at Surrey 40 years ago. The research programme was conducted by researchers at the University of Surrey’s Department of Chemistry, co-led by Dr Ian Hamerton and Dr Brendan Howlin. Hamerton continues to collaborate on the project in his new post at the University of Bristol.

The materials are known as **hydrophilic polymers**. They are based on large organic molecules composed of many repeated sub-units and bonded together to form a three-dimensional network. The test results from the new polymers (Table 2) suggest that extremely high energy density supercapacitors could be constructed in the very new future. Not only that, but the polymers age and show markedly improved conductivity with time - for reasons not currently understood, they self-organise over 30 days.

Applications of supercapacitors by useful energy density

Energy density	Application
5 Wh/kg	Current supercapacitors
25 Wh/kg	Stationary energy storage
50 Wh/kg	General transportation
100 Wh/kg	Lithium ion batteries
2500 Wh/kg	Petrol
5000 Wh/kg	Likely projected level for new materials

Table 2

polystyrene sulfonate (PEDOT:PSS) and a higher performance polymer where Imidazole is used instead of the PEDOT:PSS. Imidazole is an organic compound with the formula C₃N₂H₄.⁸

These polymers also have many other possible uses in which tough, flexible conducting materials are desirable, including bioelectronics, sensors, wearable electronics, and advanced optics.⁷

The proprietary materials developed in this project are electrically active hydrophilic polymers: an industrial grade version based on a hydrophilic structure, amalgamated with a transparent conducting polymer called Poly(3,4-ethylenedioxythiophene)

Intumescence

Intumescent materials foam and swell when exposed to high surface temperatures or flames. The objective is to contain fire and toxic gases by inhibiting flame penetration, heat transfer and transport of toxic gases from the site of a fire to other parts of a structure. The swelling creates a barrier between the flame and the structure to be protected. Intumescent materials may be water-based, solvent-based or epoxy-based, with epoxy-based materials being most widely used.

Intumescent materials are available to spray or paint on structures, or as tape, sheet, self-adhesive sheet, or other pre-formed shapes.

Magnetostrictive

[Magnetostrictive materials](#) change their shape (strain) and volume when subjected to a magnetic field. Magnetostriction is the cause of the hum of mains transformers, with the soft iron core expanding and contracting with the application of a 50Hz magnetic field, brought about by the 50Hz mains voltage in the wire wrapped around the core.

Nearly all ferromagnetic materials are metallic and exhibit a change in shape and volume resulting from a change in magnetic

field. In nickel, iron and cobalt, the strain exhibited is in the order of 0.001% and the change in volume is very small.

Giant magnetostriction - strains of 0.1% or more - was discovered in rare earth alloys during the 1960s, particularly in alloys of terbium and dysprosium, allowing high strains (about 0.1%) at room temperature. Terfenol-D, an intermetallic compound of terbium, dysprosium and iron, has since become the predominant magnetostrictive material.

New magnetostrictive materials being investigated include NiMnGa alloys exhibiting up to 9% strain in single crystal specimens and an iron/gallium alloy called Galfenol which exhibits 0.04% strain but is tougher than Terfenol-D and may be machined and used in devices where Terfenol-D may fracture.

Researchers are studying polymer matrix composites containing magnetostrictive particles that are tough and can better accommodate tensile and shear loading states. Terfenol-D powder can be added to polymers to create a magnetostrictive composite. It is also possible that pre-formed composite components or pre-made mixtures of powder with liquid polymer precursor chemicals (e.g. epoxy) may be available.

Photochromic Materials



Figure 3 Photochromic polymers (courtesy Colourchange, a division of LCR Hallcrest)

Photochromic materials change colour reversibly when exposed to different wavelengths of electromagnetic radiation (visible light and UV light, for example) at different intensities. Photochromic materials are colourless, but when sunlight or ultraviolet radiation is applied, the molecular structure of the material changes and they exhibit colour. When the relevant light source is removed, the colour disappears.

Photochromic materials may be organic and inorganic materials, the former including silver halide, which is used as fine crystals (10-20nm) which are dispersed throughout a matrix of some other material, generally glass. An alternative technique involves diffusion of the silver halide into the surface of the glass. The colouration range achievable is limited to grey and brown hues.

Organic photochromic materials exhibit different optical properties as a result of changes in the structure of the molecules. The most widely used such compounds include oxazines, pyrans and fulgides.

In pyrans and oxazines, it is believed that an electrocyclic mechanism is involved, such that when exposed to electromagnetic radiation, these compounds transform from a colourless closed ring into a coloured open ring compound. With fulgides, the transformation is from a colourless open ring form into a coloured closed ring form.

These compounds are added to polymers. The proprietary organic materials come in four base colours: blue, yellow, purple and orange/red. When combined, additional colours such as green, brown and grey and their shades can be achieved.

The rate of change in the colouration is measured as “half-life”, the time for colouration intensity to fall by half when the stimulating photon radiation is removed.

Several of the properties of organic photochromic dyes are subject to a “matrix effect” and are modified or even inactivated by interactions with different matrix polymers. The main factor determining the matrix effect is the amount of free volume available in the polymer structure. Very rigid or low free volume polymers, (highly crystalline polymers, polycarbonates, most engineering polymers) have insufficient free volume and will shift the colour of the absorption peaks by up to 40nm, accelerate the “fatigue” breakdown of the dye and reduce, or even totally prevent, the photochromic colour change. Non-crystalline polyolefins, plasticised PVC and other vinyls generally give the best performance.

Organic photochromic materials are generally produced in the form of “masterbatch” powders, for addition to polymers. Photochromics may also be supplied as paint, ink or other coating material when pre-mixed with a suitable carrier polymer. Recently, photochromic epoxy resin coatings have been patented by Essilor International⁹ to allow the preparation of photochromic plastic articles without the need to incorporate the photochromic compounds into an unsuitable plastic substrate.

3D photochromic structures

University of Nottingham research proves that advanced materials containing molecules that switch states in response to environmental stimuli such as light can be fabricated using 3D printing.¹⁰ The study findings have the potential to vastly increase the functional capabilities of 3D-printed devices for industries such as electronics, healthcare and quantum computing.

To demonstrate their concept, the team developed a photoactive molecule that changes from colourless to blue when irradiated with light. The colour change can then be reversed by exposure to oxygen from the air.

The researchers then 3D-printed composite materials by combining the photoactive molecules with a tailor-made polymer, yielding a new material that can store information reversibly.

Any molecules that change properties upon exposure to light can be printed into composites with almost any shape or size.

“In theory, it would be possible to reversibly encode something quite complex like a QR code or a barcode, and then wipe the material clean, almost like cleaning a whiteboard with an eraser,” explains researcher Dr Graham Newton. “While our devices currently operate using colour changes, this approach could be used to develop materials for energy storage and electronics.”



SOURCE: University of Nottingham



Piezoelectrics

[Piezoelectric materials](#) generate an electric charge across their surface when subjected to a mechanical stress. They also display the opposite effect, changing their shape when an electric field is applied across them. The essential feature which enables a material to be piezoelectric is that its crystalline structure is not symmetrical about its centre. This provides a net electric field within the crystal structure, which enables the structure to respond to an applied field or pressure. In piezoelectric materials the charge produced is directly proportional to the stress applied.

Piezoelectric materials are used as electromechanical transducers, converting between electrical and mechanical energy, and their uses can be divided mainly into sensing and actuating applications. They can be ideal candidates for applications which requires a lightweight, solid state system; the range of devices available as both sensors and actuators, on a bulk and micro-scale, is vast.

As actuators, the main advantages are an instantaneous and reliable response up to MHz frequencies, and a small but precise deformation (typical maximum strain ~ 0.1%). Examples include linear actuation, spark generation, precision motors, 'tweeters', ultrasonics and frequency modulators.

The materials most commonly used for actuation are the piezo-ceramics and certain piezo-composites. Single crystals in particular offer large displacement and excellent electromechanical efficiency. The most widely used polycrystalline piezo-ceramic material is lead zirconate titanate (PZT).

Piezo-composites can offer significant advantages for particular applications, chiefly within the hydrophone and medical imaging markets. The composite properties will depend on both the type of materials used and how the phases are connected, so piezo-composites tend to be manufactured to meet 'bespoke' purposes. For example, a device consisting of ceramic powder dispersed within a polymer will display different behaviour to that of a polymer containing aligned ceramic rods.

There is less choice in piezo-polymer materials. [Polyvinylidene fluoride](#) (PVDF) is the most widely used type of polymer and, although particular properties can be modified through the manufacturing process, there is less scope to optimise the material compared with the ceramic materials. PVDF is available commercially from several companies.

Piezoresistive polymers contain particles that enable the material to conduct under applied pressure. For example, 'quantum tunnelling composites' (QTC) display an extremely large change in resistance under pressure, such that they change from being electrically insulating to electrically conductive. The elastomers contain metallic particles that are isolated from each other. When pressure is applied, these particles are brought closer together until electrons are able to tunnel through the elastomer from one particle to another and hence pass completely through the material, making it conductive.

As sensors, piezoelectric materials also offer an advantage in applications where power consumption is a significant constraint, since they generate their own voltage and so do not require power. Examples include pressure and force sensors, accelerometers, hydrophones, and microphones. All forms of piezoelectric materials can be used for sensors; polymers offer several advantages over ceramic materials, such as the capability to be manufactured into large areas, a conformable nature, high impact resistance, high voltage sensitivity and low acoustic impedance.



Figure 4 Piezoelectric buzzer and sensor. Copyright: noneam / 123RF Stock Photo

Pyroelectric Materials

Pyroelectric materials generate an electrical potential (charge) when heated or cooled. This is the opposite of the electrocaloric effect. Pyroelectricity is closely related to piezoelectricity. All pyroelectric materials are also piezoelectric, but not all piezoelectrics are significantly pyroelectric.

In a pyroelectric crystal, changing temperature affects the “dipole moments” of the electric dipoles formed by pairs or groups of ions in the ionic crystal. If the effect is not symmetrical, one side of the crystal becomes charged positive and the opposite side negative. The other sides remain neutral.

The effect occurs only with changing temperature, so to measure the temperature of an unchanging object, the sensor must be switched between an object of known temperature and the object of interest.

A large number of pyroelectric materials exist, including:

- minerals such as tourmaline
- single crystals such as triglycine sulphate
- ceramics such as lead zirconate titanate
- polymers such as polyvinylidene fluoride
- biological materials such as collagen



Generally, the material will be a non-conductive inorganic or organic ionic crystal and may be in the form of a single crystal, polycrystalline, or a polycrystalline thin film.

Signals from a pyroelectric sensor may also carry interference generated by the parallel piezoelectric effect.

Self-healing polymers

When we get scratched, our skin can repair itself. Non-living coatings cannot currently do the same thing, so we cannot put self-repairing surfaces on cars, cell phones, laptops, and many other items. As the commercial applications are numerous and the financial payoffs are potentially huge, material scientists have been actively developing polymers that can self-heal. Everything from nanoparticles to expandable gels have been tried.

Early self-healing materials could only undergo the repair process once, and the recent challenge has been to devise systems that can heal themselves repeatedly.

A team at the University of Illinois under Nancy Sottos used a technique called direct-write to create an epoxy-resin base which they infused with a network of interconnected horizontal and vertical channels 200µm in diameter.¹¹ These channels were filled with healing agent low-viscosity monomeric dicyclopentadiene. The team deposited a solid epoxy resin layer on top of the vascularised substrate, incorporating Grubbs' catalyst, benzylidene-bis(tricyclohexylphosphine)dichlororuthenium into this outer coating. "After a sufficient time period the cracks are healed and the structural integrity of the coating restored. As cracks reopen under subsequent loading the healing cycle is repeated," report the researchers.¹²

A new kind of polyurethane coating works in a different way to repair its own scratches. Scratches to the surface of the new self-healing coating close up in only a few minutes when exposed to sunlight. This occurs because the damaged polymer molecules around the edges of a scratch absorb energy from the ultraviolet radiation in the sunlight and use it to form new cross-links, and so rebuild its molecular network.

The material could be useful as a clear coating for cars, electronic devices such as mobile phones, and even furniture. It combines polyurethane with a similar polymer to chitosan, a carbohydrate derived from the shells of shrimps, crabs and other crustaceans. Researchers from the University of Southern Mississippi¹³ modified the chitosan molecules by adding ring-shaped structures called oxetanes, which are composed of one oxygen and three carbon atoms. The oxetane rings give the material its ability to heal. When a scratch is formed, some of the rings break, leaving chemically reactive free ends, although the exact chemical mechanism is unknown.

Exposure to UV light creates reactive spots on other sections of the chitosan molecules which then bond with the broken oxetane rings to form new chemical cross-links that repair the damage. The process appears to begin at the bottom of a scratch, pulling it closed like a zipper.

Synthetic skin

Using an electro-conductive polymer, chemical engineers have created what is being described as a synthetic form of skin that, when injured, heals itself in a matter of seconds. Previous work involved silicon-based materials which, though electrically conductive — a necessary property of artificial skin — were also quite brittle.

Over the past decade, chemists have produced plastics that, when cut, can rejoin themselves. In 2008, a group of French engineers at ESPCI ParisTech designed a rubber compound that could restore its mechanical properties after repeated structural insults, including breaking.¹⁴ Despite these achievements, however, the materials had low electrical conductance, making them less than ideal for their intended use as sensor material for prosthetics.

But now, engineers at Stanford University have effectively combined these two desired properties to advance the science substantially. The team was able to increase both the self-healing and electrical conducting properties of their new material by incorporating nickel atoms into the polymer which allows electrons to continuously jump between the metal atoms embedded in the polymer.¹⁵

However, the new polymer is still quite sensitive to applied forces (pressure and torsion, or twisting) as these forces change the distance between the metal atoms and thus change the electrical resistance of the polymer. Therefore, it was necessary to demonstrate that this newest compound could take punishment, like real skin, and still maintain a high level of conductance.

They subsequently found that the compound retained 98 percent of its conductivity and, more impressively, it could be cut and healed over and over again - like real skin. These experiments were the first to demonstrate both mechanical and electrical self-healing.

Recycling aids

Elsewhere, scientists are reporting development of thermally self-healing polymeric materials for use in electronics products. Researchers in The Netherlands have a new plastic with potential for use in the first easy-to-recycle computer circuit boards, electrical insulation, and other electronics products that now wind up on society's growing heaps of electronic waste.

In the study "Thermally Self-Healing Polymeric Materials: The Next Step to Recycling Thermoset Polymers";¹⁶ the researchers were looking at how thermoset plastics, widely used in applications such as electrical insulation and adhesives, could be reprocessed into new products.

Lead scientist Antonius A Broekhuis and his team developed thermally "self-healing" polymeric materials based on furan-functionalised, alternating thermoset polyketones (PK-furan) and bis-maleimide using Diels-Alder (DA) and Retro-Diels-Alder (RDA) reactions to form and subsequently break polymeric crosslinking.

Shape Memory Polymers

While most shape memory materials are metallic (alloys of copper or of nickel-titanium), Shape Memory Polymers (SMP) are polymers which can “memorise a shape”, changing from shape A to shape B on exposure to external stimuli, typically heat.

SMPs can memorise shapes as a result of the polymer makeup and processes that “train” the polymer to remember shapes. Its initial, permanent shape (B) is obtained by extrusion or injection moulding. Shape A is obtained by deforming the polymer and fixing it into a temporary shape. The polymer can then be activated by external stimuli such as heat, light, electrical currents or magnetic fields. Thermal stimulus is more commonly used, where the polymer changes from a rigid to elastic body at the glass transition temperature (T_g). The effect is reversible within a certain temperature range.

SMPs have been around for about three decades and can be adapted to respond to different stimuli with the inclusion of additives or they can be made into shape-changing composites by incorporating reinforcing fibres.

Thermally activated SMPs can be tailored so the T_g is appropriate for a specific application and can range from -30 to 260°C . The polymer can be easily deformed at temperatures above the T_g ; the shape is maintained indefinitely after subsequent cooling below the T_g . The polymer will return to its original shape when heated above the T_g again.

Light-induced activation of SMPs has been achieved by incorporating reversible photoreactive molecular switches made from cinnamic acid (CA) or cinnamylidene acetic acid (CAA). Loading the polymer with respective additives yields a photosensitive polymer.

In addition, researchers are experimenting with water-activated SMPs, where the water molecules diffuse into the polymer structure and act as a plasticiser, effectively lowering the T_g of the material; this means that the shape change occurs at a constant temperature. SMPs are also showing increased potential for biological applications due to increased compatibility compared to shape memory alloys, and their ability to be made biodegradable.

Biomedical applications of SMPs are of particular interest: potential applications include a method of removing blood clots using a laser-activated device, implants that inflate to make a patient feel full, and active medical devices and implants.

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Andy Pye is a technologist, technical writer, journalist and editor based in London, England close to the Greenwich Meridian line. Having originally qualified as a metallurgist at Cambridge University, Andy spent a period as a consultant, where he specialised in advanced composites, asbestos substitutes and the methodology of materials selection, subjects on which he has published several books and technical papers.

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