

Smart materials

A talk delivered at the Department of Materials, University of Oxford
on an Open Day for school teachers

This talk is accompanied by a Powerpoint presentation

Materials science isn't what it used to be. Once, when we spoke about materials, we were speaking about *fabrics* – passive stuff to be cut and shaped and formed into components for structures and machines. Wooden beams, stone blocks, metal sheets and girders, plastic utensils (images): these were substances that were required simply to be, rather than to do. You wanted a material that would change as little as possible: that wouldn't swell, or corrode, or bend, or vibrate. All the engineering of a device or a structure was concentrated in the way the parts were put together.

Now things are different. Many of the advanced materials at the forefront of materials science are *functional*: they are required to do things, to undergo purposeful change. They play an active part in the way the structure or device works.

This both reflects and permits a change in engineering philosophy. From ancient Greece to Victorian England, we've built, or tried to build, our buildings to be impervious to changes in their environment: to withstand monolithically everything that goes on around them. Now there is an increasing tendency to look for way of making buildings adaptive, so that they do not fight change but accommodate it. The importance of this idea is evident in regions where the kinds of changes buildings face exceed our engineering capacity to override it – such as in earthquake zones. We want buildings that can respond to earth tremors instead of trying to withstand them – like trees that bend rather than snap in the breeze.

The same is true in many other areas of engineering, such as aerospace, automotive engineering, biomedicine, and robotics. Here's an indication of how this change has permeated even to popular culture: [Robbie the Robot, and Terminator II] Once we build our machines from innumerable, fixed and robust parts. In Terminator II, the villainous robot wasn't made from materials; rather, he *was* the material. He could change shape, colour and consistency at will. Poor Arnold Schwarzenegger was still made of moving metal parts, even if covered over with flesh and blood. He just couldn't compete.

Today, we already have materials that can do these things. They are called smart materials, although they are certainly not as smart as the new-style Terminator, which got its diabolical intelligence from God knows where. Smart materials have the potential to change engineering, technology and design principles completely. They do away with mechanical machines as such, and give us a new breed of device for which we don't yet have a proper word. The Japanese philosopher Kisho Kurokawa said in his book *The Philosophy of Symbiosis* that “machines do not grow, change or metabolize of their own accord.” Well, they're starting to.

Definition

What, in essence, is a smart material? We could define it as one whose properties or shape may change in response to some stimulus from the environment. But of course all materials are in fact like this. Most materials expand when they are heated, for example, and indeed a great deal of effort has gone into finding alloys, such as so-called Invar alloys, that don't show this thermal expansion, so that they can be used in delicate mechanisms such as watches that aren't at risk of jamming when they warm up. Many materials get more malleable when they are warmed; some become better electrical conductors, others become worse.

What makes a material smart is that changes like this happen by design. Typically they might respond to stimuli that would leave most materials unchanged, such as exposure to a particular chemical reagent or to light. Typically the magnitude of their response is large, for example increasing a hundredfold in volume when warmed or cooled slightly. It's a tricky business to come up with a rigid and exclusive definition of a smart material. Some researchers insist that no material by itself is truly smart, as opposed to being simply responsive. They insist that being smart isn't just a matter of producing a response in proportion to a stimulus, but includes principles such as adaptation and feedback. Others draw a distinction between merely smart and truly intelligent, in the sense of being able to do things like make decisions or repair oneself. No artificial materials are yet intelligent in this sense, although they can be combined into composite intelligent systems, made up for example of sensors, actuators, information processing and storage units, and so forth

I'm going to take a very broad definition of smart materials, and to work on the principle that, even if you can't say what such a material is, you know one when you see one.

Why smartness?

Anyone who has seen Terminator II will understand why it pays for a material to be smart. But I want to provide a few indications of what smart materials can do for us in the real world. I've mentioned already the possibility of earthquake damping, and I'll explain shortly what kind of materials might achieve it. There are several ways of using smart materials in an active system that can sense and respond to ground vibrations. Perhaps unsurprisingly, vibration-damping systems for buildings have been explored most extensively in Japan: here is one of the smart buildings in Osaka, the Dowa Kasai Phoenix Tower [image]. This has a vibration-reduction system that also reduces wind-induced sway, which can be pronounced in Osaka from time to time. Without a system of that sort, the occupants of the building might find themselves experiencing feelings of sea-sickness during high winds. The building uses a vibration control system called DUOX, which is able to quickly damp out oscillations several centimetres in amplitude at the top floor.

Vibration-control systems show that for this kind of sophisticated and adaptive control of a structure, we need more than just a 'smart' response to a stimulus. In general, we need some kind of feedback so that the response can be continuously adjusted to the stimulus.

And often the sensing of the stimulus and the production of the response might be carried out by separate entities – perhaps by two different smart materials. For example, to control vibrations we need a system that senses movement, coupled to a system that adjusts its mechanical properties to counteract that movement.

A good example might be a mechanism for noise reduction, for example in a car or an aircraft. The ‘smart structure’ that does this task might involve a smart material that senses changes in air pressure, due to sound waves, and converts that stimulus to an electrical signal that can be used to drive a loudspeaker to broadcast ‘antinoise’ – sound waves that cancel out the noise. Both parts of the system can use piezoelectric materials, which are smart materials that interconvert mechanical and electrical energy.

More generally, engineering structures might be fitted with a range of systems that use smart materials to sense problems and to do something about it. A bridge, for example, might be fitted with smart systems that sound an alert when traffic vibrations or wind sway get too great, activating automatic dampers to counteract them. An aeroplane might have wings made from a smart material that changes colour as soon as tiny cracks start to develop, or even one that repairs flaws like this automatically.

Materials that merely signal some hazard could find endless uses – wound dressings that changes colour when they need to be changed, or when infection develops, or food wrapping that changes colour when the sell-by date is past. Materials that change colour in response to an electrical stimulus are being investigated for use as ‘electronic paper’ or e-paper. The idea here is to make a sheet of plastic that can be switched from black to white and back again by a pixellated grid of transparent electrodes, rather like the LCD on laptop screens. This stuff already exists – it has been developed at MIT, but the problems of wiring it up cheaply in a high-resolution display haven’t yet been solved. [Image] Ultimately the idea is that an entire newspaper or book would be read from a single sheet of paper, on which the ink would reconfigure itself automatically as you change pages. I haven’t yet seen the film *Minority Report*, but I understand that it shows scenes of newspapers whose text changes in real time as the news develops.

Smart materials are particularly attractive for doing engineering on very small scales. [Image: MEMS] It’s possible now to make machines like this with moving parts too small to see with the naked eye. But as they get smaller, the parts get harder to make, and reliability becomes a big issue – imagine trying to change a broken cog that is as big as a bacterium. Smart materials might get around this problem because they do away with the need for mechanisms like this. Instead of having to make a machine that opens or closes a little door, for example, you simply use a smart material that swells and shrinks when appropriately stimulated. I’ll show an example of this later.

So I think one of the key concepts behind smart materials is that of the ‘invisible machine’: a device that has no cogs, gears and levers, but instead grows, extends or shapes itself to do the task at hand. You’ll notice that this sounds a lot like a living organism, and indeed a lot of the inspiration for developing smart materials comes from looking at biological materials and structures, which are able to grow, to adapt, to repair,

to harvest energy and to communicate with one another in various ways. I shall end by touching on this idea of so-called biomimetic materials science.

Examples

The concept of smart materials may be new, but smart materials themselves go back a long way. I mentioned piezoelectrics, which produce an electrical signal when squeezed. Some natural minerals are piezoelectric, such as quartz. A vibrating quartz crystal in old radio sets used to generate and receive the radio signal. The Curie brothers discovered the piezoelectricity of minerals like this in 1880. In the late 1940s a robust piezoelectric ceramic material called barium titanate was discovered, and it became used as a sensor of mechanical vibrations in sonar devices. One of the most common and important piezoelectrics in use today is a closely related material called lead zirconate titanate, which is abbreviated to PZT.

Piezoelectric materials like this can be used to make sensors for pressure and strain: both very important for engineering applications like bridges and buildings, where you want to know how much load the structure is carrying and how much it is deforming as a result. Some polymers are also piezoelectric, such as polyvinylidene fluoride – this is very convenient, because whereas ceramics are hard and brittle, polymers are tough and flexible. Thin sheets of polymers like this are used in touch-sensitive keyboards, for instance.

Here we're turning pressure into an electrical signal. Piezoelectric materials can do the reverse too: if you apply a voltage across them, they contract or expand, turning electrical energy into mechanical. This can be used to make piezoelectric drivers for inducing motion. They're used, for instance, in dot-matrix printers. A similar property called electrostriction, where a material contracts in an electric field, is used to make 'smart mirrors' for astronomy, which can change shape. The idea here is that the mirror constantly adapts its shape to compensate for the distortions of starlight caused by turbulence in the atmosphere. Adaptive optics is now widely used in astronomy to improve the sharpness of the images from ground-based telescopes.

By driving vibrations in piezoelectric materials using an electrical signal, it's possible to make composite materials with a variable and tunable stiffness. This can be used for vibration damping – you can tune the material's properties so as to absorb the vibrations and avoid resonances. Toyota have developed a suspension system for their Lexus range of cars that uses this kind of controlled-stiffness structure.

Another well-established smart material is photosensitive glass, which darkens in response to sunlight. The process is similar to the way that photographic films darken, but is reversible. The glass contains dispersed silver halide crystals doped with copper. The copper ions give up an electron to the silver ions when irradiated by sunlight, converting them to neutral silver atoms which then aggregate into tiny silver particles that scatter light. When the light is shut off, the silver atoms lose an electron back to the copper. It seems to me that this is an ideal illustration of what smart materials do – which is to say,

the smart response is dramatic and yet so unobtrusive that we quickly learn to take it for granted. It is now possible to make glass that can be switched between transparent and opaque electrically, which can be used to make smart windows that can be opened or closed without any moving parts. [Image from Blade Runner] Interior designers sometimes use this stuff to make partitions in spaces where a moving structure would be cumbersome.

Now, you've all got a piece of this [Nitinol wire]. Here's what it does. [Bend, and dip in coffee.] When people first encounter this, they jump. I did, and I knew what to expect. I think that is very telling: we don't expect ordinary-looking substances to do this kind of thing. It feels almost as though you have something living in your hand. That's a very visceral illustration of what is different about smart materials: they are counter-intuitive, acting almost as though they have intelligence and purpose.

This is a piece of an alloy called Nitinol, sometimes known colloquially as memory metal.

You can see why: it seems to remember that it is supposed to be straight. In general, it can be 'programmed' to remember any shape. Heat triggers the memory, making it return to its original shape after it's been deformed. Nitinol is an alloy of nickel and titanium, and was developed by the US Navy in the 1960s. It's an example of a so-called shape memory alloy.

This stuff has become more familiar just recently, when it was introduced for the frames of spectacles [image]. These look like ordinary glasses, but the frames are made from a titanium shape-memory alloy called Titanflex. If they get bent, you can restore the original shape just by warming them up. That's preferable to bending the bent frame back into shape by hand, which ends up weakening the metal. I'm waiting for someone to start making Nitinol tent pegs, but until then there is already a range of applications. Shape-memory alloys can be used to make temperature-controlled switching mechanisms. Just think what you'd normally need: a temperature sensor coupled to some mechanical motor-like device. The shape-memory alloy subsumes all of that in a single material, which is its own temperature sensor and mechanism in one. Nitinol wires are used as artificial muscles in some robotic devices, and as dental braces and implants that can remember their shape.

How does it work? The key is that the metal has a different atomic-scale structure at low and high temperature. When its structure changes, the movement of atoms induces a macroscopic change in shape or volume. It's possible to set things up so that, when the metal is heated through this structural change, any deformations it has accumulated get ironed out.

Well, we don't have metals yet like the one used for the new range of Terminator robots, but perhaps the closest we can get is a substance that can be switched between a solid and a liquid by an electrical field. These are called electrorheological fluids. Their viscosity is electrically controllable, which makes them useful as shock absorbers and vibration dampers. They can also be used in a contact-free clutch: two plates immersed in an

electrorheological fluid can spin freely, but when the fluid is rigidified they become locked together.

The fluids are suspensions of microscopic particles, which become strongly polarized in an electric field. This creates an attraction between oppositely polarized ends of different spheres, inducing them to aggregate into long chain-like structures [image]. Silica particles in water show this behaviour, but better electrorheological fluids are now made from polymer microspheres suspended in silicone oils, which remain active at higher temperatures. This is important since many applications, such as shock absorption, dissipate energy and heat up the fluid.

[Image] This remarkable beast is the magnetic equivalent of an electrorheological fluid, called a magnetorheological fluid or ferrofluid. The principle is the same: the fluid is a suspension of tiny magnetic particles which stick together in chains in an applied magnetic field. Here the spikes in the fluid are formed along field lines from magnets below the droplet. MR fluids are used in exercise cycles to control the resistance to the turning of the pedals.

Soft smart materials

[Image] Here's a micromachine with no moving parts. It's a smart valve for controlling fluid flow in a so-called microfluidic system. The idea here is that liquids are guided down microscopic channels carved into a material like a silicon wafer by gates, valves and pumps. Microfluidic systems are being developed for conducting analytical chemistry on very small samples, by building effectively an entire chemical laboratory on a silicon chip. Instead of all those glass tubes and flasks, the whole thing is miniaturized so that you can work with a single tiny drop of material: mixing it with other reagents and analysing the results. The lab on a chip should be useful in medicine, for instance, or forensic science, or environmental monitoring: you can do all this analysis in situ, because the lab fits easily into your pocket.

One way of making the miniature pumps and valves is to use the kind of micromechanical systems, with gears and levers, that I showed earlier. But something like this is far better, because it won't break down. This is a valve made from little posts of a polymer, reaching from the bottom to the top of the channel. Under some appropriate stimulus, the polymer swells up and closes off the channel.

The great thing is that this stimulus can be carried by the fluid itself. Here the swelling happens once the fluid gets too acidic. But it's possible also to design polymers that swell in response to light, or if they come into contact with a specific chemical reagent. So you could design a lab on a chip in which the chemical nature of the fluid itself controls where it goes.

This polymer is an example of a soft smart material: a hydrogel, a gel-like substance that can absorb a vast amount of water. This is what causes the swelling. The gel is made up of a mesh of interlinked polymer chains. If water gets between them, the volume of the

material increases hugely. Super-absorbent hydrogels like this are used for nappies and wound dressings.

A hydrogel becomes a smart material if the water uptake is controlled by some stimulus, such as heat, light, electric fields or pH. Sometimes the switch from a non-absorbent to an absorbent state can be very abrupt: the gel might remain shrunken, for example, until a particular temperature threshold is reached, whereupon it swells suddenly to many times its original volume [pic].

The amount of water or solvent the gel absorbs depends basically on whether the molecular chains in the polymer network tend to collapse and attract each other, or stretch out and repel each other. All sorts of things influence this. For example, different solvents and different temperatures make the chains more or less likely to scrunch up. If the chains contain acidic chemical groups, these may dissociate in alkaline solution, creating negatively charged regions on the chains which make them repel each other. In acidic solution these charges are neutralized and the gels shrink.

Because smart hydrogels are soft and can be biocompatible, there is a lot of interest in using them in biomedical applications such as artificial muscles.

Another potentially valuable application is for drug delivery. The idea is to use tiny spheres of the gel as microcapsules containing a drug that can be released on command, in response to some stimulus. This is typically a much better way to deliver drugs than simply by swallowing a pill or administering an injection, because it means that the drug can be accurately timed and targeted so that it is administered only when and where required.

To make a controlled-release capsule from a hydrogel, you first let the drug molecules diffuse into the polymer network by immersing the capsule in a drug solution while it is swollen. If the gel is then induced to shrink, the drug gets locked inside it. Only when the gel swells again can the drug get out.

We might think of releasing drugs only in the gut by carrying them in microspheres of a pH-sensitive hydrogel. When the spheres reach the intestine, the lower pH there triggers swelling and release. Even better is a hydrogel that swells in response to a particular biochemical trigger, so that it can sense and react to the body's chemistry. A smart delivery system for insulin has been developed using this principle. A team at the University of Washington made tiny hollow capsules with a membrane made of a pH-sensitive gel, small enough to be injected into the blood stream. They loaded the capsules with insulin and with an enzyme called glucose oxidase. This enzyme reacts with glucose in a reaction that produces acid. So when the patient's blood contains too much glucose, the reaction with glucose oxidase lowers the pH and makes the gel membrane swell, so that the insulin can diffuse out through the gaps between the polymer chains.

I came across another example like this only last week. A team in Japan have made a porous membrane that acts rather like the walls of cells. Cells regulate how much of

different substances such as salts they contain by opening and closing pores in their surface. The pores are ‘gated’: they can be opened or closed by the presence of certain ions. The Japanese team could also trigger the opening and closing of the pores in their membrane by adding certain metal ions to the solution. They made a polymer that swelled or contracted in response to these metals, and attached the polymer chains to the mouth of the pores. When the chains swelled up in response to a particular kind of metal ion, they closed off the pores. [Image – here the swelling is induced simply by humidity.]

Some polymers won’t just change shape but remember a pre-defined shape: they show the same kind of shape-memory effect as Nitinol. The first shape-memory polymer gel was made by Japanese researchers in 1995. Here’s an example [image]: the polymer can be deformed into a coil, but straightens out into its ‘remembered’ shape when warmed up. Earlier this year, two researchers reported a biodegradable shape-memory polymer which could have important medical uses. They showed that the polymer could be formed into a self-tightening knot, which constricted when warmed. This could be useful to prevent loosening of sutures in places that are hard to access surgically. A biodegradable shape-memory polymer might also be used to introduce implants by keyhole surgery, which could open out into their required shape once inside the body.

One ambitious potential use for shape-memory polymers is as flat-packed components for space exploration. NASA researchers are looking into the possibility of using a shape-memory polyurethane for the wheels of a planetary rover vehicle. The wheels would be pressed flat for compact storage en route, but would swell up again once they were warmed by the sun after touchdown on Mars.

Future perspectives

I want to end by showing how far we have to go. Here are some truly intelligent materials. The leaf, for example, is a kind of solar cell capable of adaptation, replication and self-repair. It is also a structural material, and shows properties such as automatic regulation of gas uptake and release, and sometimes self-cleaning. Wood has some kind of strain sensing mechanism that allows it to reinforce itself where needed as it grows. Shell grows in a way that is highly structured and patterned yet able to maintain a self-similar shape.

Natural materials like this genuinely blur the boundaries between a material and a functional structure—a device. We don’t question that wood and plant fibres are materials, and we use them as such. But we have no idea as yet how to make a material that can grow by gathering its raw materials and energy from its environment and processing them into new forms. Rudimentary self-repairing materials have been made, but they are usually one-shot affairs that do something like exude glue from internal cavities when they’re cracked open.

Drawing inspiration from nature is a popular theme in today’s materials science, and isn’t just confined to smart materials. But natural materials provide an abundant source of ideas for ways of developing new smart functions such as:

- sensing (think of the electro-detection systems used by some fish, or sonar used by dolphins)
- actuation (muscles, spring-loaded seed pods)
- communication
- modular behaviour and distributed intelligence (bacterial and slime-mold colonies)
- manufacturing (these are materials that carry their own factories: protein synthesis, combinatorial methods (shuffling components) as in the immune system).

Biological materials supply the ultimate example of the philosophy of smart materials: the concept that 'the material is the mechanism'. One consequence of this, I think, is that the robots of the future are never going to look like poor old Robbie, or even like C3PO or R2D2; they are more likely to look like ants, or fish, or perhaps – who knows? – even like us.