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Materials that can repair themselves

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Plastics and polymers are long-lasting but plastic can break. This article explores research to make polymers which will fix themselves. This could be useful in a wide range of applications.

Polymers are molecules containing thousands or even millions of atoms linked together into chains. They are fundamental to our lives in two quite different ways. Life itself is based entirely on the self-programmed synthesis of polymers such as the nucleic acids DNA and RNA. Nucleic acids, in turn, direct the synthesis of proteins – high molecular weight polymers that are not only biological catalysts (enzymes) but also form structures such as hair, skin, cartilage and indeed most other types of living tissue. When tissues are damaged, information stored as a sequence of different chemical sub-units in DNA is called upon to program the synthesis of new protein molecules, and these gradually replace the damaged material. Many parts of the body can thus effectively repair themselves.

The development of synthetic polymer chemistry over the past hundred years has led to the discovery of new materials that are also fundamental to modern life and society, but now in terms of their value in *technology*. Medical devices ranging from dental fillings to prosthetic limbs to replacement heart valves are all based on synthetic polymers, as are many structural components of computers, televisions, smartphones and cars. Even aircraft (apart from the engines) are no longer built from metals, but instead are produced mainly from carbon-fibre reinforced polymers, which are extremely strong and very much lighter than metals – lighter even than the lightest aluminium alloy.

Aircraft are now built mainly from polymers reinforced with carbon fibre. Such composite materials were tested extensively on this research aircraft (the British Aerospace Experimental Aircraft Programme) and are now employed in nearly all modern airliners and military planes.

However, continuous exposure of synthetic polymers to environmental stresses (abrasion, impact, pressure, chemical attack and high temperatures) can lead to progressive loss of physical strength and, eventually, to complete mechanical failure of the structure. If polymers could be designed to repair themselves when they get damaged, then such materials would show greatly improved durabilities and lifetimes in use. The development of such self-repairing polymers is currently a topic of intense investigation by scientists around the world.

Ready to repair

The problem has been approached from many different directions. Ideally, the damage itself would trigger a repair response, and such materials have indeed been developed. These generally comprise polymers containing embedded microcapsules of liquid monomer. When the polymer is damaged, the capsules are broken and the monomer is released. It then flows through the damaged region, making contact with a catalyst that causes it to polymerise and thus repair the fracture. However, this is obviously a one-shot solution to the problem, because the monomer capsules at the site of the repair are used up. A second damage-incident at the same site would not result in any repair.

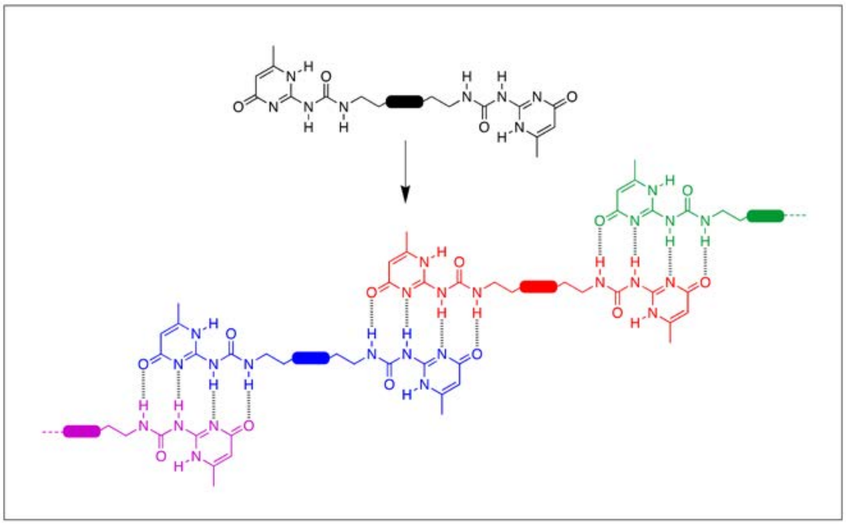
Without going to the extremes of molecular complexity found in genetically-programmed biological systems (which are still well beyond the scope of synthetic polymer chemistry), it would clearly be preferable for a repair mechanism to be somehow built into the structure of the polymer itself *at the molecular level*. That would – in principle – allow the polymer to self-repair repeatedly, at the same site, no matter how many times the damage was inflicted. Remarkably, over the past ten years or so, polymer chemists have been able to design and synthesise new polymer systems where this idea really does work in practice.

The basic principle behind all these systems is to use relatively short-chain polymers, having perhaps only tens of monomer repeat units rather than the hundreds or thousands needed to provide high mechanical strength in conventional synthetic polymers. Short-chain polymers normally have only poor mechanical properties, because the chains cannot entangle to the same degree as higher molecular weight chains. However, if the end-groups of a short-chain polymer are designed to associate together in some sort of reversible way, then good mechanical properties can still be achieved. Moreover, mechanical failure of this type of material will generally occur by dissociation of the chain-*ends*, rather than by breakage of the covalent bonds in the polymer chains themselves. The short-chain polymer molecules (not being highly entangled) can then flow easily under a stimulus such as heat or light to repair the damage. The chain ends can later re-associate to generate the original polymer structure and so restore the properties of the material.

Four hydrogen bonds

A good example of a reversible interaction is the hydrogen bond. This results from the attraction between an atom that is a tiny bit negative and a hydrogen atom that is a tiny bit positive. A hydrogen atom has only a single electron, and when hydrogen is bonded to certain elements such as oxygen or nitrogen this electron is pulled away, enabling its partly-exposed and positively charged nucleus (a proton) to attract a negatively charged atom in a neighbouring molecule.

A single hydrogen bond does not produce a tremendously strong attraction between polymer chain-ends but, in 2002, work by Meijer and colleagues at the Eindhoven University of Technology led to the discovery of an end-group (called the ureido-pyrimidinone unit) that forms *four* strong hydrogen bonds, simultaneously, to another end-group of the same type. Attaching this unit to both ends of a short-chain polymer results in the chain-ends associating strongly, but still reversibly, and produces materials that show excellent self-repair characteristics. They flow very easily on heating, to repair damage, and some polymers of this type will even repair themselves spontaneously at room temperature after being broken.

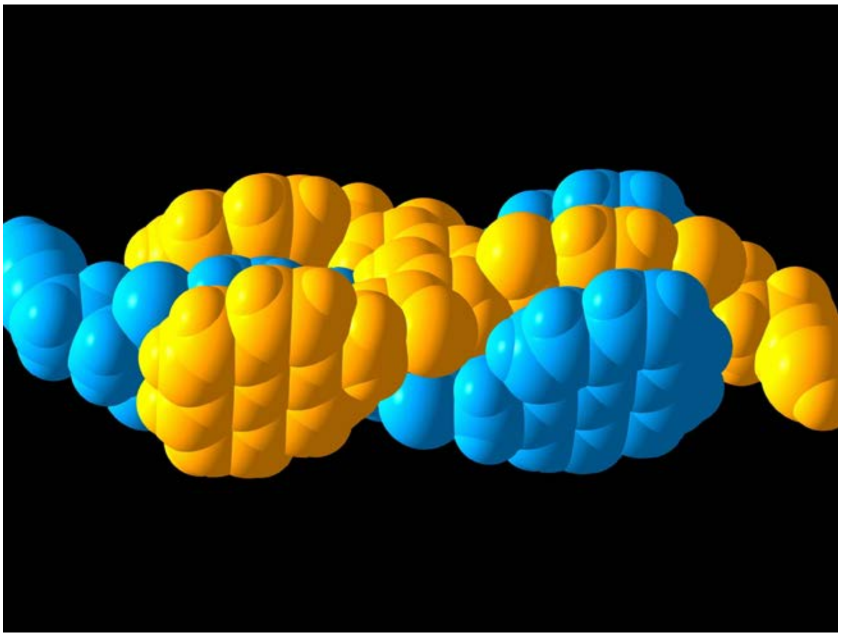


A low molecular weight polymer in which the ends are designed to associate strongly and specifically by quadruple hydrogen bonding between ureido-pyrimidinone end-groups. This gives properties (such as mechanical strength) that are usually associated with high molecular weight polymers. These materials can also show self-repair, when broken, by re-forming the hydrogen bonds.

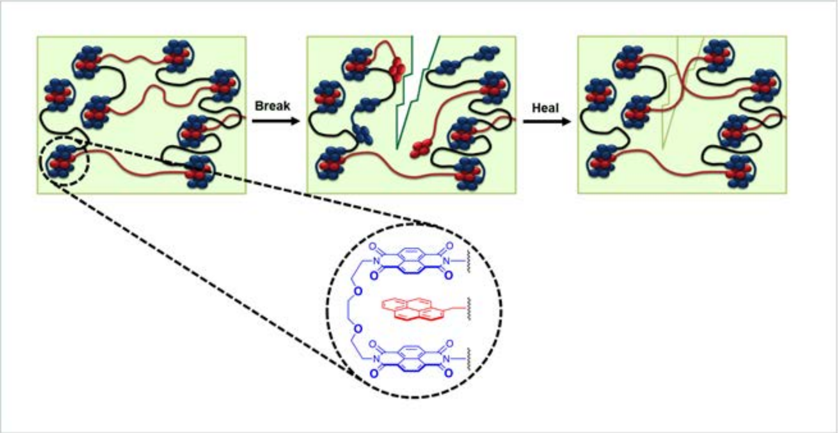
Complementary molecules

Our own work at the University of Reading has focused on a different type of interaction between molecules known as 'p-p-stacking'. This type of attractive force arises when the flat surfaces of two different molecules come into contact. Some groups attached to the p-system pull electrons away from it which leaves a partial positive charge (just as with hydrogen in the hydrogen bond). Other p-systems can develop a partial negative charge. These two units are therefore described as complementary, in that one is electron-rich and the other is electron-poor. When their flat surfaces come into contact (the situation known as p-p-stacking) the molecules are held together, reversibly, by the attraction between the positively- and negatively-charged carbon atoms in the two complementary molecules.

A hydrogen bond is an example of an intermolecular force or bond which acts between molecules.



Association of two polymer chain-ends by mutual, complementary p-p-stacking (above). This type of interaction is strongly reminiscent of the handshake often used in ancient Rome – a mutual grip of the wrist (below).

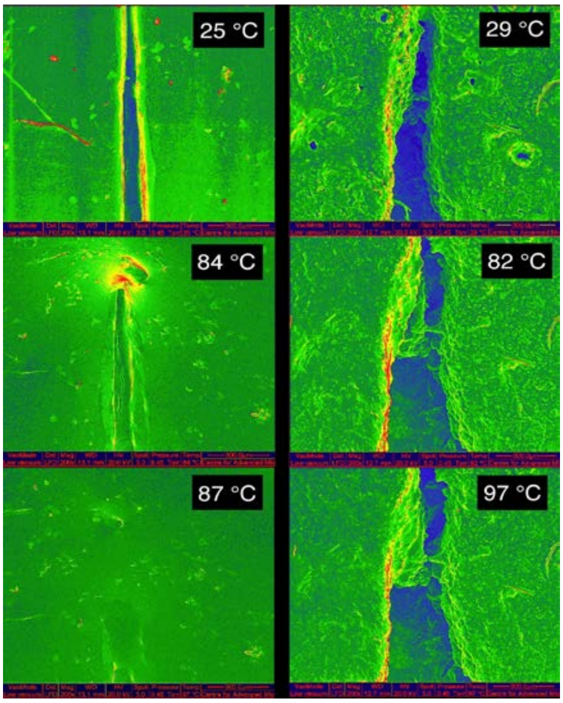


A blend of two low molecular weight polymers, one with electron-rich pyrene end groups that intercalate into chain-folds of the other polymer to form multiple p-stacks with its electron-poor naphthalene-diimide units. Fracture results in dissociation of the p-stacks, but these can re-form and so repair the damage.

It was relatively easy to attach the negative groups to the end-positions of a polymer. The resulting low-molecular weight polymer was then blended with a polymer with segments containing two positive units. These segments are designed to double upfold and so allowing double p-p-stacking. This doubling up increases the strength of the interaction between the polymer chains substantially, in much the same way that Meijer's quadruply hydrogen-bonded system multiplies up the strength of interaction between chain ends.

Self-healing polymers

The polymer blends with p-p-stacking were very good at healing themselves inat temperatures up toof about 90°C. We knew that this was entirely due to the aromatic p-p-stacking interactions, because we also usedtested a control blend of the same two polymers, but without the p stacking end-groups,s and it and this failed to show any signs of self-repair at all under the same conditions.



False-colour scanning electron microscope images of polymer blends on heating from room temperature to 100 °C. In the left-hand series a polymer blend with extensive p-p-stacking interactions shows essentially complete self-repair over this temperature range. On the right, a similar blend but without this type of interaction shows no repair at all.

Self-repairing polymers are now becoming available to industry in small quantities to allow development. The lessons learned from research in this area are therefore being directly applied, for example, in car paints that repair their own surfaces when scratched, and in the development of new self-repairing, high strength composite materials reinforced with carbon nanotubes.

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