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The weakest

How chemists are increasing the longevity of plastics

Whenever you walk along the seashore, you're bound to see some sort of plastic littering the beach and perhaps you wonder will it ever decompose? Then you go home and see your garden hose cracked and falling to pieces and you wonder why that plastic can't be made to last as long as the litter on the beach!

From an industrial point of view, longevity of polymers is something that it would be highly desirable to have more control over but as is so often the case, the way to a better product is through a better understanding of the science behind it. Professor Michelle Coote and PhD student Ms Ganna Gryn'ova are two chemists working in just this area.

Plastics are composed of polymers; long molecules built up of repetitive chains of smaller molecules known as monomers. Things like ultra-violet light or heat can break the chemical bonds that hold the chain together causing plastic to degrade in sunlight. However that's far from the whole story.

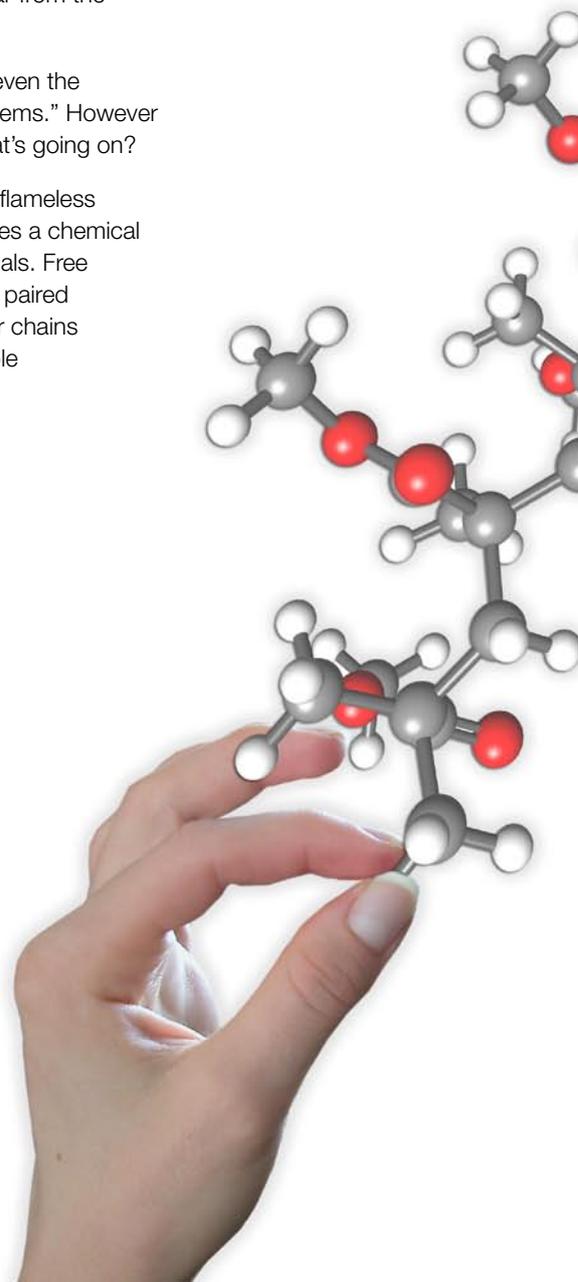
"Covalent bonds are actually quite difficult to break" Professor Coote explains, "So even the strongest sunlight will take decades to do enough damage to cause structural problems." However experience shows that polymers left out in the sun decompose quite rapidly, so what's going on?

Historical work based on lipids and rubbers suggested that autoxidation – a kind of flameless chemical combustion - was the problem in those materials. When light or heat causes a chemical bond to break, the products contain unpaired electrons and are known as free radicals. Free radicals are typically very reactive because their unpaired electrons want to become paired again. So these radicals propagate through a cascade of reactions in which polymer chains rearrange and fall apart, until they finally meet another radical and combine into stable species again.

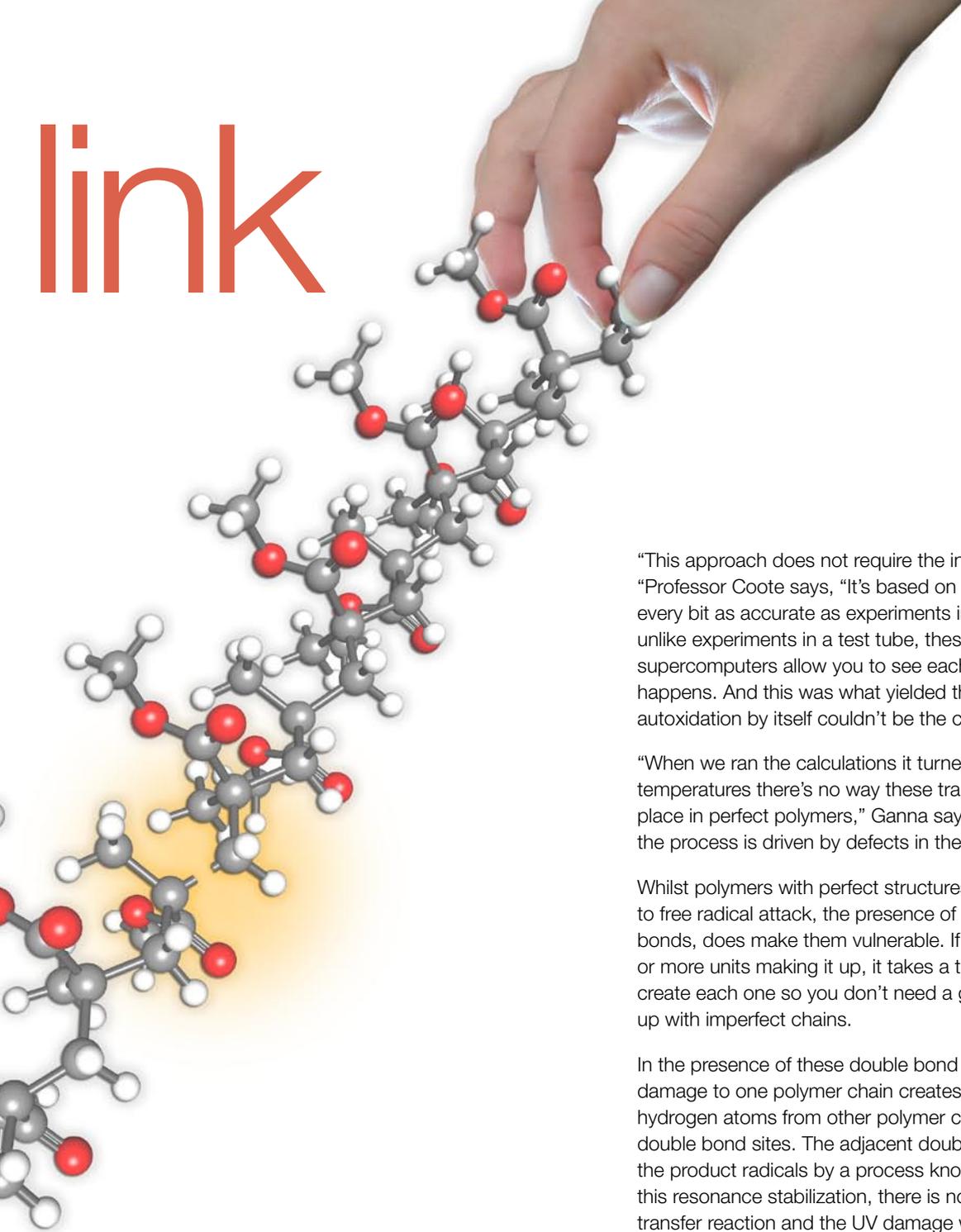
Crucially, these radicals can steal hydrogen atoms from other polymer chains, transferring the radical centre to a new polymer chain. It is this transfer process, which may be repeated 100s or 1000s of times, that allows one initial bond-breaking event to damage large numbers of polymer chains, transforming what would otherwise be a slow rate of degradation into a rapidly accelerating failure.

For many years it has been assumed that this free radical autoxidation process is responsible for the degradation of most plastics. However one of the difficulties in chemistry is that it's virtually impossible to observe reaction steps as they happen. Essentially you begin with reactants and combine them to make products but a lot of what happens in-between has to be inferred.

This is where computational quantum chemistry comes in. By applying the basic quantum modelling that underlies our understanding of atoms to complex polymers, Professor Coote and Ganna were able to build a complex model of the chemical processes involved.



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“This approach does not require the input of empirical data,” Professor Coote says, “It’s based on exact physics so is every bit as accurate as experiments in a test tube.” However unlike experiments in a test tube, these models that run on supercomputers allow you to see each step in a reaction as it happens. And this was what yielded the surprising result that autoxidation by itself couldn’t be the culprit.

“When we ran the calculations it turned out that at normal temperatures there’s no way these transfer reactions could take place in perfect polymers,” Ganna says. “Instead it turns out that the process is driven by defects in the polymer chains.”

Whilst polymers with perfect structures are relatively immune to free radical attack, the presence of defects such as double bonds, does make them vulnerable. If a polymer chain has 1000 or more units making it up, it takes a thousand reactions to create each one so you don’t need a great rate of error to end up with imperfect chains.

In the presence of these double bond defects, ultraviolet damage to one polymer chain creates free radicals that can steal hydrogen atoms from other polymer chains adjacent to their double bond sites. The adjacent double bonds serve to stabilize the product radicals by a process known as resonance. Without this resonance stabilization, there is no driving force for the transfer reaction and the UV damage would remain localized on an individual polymer chain.

“The presence of double bond defects is responsible for increasing UV damage in polymers by about 100 fold” Professor Coote says, “And since this process all hinges on those double bond defects, by controlling how we manufacture the polymer, we have a great way to engineer the longevity of the resulting plastic.”

This work opens up many exciting possibilities to control the longevity of plastic products. In principle packaging can be created that will quickly degrade when discarded. At the other end of the spectrum, plastic pipes and acrylic paints could be engineered to have vastly longer life spans than currently possible even when they are exposed to harsh sunlight for prolonged periods.

It’s yet another example of how the study of fundamental science can benefit industry and shape the world around us.