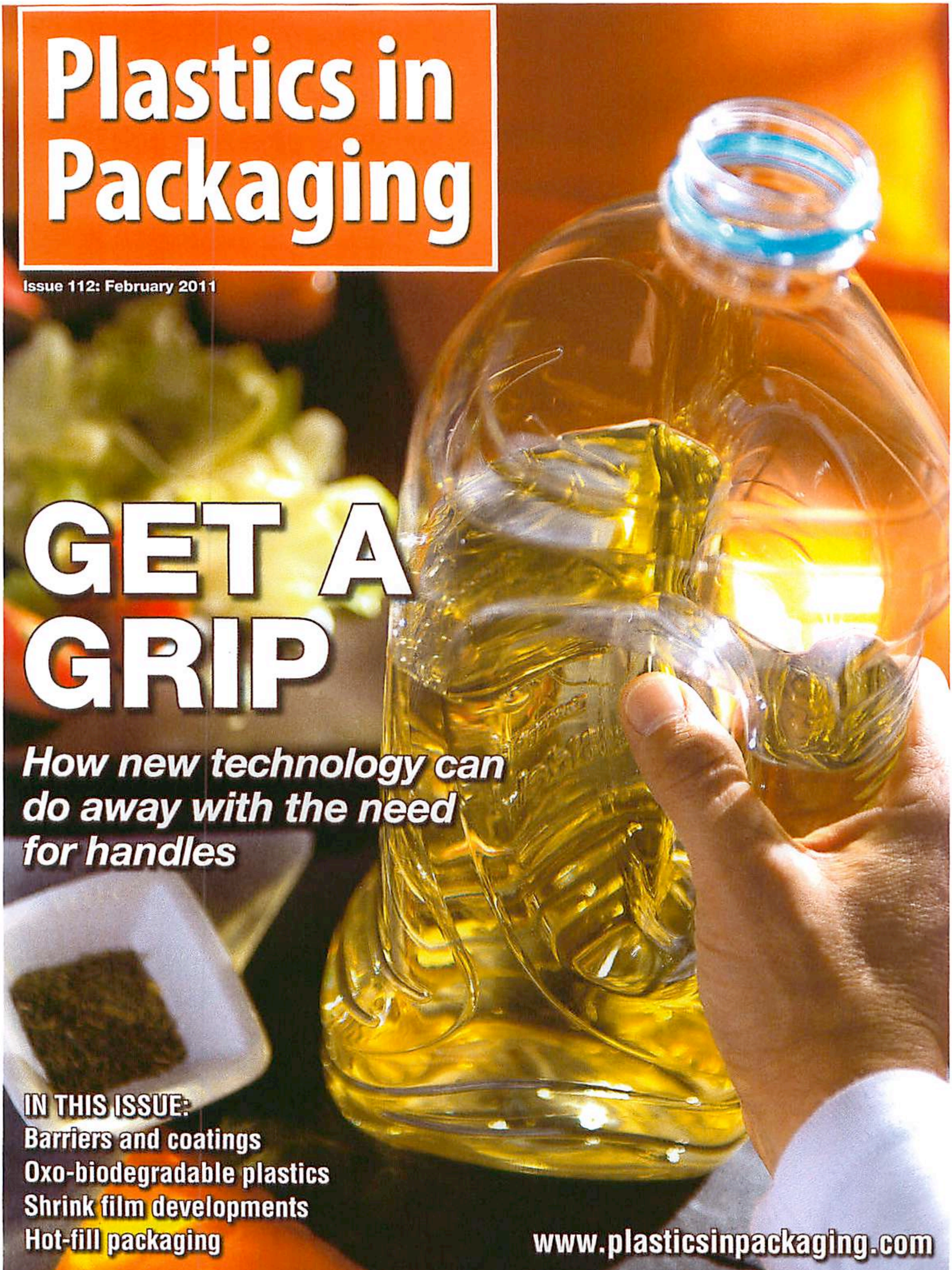
Plastics in Packaging

Issue 112: February 2011



GET A GRIP

How new technology can do away with the need for handles

IN THIS ISSUE:
- Barriers and coatings
- Oxo-biodegradable plastics
- Shrink film developments
- Hot-fill packaging

www.plasticsinpackaging.com

Quantum leap

Supercomputers and quantum chemistry could be behind the development of more robust plastics. **Steven Pacitti** talks to the scientist behind the research

What if a 'bag for life' really was for life? Or that packaging could actually last forever. The idea might not be as fanciful as previously thought according to scientists from the Australian National University (ANU), who have used supercomputers to discover how to make longer-lasting plastics.

Historically, scientists thought that plastics left out in the sun become brittle and fail due to a process called auto-oxidation, where exposure to light or heat generates free radicals, which attack the polymeric chains in the plastics, causing them to rearrange and break. Each broken polymer chain then leads to the failure of the next polymer chain, leading to a cascade that results in visible damage.

However, research led by Professor Michelle Coote and recently documented in the Royal Society of Chemistry journal Organic and Biomolecular Chemistry suggests that most types of plastics should be inherently resistant to this process. The reason that damage occurs at all is because most polymer chains contain a small number of defects in their structures, formed during their manufacture.

Interviewed by *Plastics in Packaging*, Coote said that her team had investigated a broad range of polyalkenes including polyethylene, polypropylene, polystyrene and PVC, as well as condensation polymers such as polyesters, polyamides and polyurethanes.

"Based on very accurate quantum-chemical calculations we can prove that normal plastics should not degrade via the standard auto-oxidation mechanism that everyone until now has assumed, unless the chemical structures of the polymers contain double bonds," she explains.

Specifically, the hydrogen transfer reaction that makes auto-oxidation catalytic (so that one initiation event damages hundreds or thousands of chains instead of just one) is thermodynamically impossible for most functional groups and will only happen if the target molecule has allylic hydrocarbons (as in polybutadiene).

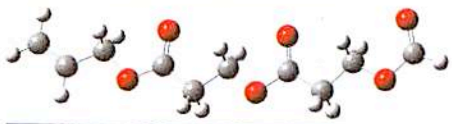
"In most polymers these chemical structures are formally absent but small concentrations of double bonds are present as defect structures. This leads to a prediction that minimising these defects would stabilise polymers considerably or that including more of these defects should accelerate decomposition, if degradable polymers were desirable," she adds.

Potentially, this would create long-lasting plastics and reduce the amount of plastics waste entering landfill every year.

"Reusable packaging such as drink bottles, lunch boxes, cookware, even reusable shopping bags would benefit from a longer lifespan, but in general we are interested in prolonging the life of materials such as surface coatings and irrigation pipes so that the use of expensive and/or toxic UV stabilisers can be avoided or minimised."

Student Anya Gryn'ova (left) worked closely with Michelle Coote (right) on the research project

Below: Polyester molecules with defects



Certainly at a time when the packaging industry is developing ways to reduce its waste impact, often by targeting the reduction of material life with biodegradable technologies, this research could actually lead to improvements in this area as well.

"If a material is intended for limited use, such as most packaging, then it would make sense to accelerate its degradation and our research highlights one strategy for doing this. Rather than minimise a defect structure, we should include them by, for example, copolymerising small amounts of butadiene in the polymer. However, if instead you are talking about surface coatings or engineering plastics or even biomedical implants, then the longer they last the better – better to keep them out of landfill altogether."

The presence of defects

Most polyalkenes have unsaturated end groups as a result of termination reactions and these could function as the catalytic sites for auto-oxidation, says Coote, explaining why defect structures are formed in the first place during resin manufacture.

"If the polyalkenes are formed by free-radical polymerisation, they can often have internal double bonds as well that form as a result of beta elimination of the mid-chain radicals formed by hydrogen and halogen transfer."

The competition, she says, between these side reactions and the normal polymerisation steps is quite complex but the team believes that many of these reactions could be minimised through small changes to the reaction conditions, such as stopping at lower conversion, or including solvents to lower the viscosity.

"In other cases, however, we believe that the defect structures form during the degradation process itself. The polymer goes through a 'pre-oxidation' stage where some chemical changes occur in a non-catalytic manner. These changes create the functional groups needed to catalyse auto-oxidation, which can then facilitate more rapid failure."

The nature of these reactions depends on the polymer, but Coote thinks that in polyesters the cis-elimination reaction is crucial as it generates double bonds. For these polymers, the way to prolong shelf-life is thus to choose different polyesters for which cis-elimination is blocked.

In addition, Coote believes that if the degradation reactions of polymers were slowed, then this would also slow down the potential discolouration of plastics over time.

On the horizon

While the initial computational study that proves the relationship between defects and degradation is complete and published, the practical synthesis of stabilised polymers has not yet been done.

"We are working with industrial collaborators Bluescope Steel [who make Colorbond steel] to use this knowledge to help them identify more stable polyester resins for their surface coatings," says Cootes. "Additionally, I have just been awarded an ARC Future Fellowship and part of the associated project is to use theory and then later experiment to investigate strategies for minimising structural defect formation in radical polymerisation of acrylic monomers. Both this grant and the industry project have a timeline of four years to experimental proof of principle."

ANU is also in talks with a pharmaceutical company about extending this research to the study of in vivo stability of pharmaceuticals.

Whether it's extending material life, or in fact reducing it, anything that improves the inherent structure of plastics used in industries from white goods to packaging is bound to be a benefit.

More information from Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia. Tel: 61 2 6125 3771. Fax: 61 2 6125 0750
http://chemistry.anu.edu.au/rsc/people/michelle-coote