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News/Views/Articles

Recycling technology: unlocking the riddle of LCD re-use

Scientists at the University of York are to play a pivotal role in new research aimed at averting a growing environmental problem caused by discarded liquid crystal displays (LCDs).

LCDs are a fixture of modern life, appearing in everything from pocket calculators and mobile telephones to wide-screen televisions.

But the liquid crystals they contain are potentially hazardous and technological advances are so rapid that society is already discarding millions of LCD screens each year. There are no viable recovery techniques and no fully safe disposal options.

Some 40 million LCD television sets were sold worldwide last year with expected sales likely to top 100 million by 2009.

"This research initiative provides a real opportunity to harness the world class expertise that we possess in the UK and direct it towards the task of wealth creation" Lord Sainsbury

Now scientists in the Department of Chemistry at the University of York have won a major DTI competition to investigate ways of extracting and recycling liquid crystals from waste LCD devices. They are part of a consortium of nine partners and supported by the Resource Efficiency Knowledge Transfer Network (KTN) and the Displays and Lighting Knowledge Transfer Network. The DTI will fund 50% of a total bid worth £1.7 million.

Welcoming the research, Science and Innovation Minister, Lord Sainsbury said: "This research initiative provides a real opportunity to harness the world class expertise that we possess in the UK and direct it towards the task of wealth creation.

"By providing a focus for collaboration and delivery, this partnership will help establish British industry as the world leader in this area."

LCD screens are usually composed of two glass sheets, between which, a thin film of viscous liquid crystal material is deposited. The material is a mixture of anywhere between 15 to 20 different compounds. EU legislation now prevents disposal of electronic materials in landfill.

Dr. Avtar Matharu, of the Department of Chemistry at York, said: "The amount LCD waste is increasing at an alarming rate and, with disposal in landfill or incineration no longer acceptable, new solutions were needed. We have developed a technology that offers a clean, efficient way to recover the mixture of liquid crystals from waste LCD devices. Once recovered, the liquid crystal mixture will be recycled in to different LCDs or the mixture will be separated into individual components for re-sale."

The following information obtained from GCN Newsletter Issue 27 April, 2007

Greener lithography?

Microlithography is an essential part of the production of ever smaller microelectronic devices and has strict and demanding chemical requirements. Photoacid generators are key materials in the processing but the most widely used of these contain perfluoroalkane sulfonates e.g. PFOS (perfluorooctanesulfonate), which are now widely regarded as being environmental hazards. In recent work published by the US Intel Corporation in collaboration with Cornell University, new PFOS-free photoacid generators have been produced and successfully tested. These use smaller perfluorogroups, which are believed to be more environmentally compatible.

R. Ayothi et al., *Chem. Mater*., 2007, **19**, 1434

Green and intelligent coatings

Corrosion leads to the depreciation of many articles in everyday use including vehicles, aircraft and buildings. Corrosion protection is a very important way to enhance lifetime and hence reduce resource consumption of such articles. Traditional corrosion protection methods often rely on hazardous substances, most notably carcinogenic chromates and it is vital that we find effective, safe replacements for future use. Groups in Portugal and Germany have worked to get her to demonstrate the use of 'intelligent ' self –healing corrosion inhibitors. The controllable delivery is based on incorporating nanocontainers of organic inhibitors in the protective films. The films are based on silica and zirconia, two reasonably abundant and safe materials, and the release of the inhibitors is triggered by pH.

M. L. Zheludkevich et al., *Chem. Mater*., 2007, **19**, 402

Green and intelligent plastics

A collaboration between four research groups in Italy has led to a new class of plastic films that can be used as sensors, responding to mechanical and temperature stresses. The plastic is biodegradable and made from a polybutylene succinate, which could be accessed from renewable resources. A brightener added to the plastic luminesces at different colours depending on its concentration – which can be affected by stresses. The authors speculate that there could

be various applications for such materials in the field of smart/intelligent films, e.g. for food packaging.
A. Pucci et al., *J. Materials Chem*., 2007, **17**, 783

From sugarcane waste to PLA

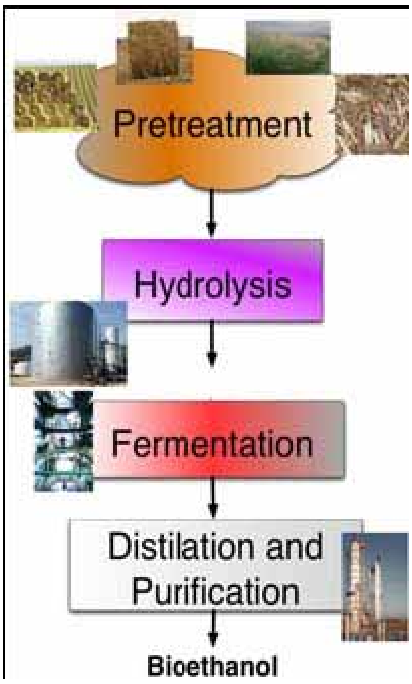
PLA is arguably the most successful example of a green and sustainable plastic material on the market. Studies on its lifecycle show the use of quite green chemical and biochemical processing methods on renewable resources to produce an environmentally compatible (biodegradable and non-hazardous) but very useful product. However, all innovations will be *greener* and never fully green and we should continually strive to improve the environmental credentials, reduce the environmental footprint, and minimise any consequential difficulties in their areas such as competitive use of raw material. PLA is typically based on corn(starch) and while local sourcing can help, the use of corn is debatable given its large scale use in food and feed. The agricultural industry produces large quantities of waste (more than food) which we should strive to use in industrial applications; lignocellulosics are the most abundant type of sustainable biomass wastes or low value products and lignocellulosic byproducts are becoming more and more abundant as new biofuel and bioenergy industries emerge. Sugarcane bagasse is a good example of that – India alone produces 45 million MT of bagasse per year largely from established industries, while Brazil in particular is rapidly increasing its production for the world's insatiable demands for bioethanol. A group at the Pune National Chemical Laboratory in India has progressed early work on the conversion of lignocellulosic biomass into lactates by proving the technology for sugarcane bagasse. This promises greatly for further improving both the environmental and economic value of PLA and hence extending its use in modern society. [Green Chem., 2007, **9**, 58]

Sustainable nanowires

The nanoscale design of materials offers much greater control over their proportion and a much higher level of activity and efficiency in operation. Unfortunately, the manufacture of such devices is not often environmentally benign or always based on sustainable resources. In research from the National Institute of Advanced Industrial Science and Technology in Japan, the use of natural fibres as templates for the preparation of titania nanowires has been described. Specifically cellulose, the most abundant material in nature, can be used to help produce good quality nanowires which have uses in solar cells, water remediation and for self-cleaning supports. [Green Chem., 2007, **9**, 18]

Second generation bioethanol

Matt Fishwick and Lucy Nattrass MRes in Clean Chemical Technology University of York



All the cars taking part in this year's IndyCar Series will run on 100% ethanol. In the EU cars are currently guaranteed to run on 5% ethanol-petrol blends.

The UK has joined the US, Japan, Germany and France in being a net importer of oil. With the majority of remaining oil reserves situated in the Middle East and predictions of a 50% rise in global energy consumption by 2030, energy security is a hot political topic. In 1973 Brazil responded to the oil crisis by investing in the process of converting sugar cane to ethanol; a biofuel which may be used as a petroleum substitute or additive. Bioethanol now accounts for half of the country's motor fuel and is exported to Europe and the US. North America, Western Europe, Canada and Sweden are now producing ethanol from wheat and corn but these programmes are coming under some criticism, due to fears of increased food prices and accelerated deforestation. Bioethanol has been marked as part of the solution to climate change, since the carbon dioxide released during combustion of the fuel is sequestered from the atmosphere in the plants cultivation stage. However energy is required for harvesting, manufacture and distribution, and while this energy is supplied by fossil fuels the process cannot be considered carbon neutral.

Next generation

The second generation of Bioethanol production involves producing ethanol from biomass, which includes agricultural residues, solid municipal waste, wood, and dedicated energy crops. This approach tackles many of the issues raised, predominantly the concern over competition for food crops. By using agricultural residues such as wheatstraw and corn stover the process adds value to what would otherwise be a waste stream, allowing the agricultural industry to grow economically without expanding into forests.

Perfect solution?

In reality the route from biomass to biofuel is a complex process as illustrated. The macrostructure of biomass reflects its role in nature as the structure and backbone of the plant; it is resilient to enzymatic degradation necessary for hydrolysis. Biomass has three main components; cellulose and hemicellulose which degrade to fermentable sugars, and lignin. Lignin inhibits enzyme hydrolysis, increasing the enzyme loading required and hence operational costs. Hydrolysis of biomass produces a mixture of sugars, which through fermentation are metabolised to ethanol by microorganisms similar to yeast. The microorganisms currently available do not metabolise effectively all the available sugars leading to poor ethanol yields.

Future

Capital and operational costs presently act as a barrier to the commercialisation of the second generation process, however much research is being done in the areas of protein engineering and process development to improve yields and reduce enzyme loading, and hence improve the economic viability of the process.

The following information obtained from Green Chemistry News

Sweet future for biodiesel 26 March 2007

Sugar catalysts can turn waste vegetable oil into biodiesel, researchers have revealed.

As fossil fuel reserves start to run dry, alternative fuel sources such as biodiesel, which is made from renewable biological material, are needed. Now, Min-Hua Zong at the South China University of Technology, Guangzhou, and colleagues have used a sugar catalyst to prepare biodiesel from waste vegetable oil. Sugar catalysts, made by the sulfonation of partially carbonized D-glucose, have previously been used for making biodiesel from new vegetable oils, but had never been successfully used in making biodiesel from waste oil.

According to Zong, one factor holding back the wide-spread use of biodiesel is the cost of the vegetable oil starting materials. And the presence of free fatty acid impurities in waste vegetable oil makes it difficult to convert this cheap and readily available potential fuel source into biodiesel. A number of solid acid catalysts, such as zeolites, have found limited success in converting waste oil to biodiesel, but they can't operate effectively under the required harsh conditions. Sulfated zirconia has shown to be a very effective catalyst for the reaction, but the cost of the rare zirconium metal is prohibitive. Zong's sugar catalysts have a higher activity than zeolites, and are cheaper to prepare than the zirconia catalysts.
Zong is committed to further research in this area. 'Environmentally-friendly production of cheap renewable fuels is very important,' she said. 'I am sure that biodiesel research is a growth area and that sugar catalysts will be an important part of it.'

Mark Keane, a chemical engineer at Herriot-Watt University, Edinburgh, UK, agreed that this work could be significant. 'The use of sugars as catalytic agents to convert waste oils is certainly intriguing and could potentially serve as a progressive approach to a burgeoning waste treatment issue,' he said.

Preparation of a sugar catalyst and its use for highly efficient production of biodiesel

Min-Hua Zong, Zhang-Qun Duan, Wen-Yong Lou, Thomas J. Smith and Hong Wu, *Green Chem.*, 2007, **9**, 434

Mild green ionic liquids 03 May 2007

Biodiesel production could become more environmentally friendly thanks to researchers in the UK who are using non-toxic ionic liquids to remove unwanted by-products.

The main by-product in the production of biodiesel from vegetable oils is glycerol. This syrupy sugar alcohol must be removed from the biodiesel as it can damage engines. Andrew Abbott and colleagues from the University of Leicester have developed a simple new approach to this sticky problem: they use green ionic liquids called deep eutectic solvents to just wash the glycerol out of the biodiesel.

Deep eutectic solvents are two or more substances mixed in a ratio that has a melting point much lower than any of the constituents. These are generally made from an organic halide salt that is complexed with something that will form a hydrogen bond. Abbott's team used quaternary ammonium salts complexed with glycerol as the washing liquid. This green washing liquid has many advantages including its low cost and toxicity; in fact, one salt used is choline chloride - vitamin B_4.

"The main by-product in the production of biodiesel from vegetable oils is glycerol."

This procedure not only has potential as a greener method of cleaning up biodiesel, but also as a method of producing pure glycerol. Alexei Lapkin of the University of Bath commented that the work 'is a very interesting development for downstream glycerol treatment and utilisation'.

Abbott hopes that 'further research will reveal a better method for recycling the salt and recovering the glycerol'. He added that the team want 'to collaborate with a biodiesel producer to test this technology on a practical scale'.

Extraction of glycerol from biodiesel into a eutectic based ionic liquid
Andrew P. Abbott, Paul M. Cullis, Manda J. Gibson, Robert C. Harris and Emma Raven, *Green Chem.*, 2007

Recent articles

A Highly Selective, One-Pot Purification Method for Single-Walled Carbon Nanotubes

J. Phys. Chem. B, **111** (6), 1249 -1252, 2007.

We report on a one-pot, highly selective chemistry to remove residual catalysts from single-walled carbon nanotubes (SWNTs). The impurities, initially present at ~35 wt % and mostly as carbon-coated iron nanoparticles, can be driven below 5 wt % with nearly no loss of SWNTs. The carbon-coated iron impurities are dissolved simply by reacting with an aqueous mixture of H_2O_2 and HCl at 40-70 °C for 4-8 h. This purification combines two known reactions involving H_2O_2 and HCl, respectively; however, by combining these two typically inefficient reactions into a one-pot reaction, the new process is surprisingly selective toward the removal of the metal impurities. This high selectivity derives from the proximity effect of the iron-catalyzed Fenton chemistry. At pH ~1-3, iron is dissolved upon exposure, avoiding the otherwise aggressive iron-catalyzed digestion of SWNTs by H_2O_2. This extremely simple and selective chemistry offers a "green" and scalable process to purify carbon nanotube materials.

Solvent-free enzymatic synthesis of fatty alkanolamides

An environmentally benign and volume efficient process for enzymatic production of alkanolamides is described. Immobilized *Candida antarctica* lipase B, Novozym®435, was used to catalyze the condensation of lauric acid with monoethanolamine. The reaction temperature of 90°C was required to keep the reactants in a liquid state. Stepwise addition of the amine minimized problems caused by the formation of a highly viscous amine/fatty acid ion-pair. The enzyme was both very active and stable under the reaction conditions, with about half of the activity remaining after 2 weeks. The maximum amide yield obtained when using equimolar amounts of the reactants was 75%, which could be increased to 95% upon water removal. Special precautions to avoid co-distillation of the amine were required. Two different strategies to avoid the amine loss are presented. Biotechnol. Bioeng. 2007;97: 447-453.

Progress Report: **Bionanocomposites: A New Concept of Ecological, Bioinspired, and Functional Hybrid Materials**

Advenced Materials 2007, 19, 1309

Bionanocomposites represent an emerging group of nanostructured hybrid materials. They are formed by the combination of natural polymers and inorganic solids and show at least one dimension on the nanometer scale. Similar to conventional nanocomposites, which involve synthetic polymers, these biohybrid materials also exhibit improved structural and functional properties of great interest for different applications. The properties inherent to the biopolymers, that is, biocompatibility and biodegradability, open new prospects for these hybrid materials with special incidence in regenerative medicine and in environmentally friendly materials (green nanocomposites). Research on bionanocomposites can be regarded as a new interdisciplinary field closely related to significant topics such as biomineralization processes, bioinspired materials, and biomimetic systems. The upcoming development of novel bionanocomposites introducing multifunctionality represents a promising research topic that takes advantage of the synergistic assembling of biopolymers with inorganic nanometer-sized solids.

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