CSEM's
Materials Monthly
March 2005 Making materials matter

Oil and water do mix

A brave new world with de-gassed water

Professor Ric Pashley holds up a vial containing de-gassed oil with de-gassed water. To mix them into a suspension in which the oil will form sub-micron droplets, all you need to do is give the vial a good shake.

ANU researchers are revolutionising our understanding of the manner in which oil and water interact. In the process, they are redefining some basic properties of water and opening up huge possibilities for the pharmaceutical and cleaning industries.

The research is being led by Professor Ric Pashley from the Department of Chemistry. He has found that when you remove the minute quantities of oxygen and nitrogen that naturally occur in water, you dramatically increase the ability of water to mix with oil. It sounds fairly simple, and it's relatively straight forward to achieve, however this breakthrough comes with breathtaking implications.

Mixing oil with water

Everyone has heard that old adage: oil and water don't mix. However, most people in the street are probably unaware of just how many problems this seemingly universal concept produces.

Most obviously there are implications for cleaning. Dirt and stains on our clothes, cars and crockery, for example, are largely composed of oils or other insoluble components. To remove the dirt, therefore, we use detergents and soap which break the oil up and allow them to be carried away by water. Beyond the price of the detergent, there's also an environmental cost of dealing with all those extra chemicals being flushed down our water ways.

"There's another problem with soaps and detergent," says Professor Pashley. "They also usually leave residues on the surfaces that they have cleaned. On most objects these trace residues don't pose too big a problem. In some situations, however, such as on some surgical instruments and microelectronic parts, these residues create major problems."

Then there are oil spills. The various detergents used to clean wildlife and shorelines impacted by an oil spill are often worse than the oil itself. Applying detergents to birds to rid them of the spilt oil, as one example, often disrupts their natural oils and leads to their death.

Mixing drugs and oil

In addition to cleaning, another major area where oils failing to mix with water produce problems is in drug delivery. Many drugs are simply insoluble in water. This fact alone means many drugs never even make it through the testing phase of approval because a suitable aqueous-based drug delivery system isn't available.

Where delivery systems have been formulated, they usually involve first dissolving the drug in a carrier oil, such as soya bean oil. This is then partially dispersed in water, usually with the aid of chemical surfactants and physical agitation. Unfortunately, the carrier oil and surfactants frequently introduce major side-effects for the patient. This adds a lot of complexity and expense to developing new drugs.

"Drug delivery is something most

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Volume VI, Issue II

Materials Monthly is produced by the ANU Centre for Science and Engineering of Materials

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people don't think about when it comes to mixing oil and water," says Professor Pashley. "The truth is that an enormous number of potentially valuable drugs are simply put up on the shelf because there is no easy way of delivering them to the body via an intravenous injection. And if a delivery system has been devised using oils and dispersants, it often comes with a range of unintended side effects because of the addition of these extra chemicals."

Oil, water & detergent?

Oils don't dissolve in water because hydrocarbon molecules (the compounds that make up oil) are fundamentally different to water molecules, and cannot replace the strong water-water bonds with equally strong water-hydrocarbon bonds. Hydrocarbon molecules are non-polar whereas water molecules are polar. Fluorocarbon, chlorohydrocarbon and silicone molecules are also non polar and have similar problems dissolving in water. Sugars, salts and alcohols, on the other hand, are polar materials and are readily soluble in water.

Detergents are made up of molecules that have non polar ends, which bind to the oil, and polar ends, that bind to the water molecules. When you add detergent to a mix of oil and water, and shake, the oil is broken up into a suspension of fine droplets, each with a thin coat of detergent. The oil doesn't dissolve in the water but it will remain in suspension for some time, during which it is carried away with the water.

"That's how detergents work. They don't dissolve oil, they simply allow it to be broken up into tiny bits which are then washed away."

So, why won't oil break up into small bits when it is agitated without detergent being present? The answer it seems, is the presence of gas molecules.

Gas in water

"For several years we have been studying the role that tiny amounts of gas dissolved in water and oil might play," says Professor Pashley. "This gas comes from the atmosphere, it's mainly oxygen and nitrogen. There's around 20 mL of atmospheric gas dissolved in every litre of water at room temperature. That's not much though it's enough to keep a goldfish alive in an aquarium."

"These gas molecules don't really fit in with the water molecules so they tend to accumulate on hydrophobic surfaces such as the oil water interface. When the mix is agitated, droplets of oil begin to break away from the main oil body. A negative (suction) pressure forms between the droplet and the main oil body, and gas cavities form between them in a process called cavitation. These gas cavities act like a glue that prevents the oil droplet from leaving the oil surface, it draws them back to rejoin the oil surface.

"The important thing is that the gas molecules nucleate this cavitation. Which begs the question, what happens if you remove the gas molecules?"

Remove the gas from the water (and the oil) and you create a significant barrier to cavitation. In the absence of cavitation, oil droplets will readily break away."

Well, that's the theory anyway. What happens in real life?

De-gassing water

In a chemical lab, removing atmospheric gas from water and oil is a relatively straight forward task. Water is de-gassed by freezing it under liquid nitrogen and then 'out-gassing' it using a vacuum pump. Following the removal of the gas, the mixture is thawed and the process is repeated another three or more times until completely de-gassed.

"There are other ways this can be achieved," comments Professor Pashley. "On oil rigs, for example, they remove gas from the water used in cooling pipes using hydrophobic filters that let out the gas while keeping the water. It obviously costs more to do this but by removing the oxygen from the water they get less corrosion and can extend the life of the pipes. The thing is, there are industrial sources of degassed water. It's not a difficult thing to produce."

And what happens when you mix de-gassed water with oil?

"The results really are quite remarkable and suggest we need to totally revisit this notion that oil and water don't mix," exclaims Professor Pashley. "It was immediately apparent that de-gassed water can remove a wide range of residual oils and oil-based solids ('dirt') from glass surfaces when the mix is agitated. We made detailed turbidity measurements on what happens when you use de-gassed water as opposed to normal gassed water but the results were also obvious by just looking at the different treatments.

"In the treatment using normal water, the oil resisted mixing and rapidly returned to its own separate layer, forming large droplets of oil that stuck to the side of the test tube. In the treatment using de-gassed water, the oil formed tiny droplets evenly mixed through the water giving the dispersion a milky appearance.

"And the effect was even more pronounced when we mixed de-gassed water and de-gassed oil. Oil has a greater capacity than water to store gas so by removing the gas from the oil, which is done in the same manner as for the water, the results are even better producing a dispersion that lasted for longer."

Cleaning sans detergent

"Now, we're not suggesting that this means we can throw detergents away," cautions Professor Pashley. "Some of the media attention that has surround this discovery has invoked visions of washing machines and dishwashers just using pure water, but that isn't very realistic. De-gassed water is still relatively expensive to produce and commercial washing mixes carry out other roles in addition to removing oil.

"However, we do envisage that this breakthrough might have some important specialist applications where detergents currently create

Professor Pashley with the equipment needed to de-gas water. "All you really need is access to liquid nitrogen and a good vacuum pump."

major problems such as cleaning some surgical equipment and silicon wafers in microelectronics industry.

"The method we've proposed involves two steps. The first has the object to be cleaned being sprayed with a de-gassed oil. The oil could be a hydrocarbon, fluorocarbon, chlorohydrocarbon or silicone liquid. This picks up the oil or dirt.

"Then, you quickly follow this with a blast of de-gassed water. This creates a suspension of water and oil that washes away.

"The mechanical action of the liquid impacting on the surface being cleaned combined with the dispersive power of de-gassed water will disperse hydrophobic dirt (oils and grease) and remove them. Other types of dirt (hydrophilic, polar dirt such as salts and sugars) will be dissolved in the normal manner.

"This represents an entirely different approach to cleaning. I'm sure there are many other areas of cleaning where eliminating detergents will be important. Cleaning wild-life affected by oil spills, for example, might be one such area."

Of course, implementing new ways of cleaning with de-gassed water and oil may take some time to develop. However, it's possible that applying this knowledge in drug delivery systems could happen almost immediately.

Drug delivery

"It's quite possible the real value of working with de-gassed water may lie more in drug delivery than in cleaning," says Professor Pashley. "And there are a several aspects to this.

"First, many important drugs only dissolve in water-insoluble oils. To be injected into the body these oils need to be dispersed in water. For some of these carrier oils there are techniques for creating mixtures with water but this usually involves the addition of stabilising agents such as surfactants and polymers. For other oils there are no methods for injecting them intravenously.

"In either case, using de-gassed oil and de-gassed water, it is now possible to create a stable dispersion without the additional stabilising agents. Over time the different phases will separate out however all you have to do to recreate it is to shake the mixture vigorously for several seconds. It doesn't get much simpler.

"And if the mixture is stored in its de-gassed condition in a sealed vial, it will retain this capacity for many months if not years.

"What's more, for reasons which we're yet to fully understand, the oil dispersion is of a nature that's close to ideal for IV injection. The oil droplets are all very close to being 0.3 microns in radius, which is exactly what pharmaceutical companies aim for when devising methods for mixing carrier oils and water. On top of that the size range has a tight distribution, superior to what's achieved when using additives to create the mix.

"Another exciting aspect is that it has been successfully applied directly to hydrophobic drugs, both liquid and solid. In other words, the carrier oil, which comes with its own side effects, has been bypassed completely. A dispersion in de-gassed water can be obtained without the use of either carrier oil or added dispersants.

"Imagine that, instead of needing a cocktail of additives to get a drug into your system, the use of de-gassed water makes it possible to be simply given a mixture of the pure drug mixed only with water."

New worlds of mixing

And this is all just the first applications of this discovery. Because there are many processes around us that are based on the assumption that oil and water doesn't mix, it's a sure bet there's a lot more that can be done with this new understanding.

"De-gassed water doesn't occur naturally," says Professor Pashley. "Maybe that's why it's taken us so long to cotton on to these possibilities. If we had known that degassed water had these properties I suspect we would have developed many applications already.

"However, as it has turned out, this field is only just opening up. It's exciting to be at the beginning of something that might be so significant.

"It's also nice to discover that the world of science still has a few big surprises to throw at us."

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Oh, and another thing!

Professor Pashley's investigations have revealed another intriguing property of de-gassed water. It seems that when trace quantities of oxygen and nitrogen are removed from water that its conductivity is dramatically increased – by around twenty times!

"It seems that the presence of significant levels of nonpolar atmospheric gases can suppress the conductivity of water, and that complete or partial de-gassing can increase it substantially," says Professor Pashley. "It's quite possible that this finding might dwarf the oil-mixing-with-water aspects of this research, but at this stage we're still to explore the full implications of this discovery."

One immediate application arising out of this discovery is that desalination of seawater via electro dialysis suddenly becomes a commercial proposition.

Looking after materials in the time tunnel

To the people that work there it's simply referred to as 'the tunnel', though 'the cavern' might be a more apt name. We are talking about the repository of the ANU Archives Program and it's located directly above the road tunnel on the Tuggeranong Parkway (around a 100 metres west of Sullivans Creek).

Hidden from public view and sheltered from the unforgiving sun, the underground storage facility holds around 13 kilometres of shelf space. And sitting on those steel shelves are a variety of records, memoirs, personal notes and pictures covering a vast sweep of Australian and ANU history.

"We have hand-written letters in the collection from back in the 1820s," says Dr Sigrid McCausland, the University Archivist in charge of the ANU Archives Program. "The University's archives contains a lot more than just records relating to the ANU. We also manage the Noel Butlin Centre Archives which contains one of Australia's most extensive collections of business and labour records."

"To manage an important collection such as this archivists require a wide range of skills. These include needing to be part historian, part materials conservator and part curator. It's not just simply storing boxes of old papers.

"Archives are all about selection, preservation and an ability to find and re use archived material.

"The first thing an archivist does when given a record is to sort through it and remove waste or redundant material. You simply can't keep everything. Some things are worth saving, some aren't.

"Next you have to know a little about the material being archived. Most of the archives exists in the form of paper so you need to know how different papers perform over time. Nineteenth Century papers often have a high rag component imparting to them a greater life span. Twentieth Century papers, especially during the wars, are usually of a poorer quality and often contain high levels of acid causing faster degradation.

Ewan Maidment

A tiny sliver of the13 kilometres of shelf space that comprise the University archives. Everytime you drive through the tunnel on the Tuggeranong Parkway you pass under this massive collection of records.

"More recently, thermal paper used in some fax machines are useless for the long term storage of information. If important information is stored in this form it needs to be copied onto a different paper stock.

"Ink jet and laser printers produce long lasting type but when a front facing page is stored over time against a plastic protective folder the type often transfers over onto the plastic.

"Once again, you can't keep everything in perfect storage, so you have to decide what's important and worth making more of an effort for. If it's a record of value it should be on acid-free paper in acid-free cardboard folders and stored in acid-free cardboard boxes. And archivist is continually making decisions – what's worth keeping and how should it be kept."

And then there are the storage conditions at the Archives, and here Canberra has a natural advantage.

"If you were going to set up an archives anywhere, it'd be Canberra," says Dr McCausland. "For a majority of the year the ambient conditions are perfect for preserving books and other paper products – basically it's cool and dry."

Which is fortunate because at this stage the University hasn't the resources to provide air conditioning to the repository. Instead the tunnel has 'conditioned air' which consists of a forced air circulation system where the air is drawn in by fans on one side of the facility and drawn out by fans on the other.

The benchmark for conditions inside archives has been established by the National Archives of Australia and is set out in the *Standard for the Physical Storage of Commonwealth Records.* This states that collections should be maintained between 18-22°C with humidity between 45-55%. Temperature and humidity monitors are scattered throughout the ANU repository to maintain a record of what conditions are actually being met.

"The entire collection also gets fumigated once a year to reduce the threat of damage from insects," says Dr McCausland.

"But it's not just the climate that makes Canberra a good place to keep archives. Because the national capital plays host to a number of museums, galleries and memorials, we're well serviced when it comes to having access to a broad range of materials conservators.

"While paper is the main material we archive, we also store film in a number of forms, material objects like union banners and a variety of other objects. Each has its own special requirements and, if it's judged to be important, we bring in specialist conservators to make sure we're caring for an object in an appropriate manner."

And, for anyone with an interest in the history of science at ANU, the Archives also holds many jewels including the personal papers of Professor Ted Ringwood (RSES), the notes of Professor Arthur Birch (RSC), the research school files of Sir Mark Oliphant (RSPSE) and the history research of Professor Frank Fenner (on JCSMR, RSBS and CRES).

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For more information on the ANU Archives Program
http://www.archives.anu.edu.au/

More information on how to preserve different materials (from the National Archives of Australia)
http://www.naa.gov.au/recordkeeping/

Unpacking the inkjet black box

The ANU Inkjet Research Facility

The world is going digital, and for all the power and precision that comes with that transition there's also often a significant cost in terms of losing control over many of the processes that we previously understood from the ground up.

Photo media is a good example of this. Any photographer or photo artist of any worth not only knew how to take photos but also how to develop and process them. They controlled the process from image capture to image presentation, and they had the capacity to work and experiment with the image at any stage. Indeed, a major part of the final product was often created while working in the dark room.

Going digital has revolutionised the industry. Digital photography has allowed for unprecedented storage and manipulation of images but when it comes to processing those images we've lost control. For most of us, outputting a digital image is as simple as pushing the print button. Working through preset software we can manipulate several variables such as resolution and colour balance but now machines are in control. And what's happening in that device known as an inkjet printer, is anyone's guess. Most of the time the product is acceptable but the inkjet is really just a black box that we don't muck around with. That means sticking with a limited set of output dimensions and working with very limited set of materials (papers and a few plastics). There is little capacity to experiment or learn.

The team behind the Inkjet Research Facility. From the left: Peter Fitzpatrick, Jason Obrien and Luisa Abello.

The Photomedia Workshop at the ANU School of Art has a tradition of building the capacity of its students such that they have control of every step of the photomedia process. Leaving the all important inkjet output phase as a black box was seen as a major limitation.

"We wanted to explore what might be possible with an inkjet," says Peter Fitzpatrick, a photomedia lecturer with the School of Art. "However, to make that possible we needed a high-end machine that would allow us to put our hands inside the 'black box' and experiment.

"We made a submission to the Major Equipment Committee and were successful. We purchased an ENCAD 880i inkjet printer. This was the genesis of the Inkject Research Facility."

The Encad has an adjustable inkhead height making it possible to work with a wide variety of materials. It is also capable of producing prints up to 152 cm wide allowing most formats to be produced.

"This printer will allow researchers, students and artists from all disciplines to output digital files on a diverse range of mediums including paper, vinyl, glass, acrylic, metal, wood, textiles, clay and film materials," says Mr Fitzpatrick. "We will also be trialling a wide range of commercial and custom-made inks and pigments.

"The facility also operates a high-resolution 10000 dpi CREO iQsmart scanner allowing for the generation of the highest quality digital files. It can also scan objects as well as 2D media.

"Research will initially proceed in three main areas," explains Mr Fitzpatrick. "We'll be investigating new ink set combinations, testing possible materials for the print support and using inkjets as an intermediary image matrix in printmedia, photomedia and textiles.

"At one end we're aiming to control the inkjet process to get as close as possible photo-quality outputs. At the other end we're trying to understand the aesthetic of the inkjet medium to discover just what's possible."

Peter Fitpatrick with an artwork produced by a student, Gary Smith. The base medium is artist-quality natural canvas, a material that is very difficult to print on. The Inkjet Research Facility developed a technique of preparing the canvas by first spraying it with a suspension of oil-based paint and gelatin. Then a print was added with the Encad printer and finally portions were painted over.

To help fund its research program, as well as passing on some of the knowledge that is being generated from that research, the facility also offers a printing service that makes use of a second high-end inkject printer, an Epson 9600.

"The Epson was purchased with the sole purpose of offering

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Unpacking the ink jet

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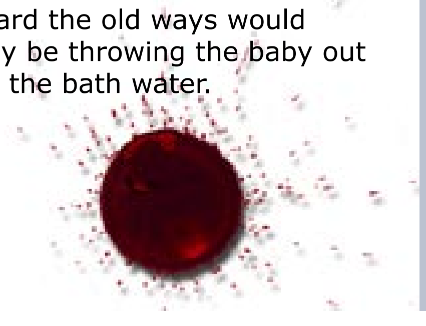
a customised print service," says Mr Fitzpatrick. "With it we can offer artists and scientists personalised consultations and advice on a wide range of printing projects. The service is ideal for small one-off runs, specialised art or edition work. The recent *flowvis* exhibit presenting images from the world of fluid dynamics was printed by us. We're competitive in price and offer the highest in quality. Clients can screen proof their images before going to print. If your requirements go beyond the mainstream offerings we might be one of the few places that can help you.

"The Inkjet Research Facility makes the Photomedia Workshop one of the most advanced facilities of this type in the country. For the first time students and visiting artists will be able to work directly and immediately at exhibition scale, having full control over all aspects of the process. The flexibility of the process allows for the exploration of methodologies, and will generate innovative inkjet applications and new kinds of work.

"Which isn't to say that the old tried-and-true analogue techniques of the dark room have been thrown away," he adds. "Indeed, the Photomedia Workshop has recently refurbished its dark room facilities making them some of the best available. Our aim is to give our students and artists access to the widest range of techniques possible. Even with the most sophisticated digital outputs in the world there are still many effects and methodologies that are only possible in the dark room. To discard the old ways would really be throwing the baby out with the bath water.



And we're always interested in exploring the possibility of new collaborations. If anyone has an idea or a challenge that involves an inkjet output, we'd be very interested in hearing about it."

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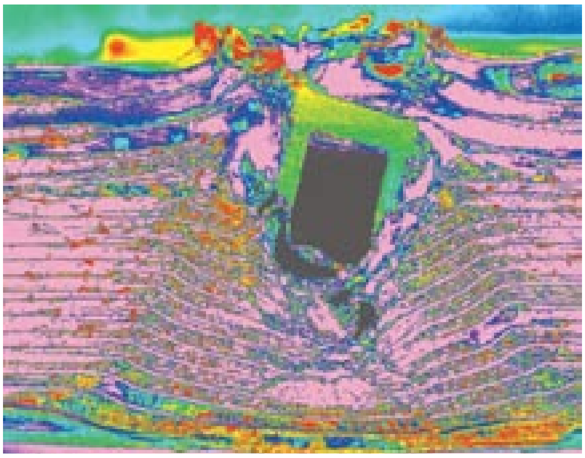

Pick the pic

Materials scientists at the University of California, San Diego (USCD), have created a new type of metallic laminate that can serve as armor and as a replacement for beryllium, a strong but toxic metal commonly used in aerospace applications.

"The new material we developed has a stiffness equalling that of steel, but it's only half as dense," says Professor Kenneth Vecchio, professor of mechanical and aerospace engineering at UCSD.

In order to test the bullet-stopping capability of his new material, Vecchio fired a heavy tungsten alloy rod into a 2 cm thick sample at a velocity of about 900 m per second. The rod penetrated only half the thickness of the test sample (see image). Vecchio said the laminate performs well as armor and has potential as a structural metal.

The new material is made primarily of two lightweight metals. Vecchio alternated layers of aluminum and titanium alloy foils, and compressed and heated them. The resulting reaction generated a laminate with two layers: a hard ceramic-like "intermetallic" layer of titanium aluminide, and a pliable layer of residual titanium alloy. The layers can be stacked like 1-millimeter-thick pages of a book, and even contoured into desired shapes prior to heating.

The laminate architecture mimics the the tough shell of the abalone. The mollusc makes its dome-shaped home by slowly adding layers of brittle calcium carbonate, each about one-thousandth the thickness of a human hair, between even thinner layers of a stretchy protein adhesive.

"The intermetallic phase of titanium aluminide is the complement of the mollusk's hard calcium carbonate phase, and the titanium alloy layer mimics the abalone shell's compliant protein layers," said Vecchio.

More info: http://ucsdnews.ucsd.edu/newsrel/science/030705_Vecchio.asp

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Materials Monthly comes out 10 times a year (February to November). We welcome your feedback and contributions. Please send them to David Salt, Editor, *Materials Monthly*, care of CSEM.

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