CSEM's
Materials Monthly
October 2006 Making materials matter

Getting stuck into resin

What began as an investigation of the chemical structure of the resins in wood composites has led one research chemist to making and testing her own particle boards. Dr Amy Philbrook went in as an organic chemist but suspects she might be transforming into a materials scientist.

MF, UF and MUF resins hold together many of our most commonly used products. They're all thermoset resins, meaning they set hard when heated, and they're used in the manufacture of wood adhesives, laminates, dinnerware and paper additives. The production of these resins is big business. In 2004 alone Orica Australia manufactured approximately 18,000 tons of them.

World-wide it's a multi-billion dollar industry and yet, despite their widespread use, there is much that is not understood about the chemical bonds that form as these resins cure. Scientists at the Research School of Chemistry are now applying advanced nuclear magnetic resonance spectroscopy to the problem and are coming up with some interesting results.

Meet the resins

Melamine-formaldehyde (MF), urea-formaldehyde (UF) and melamine-urea-formaldehyde (MUF) are amino resins formed in a two-step chemical process between amines (and their derivatives) and formaldehyde. When manufactured for wood adhesives the first stage is the formation of a homogeneous solution of low molecular weight species. This liquid resin is then mixed with wood fibre and pressed where it undergoes further condensation resulting in covalently cross-linked networks, which bind the wood fibre.

Urea-formaldehyde resins are the cheapest of the resins to produce. They possess good thermal properties with excellent hardness and an absence of colour. However, once cured, UF resins are susceptible to acid hydrolysis when they come into contact with water resulting in the release of toxic formaldehyde. To make wood adhesives more durable and less likely to hydrolyse, additives like melamine (1,3,5-triazine-2,4,6-triamine), are added to the resin.

MF resins are used for dinnerware, automotive top coats, textile finishes and exterior wood adhesives. MF resins are more heat resistant, less susceptible to acid hydrolysis and more water resistant than UF resins, but are more expensive to manufacture because of the relatively high cost of melamine.

MUF resins utilise the cost-effective strong UF component and the hydrophobic durable properties of MF resins. When compared to a UF resin, an MUF resin is more durable and therefore emits less formaldehyde.

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Dr Amy Philbrook with her test rig for making mini MDF boards. "The particle board industry is enormous and it's amazing how little we understand about the basic resin materials we're working with," she says.

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But what's in the mix?

In principle, urea and melamine could co-polymerise in the condensation stage of the reaction to produce the co-polymers methylene (A) and dimethylene-ether (B). However, it could also be that the MUF resins are simply mixtures of MF and UF resins – a mix of monomers from these two resins. Available tests are unable to distinguish between a mix of monomers or a mix containing the co-polymers A and B.

If the co-polymers are present, or if the process of curing could be manipulated to encourage their formation, it's likely they would confer superior physical properties on the resin in terms of durability and stability. However without a procedure for detecting them there has been no possibility of a coordinated investigation into how they might be created or what physical properties result.

In other words, while these resins have widespread use and are manufactured in prodigious quantities, because we've lacked the capacity to analyse what types of bonds are forming in them, we're limited in our ability to explore how we might create a more effective mix (in terms of cost and performance).

"The particle board industry is enormous and it's amazing how little we understand about the basic resin materials we're working with," says Dr Amy Philbrook, a postdoctoral researcher based in the Biochemical Reactions and Molecular Recognition Group at the Research School of Chemistry. She has spent several years now investigating the chemical structure of resins used by Orica in many wood composite products. Her current work is funded by an ARC Industry Linkage grant (with Orica).

Industry orientated chemistry

"We're looking at correlating the chemical structures of these amino resins to the resulting physical properties," she explains. "So we're trying to determine which bonds perform better in the final reconstituted wood product.

"This builds on the research I undertook during my PhD, which was also carried out here at RSC, where I was looking at the chemical structure of the resins at the initial stages of the resin making. I was looking at how bonds were forming and which bonds were forming using Nuclear Magnetic Resonance (or NMR) spectroscopy.

"At the time that I was doing this research it was known that you could increase the durability of UF resin by mixing in melamine. However, why this occurred wasn't understood. Could it be simply attributed to the melamine being present, or was it because components in the melamine were reacting with components in the urea thus changing the actual structure of the resin? Were monomers in the urea and the melamine cross linking to form co-polymers?

"The reason for the uncertainty was that there was no tool to identify co-polymer links in MUF reactions. Therefore the initial aim of my research was to develop a tool to assess co-polymerisation. Such a method would be valuable to correlate structure to resin properties and could then be used to maximise manufacturing or mixing techniques and to produce resins with superior properties."

An NMR tool

"We therefore set out to establish procedures to identify and characterise any co-polymerisation in the MUF reactions," says Dr Philbrook. "The technique we used employed NMR spectroscopy because this is a tool that has been widely used in the past to elucidate amino resin structures.

With the assistance of Dr Max Keniry, leader of the NMR Group at RSC, Dr Philbrook was able to identify a unique NMR signature for the co-polymer fragments A and B and then demonstrate that these were present in the MUF resin. She also showed that these signatures were missing in the UF and MF spectra. By so doing she had, for the first, demonstrated co-polymerisation has been taking place. Just as importantly, she had developed a tool that promises to open up studies on wood resins.

"These techniques are suitable to be applied to industrially prepared MUF resins," she says. "Therefore, it's now possible to correlate the molecular structure of the resin to its physical properties. Furthermore, it is now feasible to investigate the extent of co-polymerisation in MUF

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NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) is a cornerstone of molecular chemistry, biology and modern materials science. It's one of the few non-destructive methods for analysing molecular structure, and provides a wealth of information on what atoms make up a molecule, how they are arranged (eg rings, layered molecular segments, etc) and how the molecule is folded or twisted in three dimensions.

NMR grew out of basic molecular science in the 1940s. It was first demonstrated by Felix Bloch and William Hansen at Stanford University and Edward Purcell at Harvard University in 1946. They showed that when certain atoms are placed in a strong magnetic field, they absorb energy at a specific frequency. By measuring the energy that is absorbed and then radiated by these atoms, it is possible to identify what they are. NMR spectrometers are based on this concept and are capable of detecting and amplifying the absorption and emission of energy from atoms with such precision that it's possible to calculate the structure of molecules.

NMR has been one of the basic enabling technologies that have been behind the development of the materials that have characterised the 20th century such as polyester, paints and a variety of other plastics and petrochemical products. Today, many labs operate whole batteries of NMR systems performing a wide range of duties including measuring the moisture content of food, doing quality control in pharmaceuticals and performing advanced biomedical studies.

Dr Amy Philbrook and Dr Max Keniry. Dr Keniry wrote the NMR pulse sequence used to fully assign MUF co-polymer fragments.

A force of Nature

Henry Wilson designs furniture, and his passion is using composite wooden materials and driving these materials to their structural limits. He's produced a number of innovative designs that are light, portable and storable while still being strong and robust – perfect for modern living, compact homes and constant moving. He's also set up his own company and modified his designs so they can be commercially manufactured. And he's achieved all this while still an undergraduate in the Furniture/ Wood Workshop at the ANU School of Art.

The 'Force of Nature' table designed by Henry Wilson - it's elegant, portable and needs no additional tools or fastenings.

The table he's designed is called the 'Force of Nature', and uses beech wood in the trim and legs, and laminated styrofoam in the table top to keep the weight down. The legs and supporting rail are made from beech, and the supporting rail is flexed and inserted into a slot on the underside of the table where it's held under tension. When not in use the table can be pulled apart and stored. It's stylish to look at and requires no additional tools.

"I was striving for a simple design with no applied fastenings, a simple structure that's easy to assemble and transport," says Mr Wilson. "I particularly wanted to explore the properties of beech. It's a friendly and forgiving wood, especially resilient to bending, and is a plantation timber and therefore a renewable resource."

Henry Wilson with his Racquet chair, a light weight stackable chair that incorporates traditional wood with a range of advanced composites.

Dr Rodney Hayward, Head of the Furniture/Wood Workshop where Mr Wilson designed the table, believes the 'Force of Nature' table is an elegant and innovative solution to an age old problem. "It's strength comes from its simple beauty," he says. "Hidden is the engineering, the secret architecture."

Mr Wilson designed the table to specifically match the aesthetic style of his slatted chairs, also made from beech and hoop pine plywood.

"The principle behind the slatted chair design was to create a pleasing lightweight, ergonomically-sound wooden chair," says Mr Wilson. "I wanted to bridge the gap between a hard-finished wooden chair and an upholstered chair."

He achieved this by using beech wood slats for the backrest and seat. Each slat is made of two pieces of wood with a void in the middle. These flex and bend to the shape of the sitter, and flex back when the person stands up.

In attempting to translate these designs into templates for manufacture, Mr Wilson also came up with designs for a 'zig zag' stool and a bookcase that made use of the excess plywood sheet in order to minimise wastage.

If all that wasn't enough, he's also been working on a racquet chair that uses a webbing of braided polyethylene cord as a seat and backrest strung inside a frame of laminated plywood. His aim is to produce a light and strong stackable chair. The first prototypes of the chair demonstrated elements of the frame weren't strong enough, so, with the help from the Department of Engineering, Mr Wilson tested designs that incorporated carbon-fibre lamination on the stressed sections of the plywood frame. The result is a super-light chair which features the carbon-fibre laminate as a design element. The chair is still being developed.

For a student in his Honours year of a Bachelor of Visual Arts, Henry Wilson is a force to be reckoned with.

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Nr Wilson's slatted chair maintains the hard finish of wood but flexes to move with the seated person. The slats are made from beech.

reSkin

Wearable technology

An ANAT Media Lab being run at ANU from 15 Jan - 3 Feb, 2007

The idea is simple but there's no telling where it might lead. Bring together 20 artists including jewellers, textile artists, fashion designers and media artists, and put them with six internationally renowned media arts and design facilitators for an intensive three-week workshop focussing on wearable technology – and see what happens.

The format is known as a Media Lab and the Australian Network for Art and Technology (ANAT) runs one each year. The next Lab will be run at the beginning of 2007 at ANU and is titled *reSkin*. It will focus on wearable technology, with a focus on the skill-based practices of object, jewellery, fashion design and media art.

reSkin will engage a team of renowned media arts facilitators who will guide and work with 20 artists as they research, develop and rapid prototype sensor, time-based and reactive clothing; jewellery, shoes, bags; and personal, environmental and device designs – anything wearable and technologically integrated.

ANAT's annual Media Labs and Summer Schools have traditionally concentrated on introducing the skills associated with emerging technological-based forms and practices to a wide sector of Australian media arts practitioners, writers and curators. Building upon the success of these initiatives, including the 2005 Create_Space Lab, *reSkin* will place four international and national facilitators with 20 participants including jewellers, textile artists, fashion designers and media artists.

About the Facilitators

Elise Co (USA) is a multimedia designer and programmer. Her practice includes the exploration of the synthesis of fashion and technology and recent projects include a luminescent raincoat and modular reactive bracelet.

Joanna Berzowska (Canada) is an Assistant Professor of Design and Computation Arts in Montreal. She works primarily with 'soft computation': electronic textiles, responsive clothing as wearable technology, reactive materials & squishy interfaces.

Susan Cohn (Australia) is an internationally acclaimed goldsmith and designer who has exhibited extensively. Her many accomplishments include being the first Australian to have a product manufactured by Alessi.

Nikita Pashenkov (USA) investigates the intersections between design, programming and electronics technology. He has worked with the Aesthetics & Computations Group in the MIT Media Laboratory and won the 2001 Tokyo TDC Award for Interactive Art.

Cinnamon Lee (Australia) is a metal smith whose focus is on the relationship between the body and object through interaction. She uses a range of traditional skills and new processes, most recently working with electric illumination and rapid prototyping.

Stephen Barrass (Australia) is Associate Professor in the School of Creative Communication and co-Director of the Sonic Communications Research Group at the University of Canberra. His artistic works include animated couches, haptic poems and edible soundscapes.

Alistair Riddell (Australia) lectures in computer music in the Centre for New Media Arts, ANU, and is a composer, performer and programmer. He has been active in a wide range of interactive digital arts including collaborations with many textile artists.

The Kukkia dress created by Joanna Berzowska, one of reSkin's facilitators, serves as a good example of what reSkin might create. It is decorated with three animated flowers constructed out of felt and silk with the shape-memory alloy Nitinol stiched through it. When heated the wire shrinks and pulls the petals together. As it cools down, the rigidity of the felt counteracts the shape of the wire, allowing the flower to open. It is an expressive and behavioral kinetic sculpture that develops a visceral relationship with the wearer.

Alexandra Gillespie is Project Manager for *reSkin*. She brings valuable experience to the position in her work as an artist, project manager, and university educator in the field of media and time-based art. She believes *reSkin* will be an exciting opportunity for Australian artists and designers to explore materials and processes towards creating wearable computing prototypes.

reSkin will end with a one-day forum of critical dialogue looking at Wearable Futures on Saturday 3rd of February. The forum will be run at the National Museum of Australia, and streamed on the net for international and national audiences. ANAT is currently exploring other opportunities for sharing the innovative and exciting outcomes that will result.

Materials interest

CSEM is hoping to stage a materials seminar in the first week of *reSkin* in which six materials researchers at ANU share their insights on their material with the workshop participants. If you would be interested in being a part of this seminar please contact David Salt <David.Salt@anu.edu.au>

For further information about reSkin, please contact Project Manager Alexandra Gillespie at alexandra@anat.org.au

Or visit the web site www.anat.org.au/reskin

About ANAT

ANAT
Australian Network for Art and Technology

ANAT is Australia's peak network and advocacy body for media artists working in screen, sound, installation, performance, literary and networked arenas; creating opportunities for connection, collaboration, innovation, research and development both nationally and internationally. ANAT brokers the synthesis between art and culture, science and technology. ANAT is supported by the Visual Arts and Craft Strategy, an initiative of the Australian, State and Territory Governments; the Australian Government through the Australia Council, its arts funding and advisory body, and the South Australian Government through Arts SA.

Multi-point annealing

in the Glass Workshop, School of Art

One of the most challenging aspects of creating innovative glass art is dealing with the tension that can build up in the glass as it cools. Not only can this tension warp the shape of the form being created but, because glass is such a brittle material, it can lead to the glass cracking or even shattering when subjected to a bump or a small temperature change.

To ensure this doesn't happen all glass products produced from a molten state need to go through an annealing process while cooling back to room temperature. Annealing involves stabilising the temperature at a specific point so internal stresses can ease. Then the glass must maintain precise cooling rates back to room temperature to produce a work with low internal tension.

Annealing larger and more complicated shapes in glass is a highly technical business in industry and research. Sophisticated industrial annealing approaches use targeted multi-point readings in the kilns to maintain a tight corridor of maximum/minimum thermal parameters for precise annealing for glass of larger size or complexity in shape. For example, the Mirror Lab facility at the University of Arizona produces the world's largest, lightweight land-based reflecting telescope mirrors. It uses a kiln some 10 m in diameter to anneal the glass for its large mirror blanks. At close to 20,000 kg they are the world's largest objects of cast glass. This kiln has over 200 thermocouples (temperature sensors) to allow the precise control of the annealing process. It was after seeing this facility that the head of the Glass Workshop, Richard Whiteley, got the idea to translate this approach for artists.

Cobi Cockburn, an Honours student in the glass workshop, with her artwork titled Shifting Fields. *The work consists of many fine glass tubes fused together and then reformed to create a canoe-like form. Works such as these are very difficult to create using single-point annealing because of the complexity of the form. Ms Cockburn won the prestigious 2006 Ranamok Glass Prize in August for* Shifting Fields. *The acquisitive $10,000 prize, now in its 12th year, is open to all contemporary glass artists from Australia and New Zealand.*

This cast glasswork by Charles Butcher, an Honours student in 2006, is a good example of the complex glass objects that require close control of annealing. Butcher's work is featured at a solo exhibition at Sabbia Gallery in Sydney this month.

In stark contrast, the kilns used by glass artists have only a single thermocouple and the annealing profile can often be unstable due to temperature variations in the kiln at any one time. This has been a limiting factor to artistic innovation for many years. The Glass Workshop at the School of Art is embarking on a project to translate the complicated industrial approach so studio-based artists can improve their efficiency in annealing and success rate. The aim is to be able to provide artists with the tool to achieve accurate thermal profile information, and importantly, be able to control this without a cost-prohibitive infrastructure.

Developing a multi-point annealing facility for artists will take the guesswork out of the annealing process by providing accurate temperature readings of the kiln environment and allow the annealing computer to make necessary adjustments for the cooling profile of the glass.

The advantage is that complex innovative and larger scale creative works can be more easily and reliably produced, saving time and money. The Glass Workshop is proposing to build a set of four kilns featuring the facility of multi-point annealing support and zone temperature control so that the heat of individual kiln chambers can be controlled separately as required.

Richard Whiteley holds up a transparent glass book, an artwork by Sue Kesteven, one of the Workshop students. The book is made by fusing together several glass elements and poses many challenges when it comes to annealing.

A better understanding of thermal dynamics within kilns will give researchers real information as opposed to the blunt instrument of single-point annealing. Through the sensitivity of equipment, these kilns will allow senior students and staff the ability to cross over between forming processes with much more certainty and success.

To assist in the project Dr David Ellis from Earth and Marine Sciences has been offering advice and support with approaches to setting up the technical side of the research. The Glass Workshop is currently seeking support to develop a Glass Research Laboratory, which will be the world's first and only education-based facility in the art of multi-point annealing. The aim is to develop a state-of-the-art glass facility to promote and support the crossover potential between hot- and kiln-cast glass, while also providing a facility to foster and broaden in-depth investigation in multi point annealing of kiln cast glass.

"We have established a excellent reputation for our artistic outcomes," says Mr Whitely. "Additionally, many of our senior students have a strong technical research component as part of their practice. We have identified this as an area that needs more collective research to assist the whole sector move forward."

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Getting stuck into resins

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resins and experiment with ways of modifying it.

"This NMR tool enabled me to start looking at the resin components, the monomers, that industry is actually using and devise model systems to test alternatives. I was looking at how bonds were forming with known monomers and then making new monomer units to replace the more expensive melamine monomer."

Bonding with wood

One of the investigations that Dr Philbrook employed these new NMR techniques on involved studying covalent bonds between the UF resin and the wood particles.

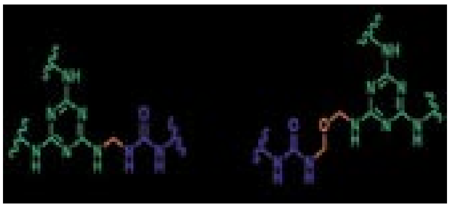
"There's interest in the industry as to whether or not these resins actually form covalent bonds with the wood or if it's just different adhesive interactions between the wood fibre," says Dr Philbrook. "It's believed covalent bonds would result in stronger strength properties but so far no one has been able to determine whether or not these resins actually form co-valent bonds with the wood. So, part of my study was looking at these amino resins to see if they can form covalent bonds with the cellulose monomer unit.

"I should point out that the cellulose monomer unit is not wood itself but the functional group that would react with the resin if these co-valent bonds were forming. So, using the same NMR techniques we've shown that co valent bonds do form with the cellulose monomer unit. That gives us the green light to undertake further investigations. Now we need to demonstrate that it's happening with the actual wood fibre. If we can demonstrate that then we need to explore processes to ensure that when you press boards these bonds are forming."

From resin chemistry to wood composites

Now that Dr Philbrook has developed techniques for measuring bonds in the resin she's moving into areas somewhat unfamiliar for most research chemists – manufacturing her own test boards and measuring their physical properties.

"So, the idea is to make mini boards for testing," she explains. "We can measure the board's physical



Possible products from melamine-urea-formaldehyde reactions: methylene linked co-polymers (left) and dimethylene-ether linked co-polymers.

properties and then grind up little pieces of board and test them using NMR spectroscopy to see what type of bonds are found in the resin. We can then correlate the resin chemistry with the resulting physical properties.

"So, maybe we'd have one resin that formed covalent bonds and another that didn't. We'd then determine which resin gives you better physical properties. This helps us decide whether it's worth jumping through hoops to achieve certain types of bonds by understanding that some provide additional strength or water resistance or a whole variety of physical properties.

"With advice from Orica the RSC workshop has designed a test system for making mini MDF boards. I'm making resins using Orica's recipes and using the hot press in the Department of Engineering to produce the boards. So far I've demonstrated that we're getting similar strength properties to the commercial products. This means the test system works and we're now ready to start testing some new monomers. Though there's a lot to figure out along the way.

"So, say for example, you have a new compound that looks like being a promising new ingredient for the wood resin. Next you have work out how much you put in and how you'll treat the resin. There are endless different temperatures and process conditions you could choose.

"I've found some compounds that form co-polymers more readily with urea than melamine so we'd like to see if they are going to give us better resulting physical properties.

"Melamine is much more expensive than urea but melamine gives water resistance because of its chemical structure. So, if I've made water resistance molecules or hydrophobic compounds that we're testing with urea and formaldehyde, maybe instead of using 30% melamine I could use 2% of one of my additives and get better performance."

Dr Philbrook is happy to acknowledge that she's on a steep learning curve when it comes to materials testing. She also believes this is a productive partnership between industry and research.

"It's unusual for an organic chemist to take on the materials testing but I've found it to be a very rewarding challenge that has extended my understanding of wood composites and deepened my appreciation of the role of resin chemistry.

"Orica has been very supportive of the research, and very happy with what's been achieved so far. It's a good partnership because we have the scientific and analytical resources here at ANU that simply don't exist in most companies. It will be interesting to see what comes out of this partnership in the coming years."

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