J. W. GOTTSTEIN MEMORIAL TRUST FUND

The National Educational Trust of the Australian Forest Products Industries

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TRUST

ADVANCES IN PAPER COATING RESEARCH

CHRISTIAN KUGGE

2008 GOTTSTEIN FELLOWSHIP REPORT

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Joseph William Gottstein Memorial Trust Fund

The Joseph William Gottstein Memorial Trust Fund was established in 1971 as a national educational Trust for the benefit of Australia's forest products industries. The purpose of the fund is *"to create opportunities for selected persons to acquire knowledge which will promote the interests of Australian industries which use forest products for the production of sawn timber, plywood, composite wood, pulp and paper and similar derived products."*

Bill Gottstein was an outstanding forest products research scientist working with the Division of Forest Products of the Commonwealth Scientific Industrial Research Organization (CSIRO) when tragically he was killed in 1971 photographing a tree-felling operation in New Guinea. He was held in such high esteem by the industry that he had assisted for many years that substantial financial support to establish an Educational Trust Fund to perpetuate his name was promptly forthcoming.

The Trust's major forms of activity are:

1. Fellowships and Awards - each year applications are invited from eligible candidates to submit a study programme in an area considered of benefit to the Australian forestry and forest industries. Study tours undertaken by Fellows have usually been to overseas countries but several have been within Australia. Fellows are obliged to submit reports on completion of their programme. These are then distributed to industry if appropriate. Skill Advancement Awards recognise the potential of persons working in the industry to improve their work skills and so advance their career prospects. It takes the form of a monetary grant.

2. Seminars - the information gained by Fellows is often best disseminated by seminars as well as through the written reports.

3. Wood Science Courses - at approximately two yearly intervals the Trust organises a week-long intensive course in wood science for executives and consultants in the Australian forest industries.

Further information may be obtained by writing to:
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Christian Kugge is a Research Scientist in the Advanced Biopolymers group in CSIRO Division of Materials Science and Engineering.

His research centres on the adding value to paper products through both conventional coating and barrier coating. He has responsibilities in the 5G coatings project.

Prior to joining CSIRO, Christian worked as a CRC post-doctoral fellow at the Australian National University, and as a R&D manager in the Australian coating industry.

Christian has a PhD from the Royal Institute of Technology in Sweden and a M.Sc. in Chemistry from the Mid Sweden University.

Executive Summary

This report summarises the findings of visits to a number of research institutions in North America including the Nano Science and Technology Institute (NSTI), the Nanotech conference in Boston and the 10^{th} TAPPI Advanced Coating Fundamentals Symposium held in Montreal as well as an experimental study in Sweden.

The work presented at the NSTI Nanotech conference covered many different research disciplines. Three presentations relevant to paper, coating and wood applications were discussed in terms of synthesis of chitosan and starch nanoparticles and the designing of superhydrophobic surfaces.

The research discussed at the TAPPI Advanced Coating Fundamentals Symposium addressed all aspects of paper coating chemistry and applications. The symposium was well represented by the traditional schools from Scandinavia and North America which gave an up-to-date view of their current research. Each school is continuing in their domain of interest although researchers at Omya (a pigment supplier) are presenting a slightly new direction of research with a focus on moisture pickup in calcium carbonate and its role on surface and pores structure. Replacing latex by starch is still an area of interest.

An atomic force microscope – confocal Raman spectrometer – scanning near optical microscope (AFM-CRS-SNOM) located at the Institute for Surface Chemistry in Stockholm, Sweden was assessed for its ability to analyse paper coatings and wood samples. Starch and latex binders in paper coatings were successfully detected by a 785 nm laser. The finding of starch in an aggregated form in the coating layer was unexpected. Wood adhesives were also detected in wood samples placed under water, to avoid damaging the wood.

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Introduction

Paper, commonly used in everyday life, is a complex man-made material, requiring a rather fine arrangement of cellulose fibres to occur at rapid production speeds. It is made more complex by the addition of a coating layer. The paper is coated for several reasons, such as improving print quality, printability, brightness and opacity.

A typical 'wet' paper coating suspension consists mainly of three components, a mineral pigment such as calcium carbonate or clay, a water-soluble thickener or co-binder such as carboxymethyl cellulose or starch, and a binder such as styrene butadiene or styrene acrylate latex. A range of other additives such as lubricants, defoamers and brightening agents are used in small quantities to improve the overall runnability and end-use properties. Variations in the coating composition will yield different consolidation behaviour and thus different end-use properties. One parameter varied in this study has been the latex content as parts of the latex binder were replaced by starch. The aim with the experimental study performed at the Institute for Surface Chemistry was two-fold, a) investigate latex and starch distribution within the coating layer and b) investigate wood, wood adhesive and the usefulness of a combined atomic force microscope – confocal Raman spectrometer – scanning near field optical microscope (AFM-CRS-SNOM) analysing those kinds of samples.

The Australian industry mostly produces traditional coating grades for packaging using linerboard of 140-200 g/m^2 grammage. Most known products are the cereal box and the box for carrying a six-pack of drinks. More unknown is the barrier coating for water and water vapour as the coating is transparent and often applied on the inside of a box. Typical barrier coating products are packaging of frozen food and dry cookies. The main difference between a conventional paper coating and a barrier coating is that the barrier coating contains much less mineral pigment (being transparent) and more latex and/or other water-repelling polymers. The advantage is

that both coatings can be applied by traditional coating techniques such as blade, rod or airknife.
The coated board manufactured in Australia can be found in an endless range of products used everyday from foodstuffs to cosmetics, wines to hardware. They tend not to be used in the highest value packaging where imported grades mainly dominate because of a superior base sheet. In case of cigarettes packaging, the market would be interested in a method for counterfeiting. In long-term thinking the Australian industry would benefit if this type of packaging with novel solutions (niche products) were produced although it need substantial investment in both research and equipment.

Materials and methods

Pigments

Pigments have been used in paper coatings since the 1870s. Kaolin clay, a platy particle and a relatively inexpensive material, was the first in use. Clay coatings provide a white (or near white) glossy surface and a good area coverage. This structure is not very porous after calendering giving poor ink absorption. This was addressed in the 1960s by introducing a more spherical pigment like ground calcium carbonate (GCC). Nowadays precipitated calcium carbonate (PCC) is attractive as the opportunity to engineer and to fine-tune particle shape opens new avenues of niche products. This development has to some extent been slow as the costs of these pigments are higher than conventional GCC. Today's industrial formulations often combine three types of pigments, clay, GCC and TiO_2 (anatase or rutile) to optimise performance and appearance. TiO_2 is added for its high refractive index contributing to an improved opacity and whiteness.

Binders

Latex binder was introduced to the paper industry in the late 1940s by the DOW chemical company. At the time the binders were called adhesives as the function is to adhere to the pigment surface and to the paper surface creating a strong surface that can withstand printing operations. The first binders were styrene-butadiene emulsions with a particle size of about 100-150 nm. These binders are still in use due to their good performance. The binders are 50% solids and the glass transition temperature (T_g) used in industry typically range from -7 to 28 °C depending on the ratio of styrene (high T_g) to butadiene (low T_g). Binders are often stabilised by both carboxylic groups and anionic surfactants as most pigments are stabilised by the negatively charged polyacrylic acid. Other common binders are styrene-acrylate and polyvinyl acetate.

As the styrene-butadiene binders have been used for over 6 decades they have been proven to be good product. However, in recent years increased awareness of environmentally friendly products in line with global warming has put pressure on the paper industry to not use products derived from the oil industry. This is the reason for studying conventional paper coatings in which parts of the latex has been replaced by a starch binder. We all know that starch can be sticky as for example freshly cooked pasta is quite sticky. The binding strength of starch is not as high as for synthetic binders such as styrene-butadiene, although other qualities such as ink spreading and print quality may improve.

DOW coater

Linerboard samples analysed by the combined AFM-CRS-SNOM instrument were coated using CSIRO's DOW coater displayed in Figure 1. The coater was utilised in a rod configuration meaning that a rotating rod is metering off the coating excess. The coating speed was 20 m/min with both IR dryers set at maximum power and the oven at 230 °C. The coat weight applied is typically around 10-15 g/m^2.

Figure 1. CSIRO's laboratory (DOW) coater

The samples coated and analysed were based on clay, calcium carbonate and latex binder. The control sample (sample 1) contains 14 parts per hundred (pph) latex styrene-butadiene binder on dry pigment. In three other samples the latex were replaced with starch as of sample 2; 12 parts latex and 2 parts starch, sample 3; 10 parts latex and 4 parts starch, and sample 4; 6 parts latex and 8 parts starch.

Starch from Roquette was cooked by conventional methods for 20 minutes at 90 °C and immediately added to the coating suspension during stirring.

AFM-CRS-SNOM instrument

Confocal Raman microscopy offers the possibility to acquire chemical information of a sample with a resolution down to the optical diffraction limit (~ 200 nm). This method allows analysing the local distribution of different components within a sample in ambient conditions and without requiring any special sample preparation.

Confocal Raman microscopy combines two different techniques, namely confocal microscopy and Raman spectrometry. In confocal microscopy a small pinhole sitting in conjunction to the focus of the objective allows only the light coming from the focal plane to pass into the detector. This focal plane can be moved a few micrometers into the sample which gives the opportunity of gaining 3d information. Raman spectroscopy uses the effect of inelastic scattering of monochromatic light on molecules. Raman spectra show in addition the elastic scattered light energy-shifted peaks which are characteristic for the scattering molecule and result from the excitation of vibrations in the molecule. Performing Raman microscopy, a Raman spectrum is recorded on every image pixel. When analysing dedicated peaks of the spectra, a variety of images can be generated using only a single set of data. Post-measuring data evaluation makes identification of different components in the sample possible.

The measurements were performed with a WITec alpha300 (see Figure 2) system which has a lateral resolution of 200 nm and a vertical resolution of 500 nm. The scan range for one image was 50x50 μm or 20x50 μm and 1024x128 pixels using a 785 nm laser for excitation. The integration time per Raman spectra was 110 ms.

Figure 2. YKI's AFM-CRS-SNOM (WITec) instrument

Both paper and wood samples were microtomed and analysed in the *z*-direction (cross section) by confocal Raman spectroscopy. The top surface was analysed by AFM. To be able to use the SNOM part of the instrument samples need to be transparent.

Results and Discussion

Wood samples were glued together by an adhesive and microtomed across the interface. The objective was to analyse adhesives penetration into the wood fibres.

One found that both the 532 nm and the 785 nm laser was too powerful to use in air as the lasers burned a hole in the wood but not the adhesive as shown in Figure 3. The wood sample and the 785 nm laser were later used successfully under water which prevents damaging the sample.

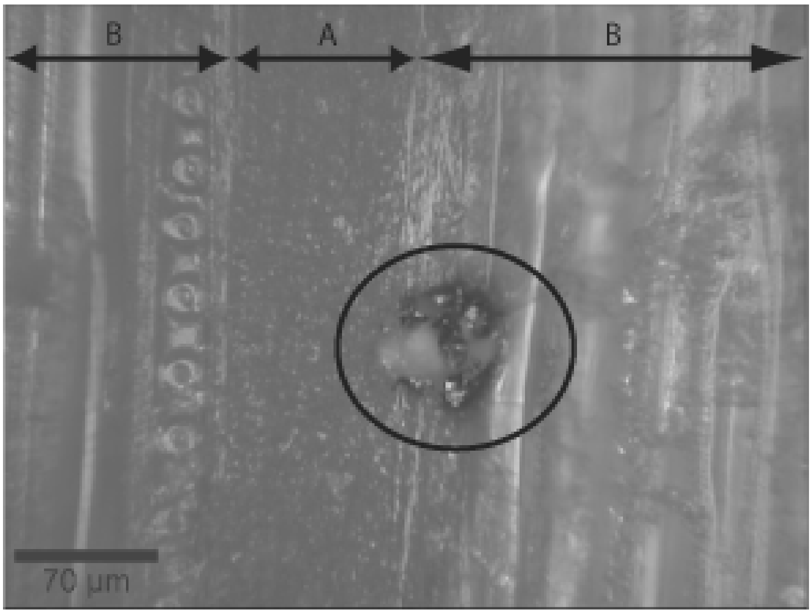

Figure 3. Optical image of the wood (B) / adhesive (A) interface. The circle indicates a burned area caused by the laser.

The first step is to analyse the wood and adhesive separately creating a reference spectrum for each material in order to map the intensity over a specific area across the wood/adhesive interface.

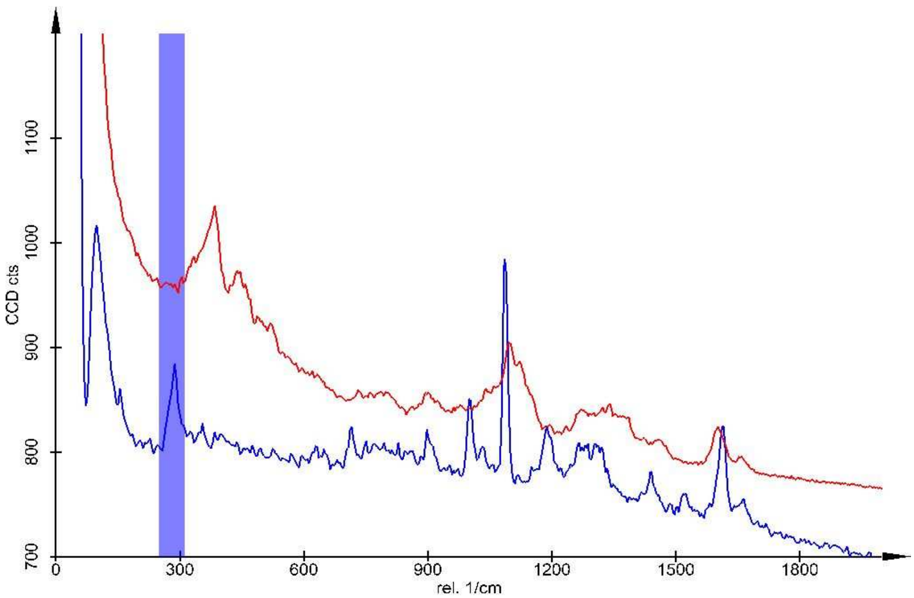

Figure 4. Raman spectra of wood (red) and adhesive (blue).

Figure 4 shows Raman spectra's (fingerprints) of wood (radiata pine) and adhesive. The marked area at 300 cm^{-1} differentiates adhesive from wood. The wood peak at approximately 390 cm^{-1} and the adhesive peak at approximately 300 cm^{-1} are later used for analysing large areas. Figure 5 displays good repeatability of the adhesive.

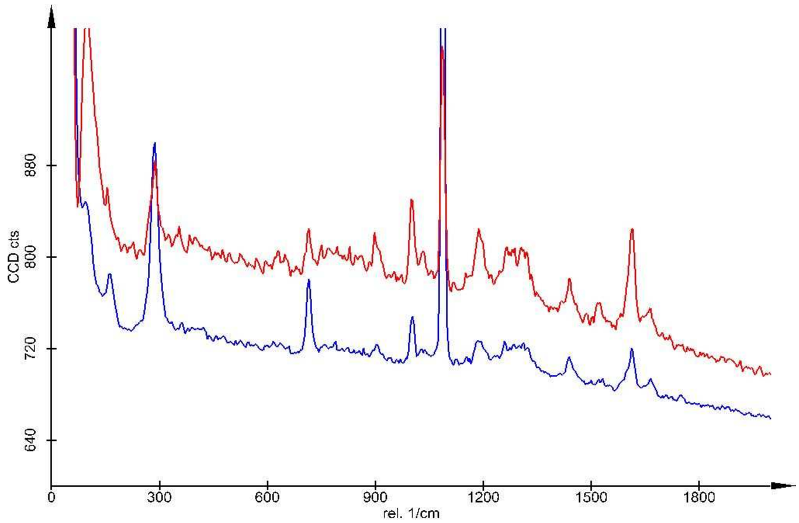

Figure 5. Raman spectra of two adhesive scans indicating good repeatability.

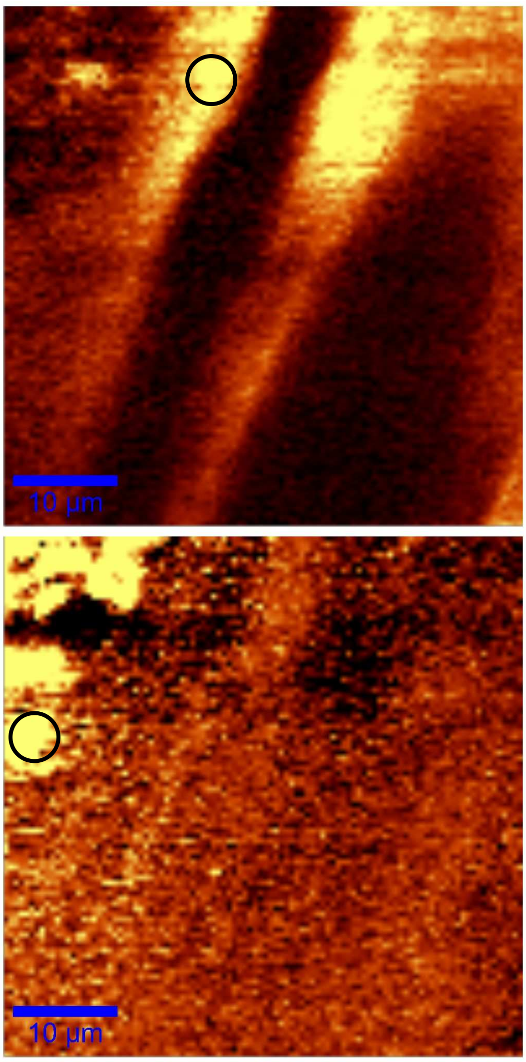

Figure 6. Top: Raman intensity map (50 x 50 µm) of wood at the interface of wood and adhesive. Bottom: Raman intensity map of adhesive at the interface of wood and adhesive. Raman spectrums of circular areas are shown in Figure 7.

Figure 6 show high intensity of adhesive in the upper left corner and high intensity of wood right next to the adhesive. As the intensity of the adhesive is on the same level as normal noise where the intensity for wood is high one can suggest that the adhesive does not penetrate the wood fibre.

The map of wood intensity shows a dark area in the middle which is likely to be due to surface roughness, meaning that the laser is out of focus. Analysing this surface with an even more roughness-sensitive method such as AFM was not possible.

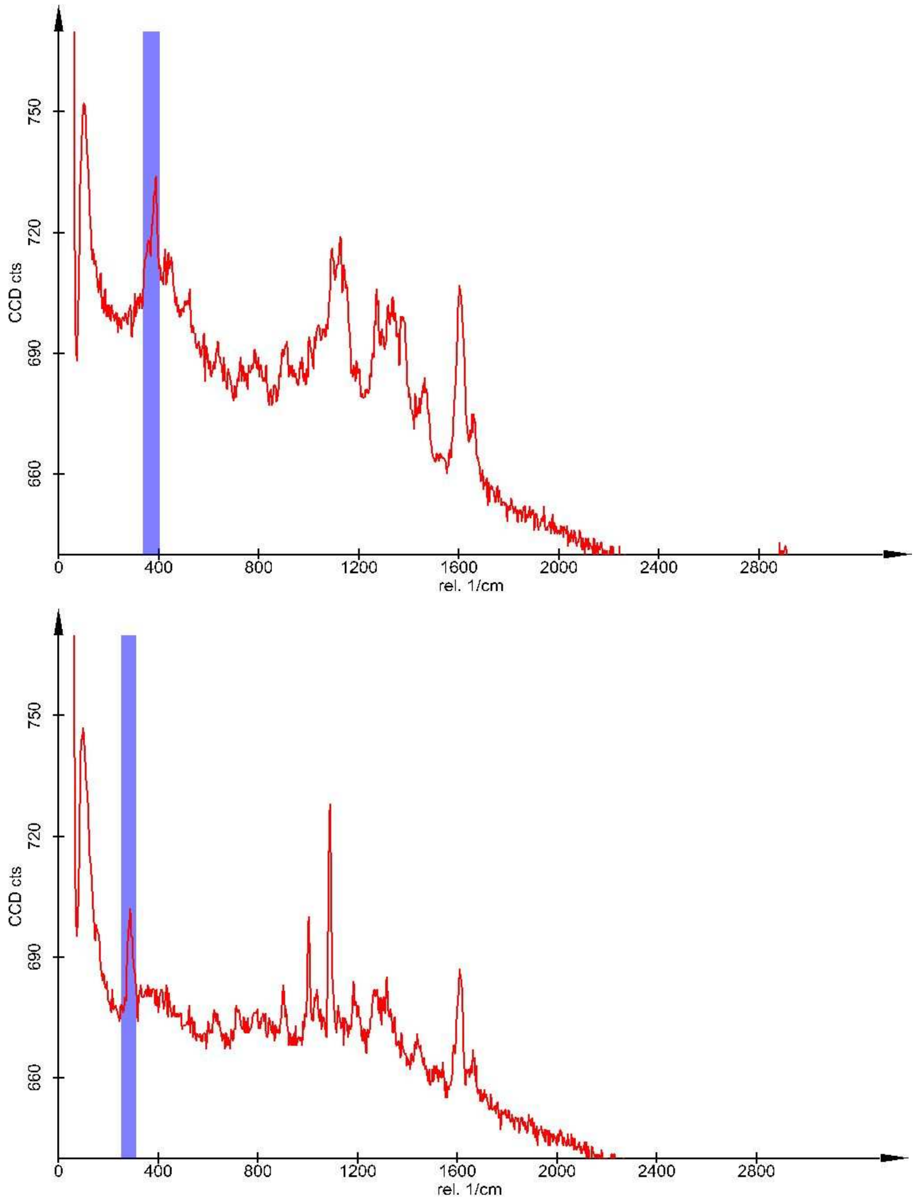

Figure 7. Raman spectra for the high intensity areas circled in Figure 6.

Paper coated samples were analysed in air using the same 785 nm laser. Starch and latex reference spectra are shown in Figure 8.

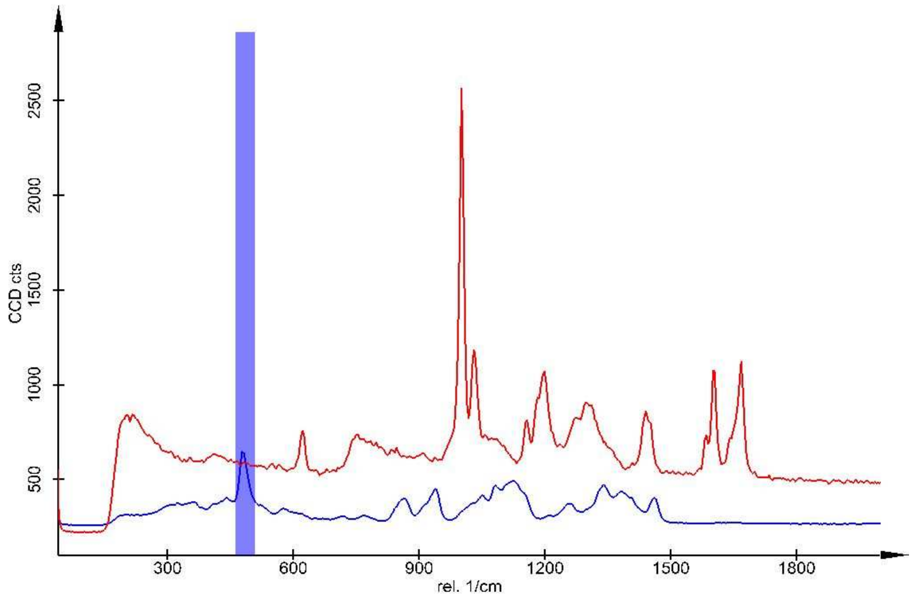

Figure 8. Raman spectrum for starch (bottom) and latex (top).

The marked peak at approximately 480 cm^{-1} (starch) and the large peak at approximately 1000 cm^{-1} (latex) are used for further analysing of starch and latex in the intensity area maps below.

An example of cross section maps of sample 4 (6 parts latex and 8 parts starch) are shown in Figure 9.

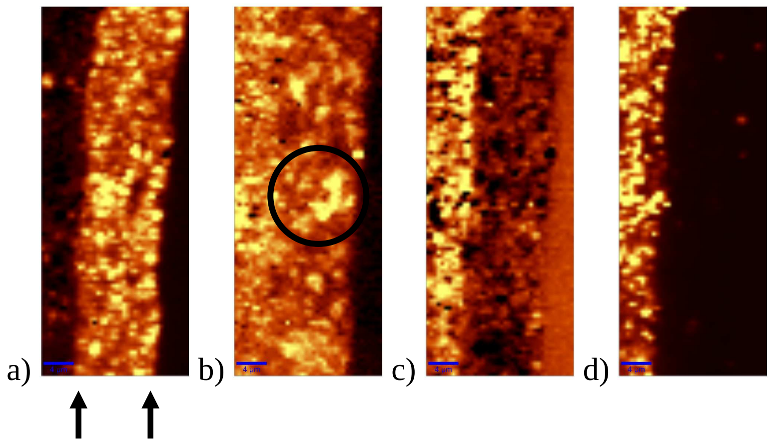

Figure 9. Raman intensity maps of a) $CaCO_3$, b) starch, c) latex and d) TiO_2. Left arrow indicates the pre-coat / top-coat interface and the right arrow indicate the top-coat / air interface.

Figure 9a shows that there is no $CaCO_3$ in the pre-coat and some $CaCO_3$ is present in the top-coat. One can determine starch in the top-coat being more distinctive as a large aggregate (≈5 µm) of starch is circled in Figure 9b. This type of starch aggregate was repeatedly found in this sample containing 8 parts of starch but not shown in samples containing less starch. It appears to be starch in the pre-coat but this was falsified as the peak of TiO_2 overlap the peak of starch. Figure 9c shows the latex intensity to be moderate in the top-coat and more concentrated in the pre-coat.

Some latex signal is detected in air as shown by a weak brown colour although this is considered to be noise. Figure 9d show that TiO_2 is present in the pre-coat and not in the top-coat.

The other technique used in this study is the AFM. Figure 10 show typical AFM phase and topography images for paper coating.

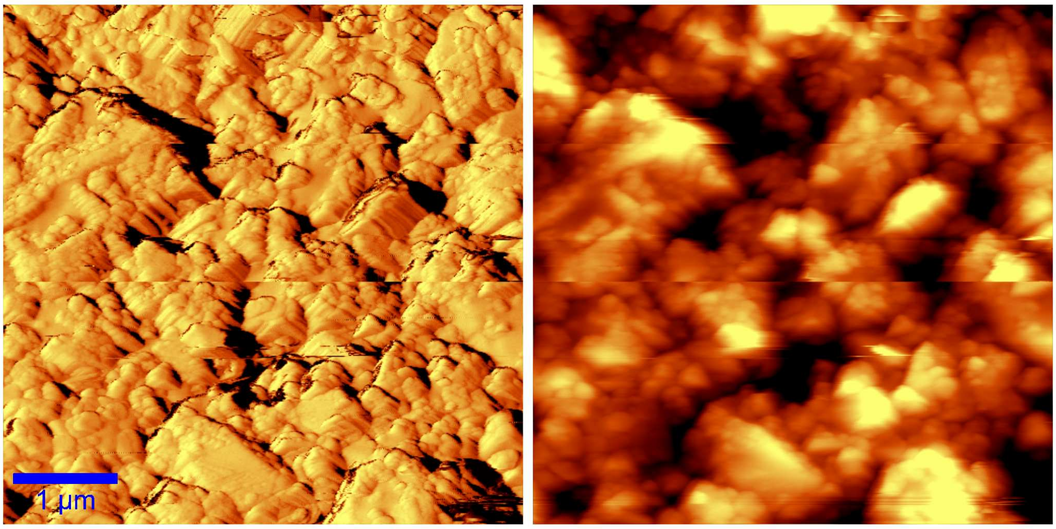

Figure 10. A 5x5 µm AFM phase (left) and topography (right) image of coated paper.

Conclusions

Both Raman and AFM analysis are powerful tools for the Australian paper industry in terms of optimising performance, troubleshooting and developing new products. For the wood industry the Raman spectroscopy would be useful in determining the type of adhesive used in different products.

Visiting institutions and conferences in North America as well as carrying out an experimental study and evaluating a new instrument in Sweden have been very fruitful. I believe the Australian paper and wood industry will see the benefits of this kind of analysis in their development program. Notes from the conferences and visits are given in Appendix A and B.

Acknowledgments

Dr. Birgit Brandner and Assoc. Prof. Agne Swerin at the Institute for Surface Chemistry (YKI) are acknowledged for their great hands-on support and discussions during this experimental study.

APPENDIX A – Notes from conferences

NSTI Nanotech –The Nanotechnology Conference and Trade Show
(http://www.nsti.org/Nanotech2008/)

Located in the heart of Boston this conference attracted a large number of researchers in the nanotechnology field. The Nano Science and Technology Institute (NSTI) organise the annual Nanotech conference and trade show, the most comprehensive international nanotechnology convention in the world. This year's event was held jointly with CleanTechnology and TechConnectSummit.

The conference started with a free of charge one-day course on various subjects. I attended the course on carbon nanotubes held by Prof. Wolfgang Bacsa (http://wsb000.googlepages.com/). The course covered all aspects of carbon nanotubes synthesis and applications. This has been useful in planning future niche products for the Australian paper industry involving cellulose, carbon nanotubes and ionic liquids.

During the conference three presentations relevant to paper, coating and wood applications were discussed in terms of synthesis of chitosan and starch nanoparticles and the designing of superhydrophobic surfaces. There is a group in Asia which produce starch nanoparticles down to 200 nm which is very interesting in terms of replacing latex binder in paper coatings. Adding starch nanoparticles would likely provide a more uniform starch distribution, avoiding starch aggregates as shown in Figure 9. The main benefit of this would be a stronger coating, as the starch would be a more effective binder. A similar case is possible with chitosan nano particles as a group in Western Australia has the potential to scale-up their production of chitosan nanoparticles. A group at MIT presented their recent work on superoleophobic surfaces (Science 318, 1618 (2007)) which has similarities to superhydrophobic surfaces. This is interesting science for future research on products such as grease-proof paper and water-repelling products for the Australian wood and paper industry.

TAPPI Advanced Coating Fundamentals Symposium

Located in the heart of Montreal this conference attracted both local researchers and international visitors mainly from Scandinavia.

TAPPI was founded in 1915 and is the leading association for the worldwide pulp, paper, packaging, and converting industries. TAPPI organise this biannual conference traditionally in different locations in North America but in 2010 Europe will host this event for the second time in order to attract more attendees.

The conference started off with a poster session followed by speakers. Keynote speaker Prof. Robert Pelton talked about the bioactive paper network called Sentinel which is a large consortium between industry (25% funding) and academia in Canada. A major area lies within detecting, repelling and deactivating waterborne bacteria. One great challenge is to create a colour change when capturing bacteria. Other key presenters were Prof. Pat Gane (Helsinki University of Technology and Omya), Dr. Göran Ström (STFI), Prof. Lars Järnström (Karlstad University), Prof. Douglas Bousfield (University of Maine) and Assoc. Prof. Agne Swerin (YKI).

Prof. Pat Gane presented his work on pigment moisture uptake by hygroscopic dispersing agents and its effect on surface and pores structure. Dr. Göran Ström introduced their MicroDAT (micro Drop Absorption Tester). Their device can deliver 320 pL drop volumes at a speed of 1.4 m/s which simulates inkjet printing operations. A high speed camera takes an image of the drop every 8 ms. Prof. Lars Järnström continues to work with barrier coatings in collaboration with the National University of Singapore. In this project they study latex dispersions as carriers for glucose oxidase oxygen scavenging systems. They are using enzymes in latex barrier coatings in order to create active oxygen absorbing packaging materials. Prof. Douglas Bousfield demonstrated a new test method and model for short-time (<5 ms) dewatering in collaboration with BASF. Assoc. Prof. Agne Swerin presented his work on silica pigments for inkjet printing. Different types of silica and silica/clay blends were studied in terms absorption and porosity effects on printing performance. Inkjet penetration into the coating was analysed by confocal Raman spectroscopy. The binder used was polyvinyl alcohol and it appears to be an optimum dosage of binder to maximise print quality in terms of colour gamut. Experimental grades of silica/clay blends (provided by Eka Chemicals) have a great potential to improve print quality.

APPENDIX B – Notes from organisational visits

The University of Maine (9 June 2008)

Key contact: Prof. Douglas Bousfield

The surface treatment program at the University of Maine (Chemical Engineering) is a rather unique institution as they attract funding from industry world-wide. Approximately 50% of the funding is external. Most of their current research lies within coating modelling, rheology, structure and ink settling. The group use a confocal laser microscope in many aspects of their research. They have a very strong link to the Laboratory for Surface Science and Technology (LASST) located next door. LASST recently obtained a new state-of-the-art SEM with the capability to cut samples inside the SEM.

Coating equipment consists of a 300 mm pilot paper machine, equipped with Gate-roll size-press; a CLC coater and a laboratory super- and soft-calenders. All this is part of the Pulp and Paper Process Development Centre directed by Mr Michael Bilodeau.

An area of collaboration with Prof. Douglas Bousfield was established. We expect to publish jointly in the near future. A long term collaboration with this hub of coating technology and knowledge would benefit the Australian industry.

Cerealus (9 June 2008)

Key contact: Mr. Tony Jabar

Cerealus is a spin-off company from the University of Maine who develops new barrier coatings and in particular coatings for grease proof paper. The barrier coating is based on corn and is very promising as a replacement for current non-environmentally friendly fluorocarbon treatment. Discussions were held on a future collaboration which could benefit the Australian industry.

PAPRICAN (13 June 2008)

Key contact: Dr. David Vidal

PAPRICAN, now known as the FPInnovations PAPRICAN, is the largest pulp and paper research organisation in Canada as well as publisher of the Journal of Pulp and Paper Science. The organisation is mostly funded by the industry with more than 30 member companies. Researchers at PAPRICAN have a strong background of modelling, numerical simulation of coatings and ink/coating interactions. A few weeks before my visit they received their own supercomputer. They are also in a complete upgrade phase of many instruments as well as extending their instrument park.

PAPRICAN have one of the first patents (1980's) on making nanocellulose and their current equipment can make 2-5 kg/day. This equipment will be upgraded to a much larger scale in the near future. Xuequan (Shirley) Tan is a postdoc working in this area and she is concentrating on finding new applications for nanocellulose. Nanocellulose has been recognised as a future direction for wood scientists creating novel applications and niche products.

OrganoClick (3 July 2008)

Key contact: Mr. Mårten Hellberg

OrganoClick has been appointed as the most promising Swedish start-up company 2008 as they have developed a number of improved paper based materials and chemical formulations used to enhance the performance of paper and packaging products.

After a meeting with Mr. Mårten Hellberg (CEO), Dr. Armando Córdova (Assoc. Prof. in organic chemistry at Stockholm University) and Dr. Joseph Samec (Project manager) we find mutual interests in barrier coating performance and a future collaboration is currently being discussed.

APPENDIX C – Itinerary

Date	Venue	Visit
Friday May 30		Depart Australia
Sunday June 1	Boston	NSTI Nanotech conference
Friday June 6	Orono	University of Maine
Monday June 9	Orono	Cerealus Holdings
Tuesday June 10	Montreal	TAPPI Coating Conference
Friday June 13	Montreal	PAPRICAN
Monday June 23 – July 3	Stockholm	Institute for Surface Chemistry
Thursday July 3	Stockholm	Organoclick AB
Thursday August 28		Return to Australia

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