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**MAGNETIC RESONANCE
SPECTROSCOPY AND IMAGING
AS APPLIED TO THE FORESTRY SECTOR**



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by

Albert Roger Meder

Massey University

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ABSTRACT

The forestry sector in New Zealand ranks as the third largest export earner. The individual industries within the forestry sector have, in some cases, grown up on the basis of institutionalised knowledge, sometimes without a full understanding of the underlying fundamental physico-chemical relationships and the changes that occur during wood material processing. At the same time the commercial pressures of operating within the forestry sector have resulted in demand for more uniform, high quality, fit-for-purpose product, faster throughput and less downgrade from what is becoming a lower quality feedstock as harvest ages decline. In the 21st century, the forestry sector is being transformed into an “engineered ligno-cellulosic materials processor” and this in turn is requiring a more sophisticated knowledge of the material feedstock and the processes involved in wood products manufacture.

The aim of this work was to use magnetic resonance techniques to explore aspects of ligno-cellulosic materials processing at points along the value-added process chain, namely drying, chemical modification (preservation) and re-engineering (gluing) of wood products.

Magnetic resonance mini-imaging studies of the water transport during the drying of radiata pine boards have shown differences in the directional movement of water within the wood structure. These effects show a dependence on the surface area to volume ratio of timber and the orientation of the annual rings with respect to the larger drying face. Narrow, flat-sawn boards exhibit anomalous drying behaviour in terms of water mass transport, whereas thicker boards display more conventional core-shell drying behaviour. These restrictions to flow have been further investigated using diffusion tensor imaging *via* a modified pulsed field gradient spin-echo sequence to elucidate the nature of anisotropic diffusion in wood. The direction of least restriction to self-diffusion is in the longitudinal direction, as would be expected with it being the direction of active transport within a tree stem, whereas the direction of greatest restriction to self-diffusion is in the radial direction, with the higher density latewood acting as a barrier.

Preservation of radiata pine sapwood with novel boron-based preservatives has been investigated using magnetic resonance imaging to determine the penetration and retention of the incipient compounds. An apparent anomaly in retention for trimethylborate-treated *Pinus radiata* sapwood was investigated by ^{11}B MAS NMR spectroscopy of excised sections of latewood and earlywood, which showed hydrolytic decomposition of trimethyl borate to form boric acid. The rate of hydrolysis of trimethylborate was monitored by ^{11}B MAS NMR spectroscopy and was shown to occur very rapidly in the latewood (within 24 hours), and over a longer time scale of several days in the earlywood. The resulting publication has reported some of the first published ^{11}B MRI images.

Magnetic resonance spectroscopy has provided (in conjunction with separate mass spectrometry studies) mechanistic evidence for the accelerated curing of phenol-resorcinol formaldehyde resols, using ammonia in combination with the conventional paraformaldehyde hardener - a process known as GreenWeld™. Carbon-13 and nitrogen-15 NMR spectroscopy has shown evidence of both benzylamine and aniline type bridging structures formed during cure, compared to only methylene structures being formed under conventional curing conditions.

Poly(vinyl acetate) emulsion polymer adhesive has also been examined using NMR spectroscopic methods, with particular focus on the effect of addition of aluminium chloride, which is often commercially added to PVAc formulations as a crosslinking agent. Multinuclear magnetic resonance spectra obtained during the cure of AlCl_3 modified PVAc adhesive, shows a low frequency ^{27}Al shift of *ca.* 3 ppm suggesting a local change in environment as the aluminium changes from a solvated to a covalently bonded octahedral environment.

Finally, as a preliminary study, a new device for measuring uniaxial extension of visco-elastic solids was trialled on poly(vinyl acetate) hydrogels to study the effect of addition of aluminium chloride on the visco-elastic properties of the adhesive. A similar, manually operated device was used to obtain NMR spectroscopic data during compression of the gel. These studies have shown that addition of aluminium chloride as a crosslinking agent, in fact produces a cured adhesive with fewer crosslinks than the corresponding unmodified adhesive, but with increased resistance to shear-induced creep.

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I have learned more from my mistakes than from my successes.

Sir Humphrey Davy

During the period of research that has led to the completion of this thesis I have certainly learned a great deal about magnetic resonance imaging and about myself. There have been a number of “practical lessons” learnt. None of it however would have been possible without the support, encouragement and assistance from a number of people.

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To my mother, Betty and the memory of Adam, I say to you all ...

Kia kaha, kia tara

Have strength, have courage

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ABBREVIATIONS USED

B_0	external (static) magnetic field
B_1, B_2	applied magnetic fields
cm	centimetre
COSY	(^1H - ^1H) correlation spectroscopy
CP/MAS	cross polarisation - magic angle spinning
CPMG	Carr-Purcell-Meiboom-Gill
CSA	chemical shift anisotropy
D	diffusion coefficient
dB	decibel
DIFFSE	diffusion spin echo (pulse sequence)
DCM	dichloromethane (CH_2Cl_2)
DEPT	distortionless enhancement by polarisation transfer (pulse sequence)
FID	free induction decay
FOV	field of view
FT	Fourier transform
G	Gauss = 10^{-4} Tesla
G/cm	Gauss per centimetre (1 G/cm = 10 mT/m)
G_e	field gradient (applied in direction e)
h	Planck's constant (6.625×10^{-34} J s)
\hbar	$h/2\pi$
HMMM	hexamethylmethyloimelamine ($\text{C}_3\text{N}_3(\text{N}(\text{OH})_2)_3$)
HMTA	hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$)
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum correlation
HSQC	heteronuclear single quantum correlation
HPDEC	high power decoupling (MAS pulse sequence)
I, S	nuclear spin quantum number
k_B	Boltzman constant (1.38×10^{-23} J K^{-1})
kHz	kilohertz
L	angular momentum
MAS	magic angle spinning

MC	moisture content
MHz	megahertz
ML	middle lamella
mM	millimolar (concentration)
mm	millimetre
MRI	magnetic resonance imaging
MSME	multi slice, multi echo (imaging pulse sequence)
m_x, m_y, m_z	magnetisation in x, y, z axes
M_0	bulk magnetisation
N_A	Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$)
N-MAM	N-methylolacrylamide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
od	oven dry
PCA	principal components analysis
PFGSE	pulsed field gradient spin echo
PLS	projection to latent structures (regression)
ppm	parts per million
PVAc	poly(vinyl acetate)
PVOH	poly(vinyl alcohol)
QCC	quadrupolar coupling constant
r	radius
rf	radio frequency
R	universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
S/N	signal-to-noise (ratio)
T	temperature or Tesla (magnetic flux density)
T_1	spin-lattice or longitudinal relaxation constant
T_2	spin-spin or transverse relaxation constant
T_E	echo time
T_R	repetition time
TBTO	tributyltin oxide ($((\text{C}_4\text{H}_9)_3\text{Sn})_2\text{O}$)
THF	tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$)
TMB	trimethyl borate ($\text{B}(\text{OCH}_3)_3$)
TMS	tetramethylsilane ($(\text{CH}_3)_4\text{Si}$)

Δ	“big delta” – duration between gradient ramps in diffusion sequence
δ	“little delta” – duration of gradient ramp in diffusion sequence
θ, α_E	angle, Ernst angle
π	angle of tip in radians = 180° tip
$\pi/2$	angle of tip in radians = 90° tip
η	asymmetry parameter (NMR), intrinsic viscosity (rheology)
μ	magnetic dipole moment
σ	NMR chemical shift (ppm), stress (rheology)
ρ	density
ω_0	Larmor frequency (rad s^{-1})
ν	concentration (rheology)
ν_0	Larmor frequency (Hz)
ω_Q	quadrupole frequency (rad s^{-1})
ν_Q	quadrupole frequency (Hz)
ω_{rf}	excitation frequency
ϵ	strain
ψ	functionality of polymer crosslinks
τ	variable delay (NMR) or stress or torque (rheology)
γ	NMR gyromagnetic ratio ($\text{rad T}^{-1} \text{s}^{-1}$)
$\dot{\gamma}$	shear rate (rheology)
Ω	frequency of rotation of rheometer drive spindle (Hz)

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