Accessibility and reactivity of hydroxyl groups in wood

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To Improve Performance of Wood and Wood Composites:

Chemical modification of cell wall polymers

- What reactive chemical to use?
- How does the chemical get to a reactive site?
- How does it react?
- Where does it react?
- Does it improve properties?
- How/Why?
- What did you learn to improve the process?

Outline

Overview of wood modification

Penetration of reagent – accessibility/swelling

Differences between soft and hard woods

Distrubition of bonded chemical

Conclusions

Performance of Modified Wood

Dimensional stability – Due to the bulking effect of the bonded chemical or crosslinking.

Decay resistance – Due to change in configuration and conformation of polymer and moisture level too low to support fungal attack

Fire retardancy – Due to the chemistry of the bonded group (N, P)

Ultra violet resistance – Due to chemistry of the bonded group

Do of these properties depend on where bonding has taken place?

Dimensional stability – No - If bulking the cell wall back to its green dimension. - ? For cross linking.

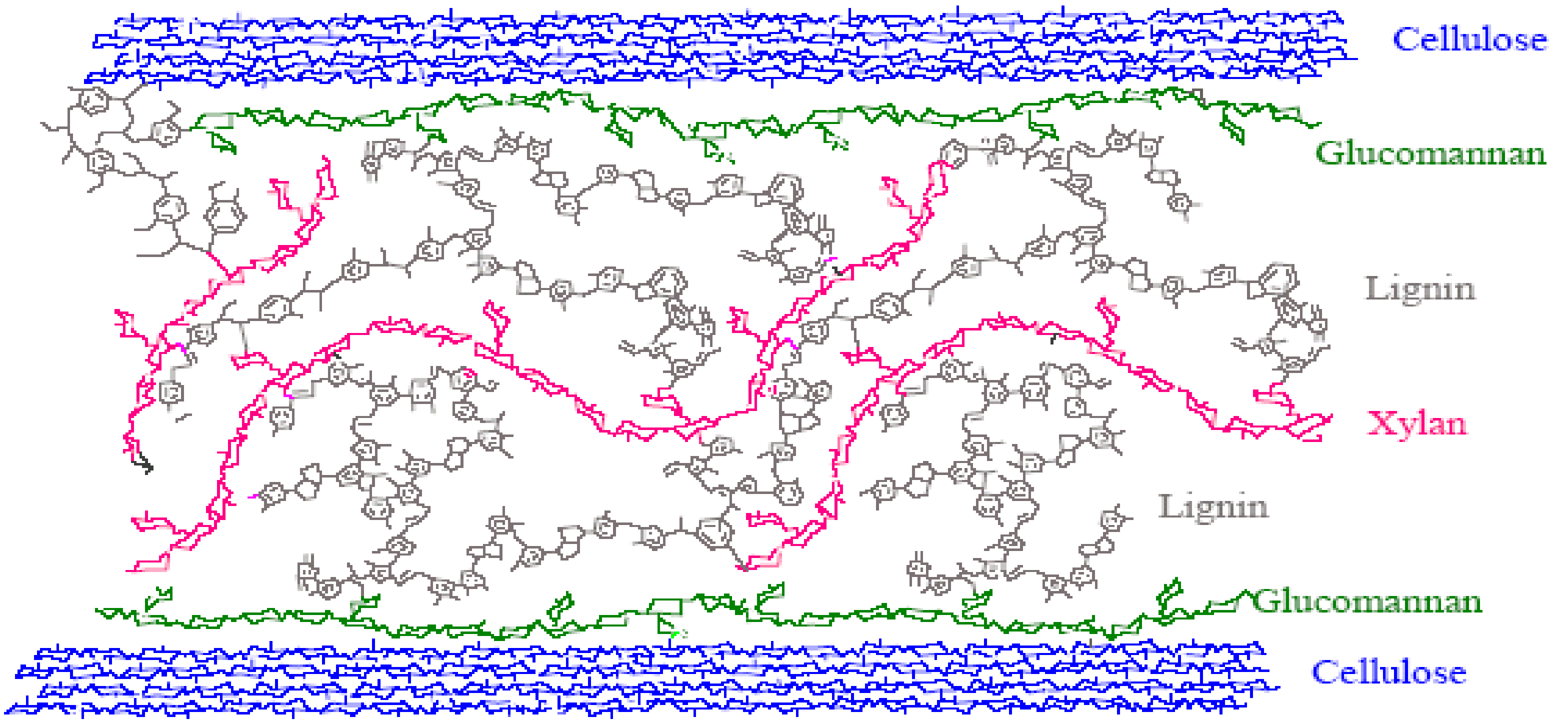
Biological resistance – Yes, mainly in the carbohydrate polymers – hemicelluloses.

Fire retardancy – No, but bonded chemical must be released.

Ultra violet resistance – Yes, stabilize lignin.

Cell Wall Crosssection (S_2 Layer)

Where are the hemicelluloses, cellulose and the lignin located in the wood cell wall?



Penetration – Accessibililty
Volumetric Swelling

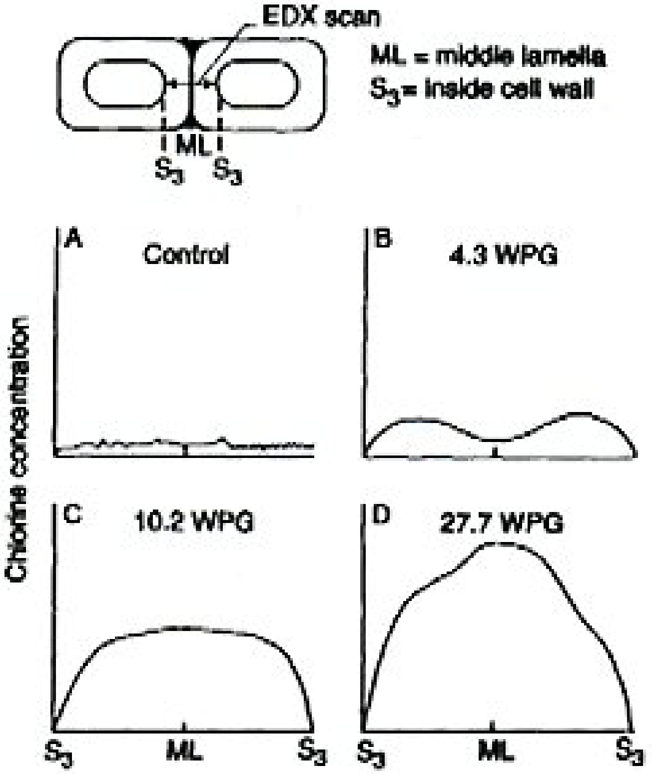
Southern Yellow Pine

Solvent	Swelling at 25°C 24 hrs	Swelling at 120°C 1 hour
Water	10.0	10
Acetic acid	8.8	11.1
Acetic anhydride	1.5	Reaction
Pyridine	11.3	13.1

Accessibility of cell wall polymers depends on swelling

In acetylation, acetic acid and pyridine are swelling agents not catalysts

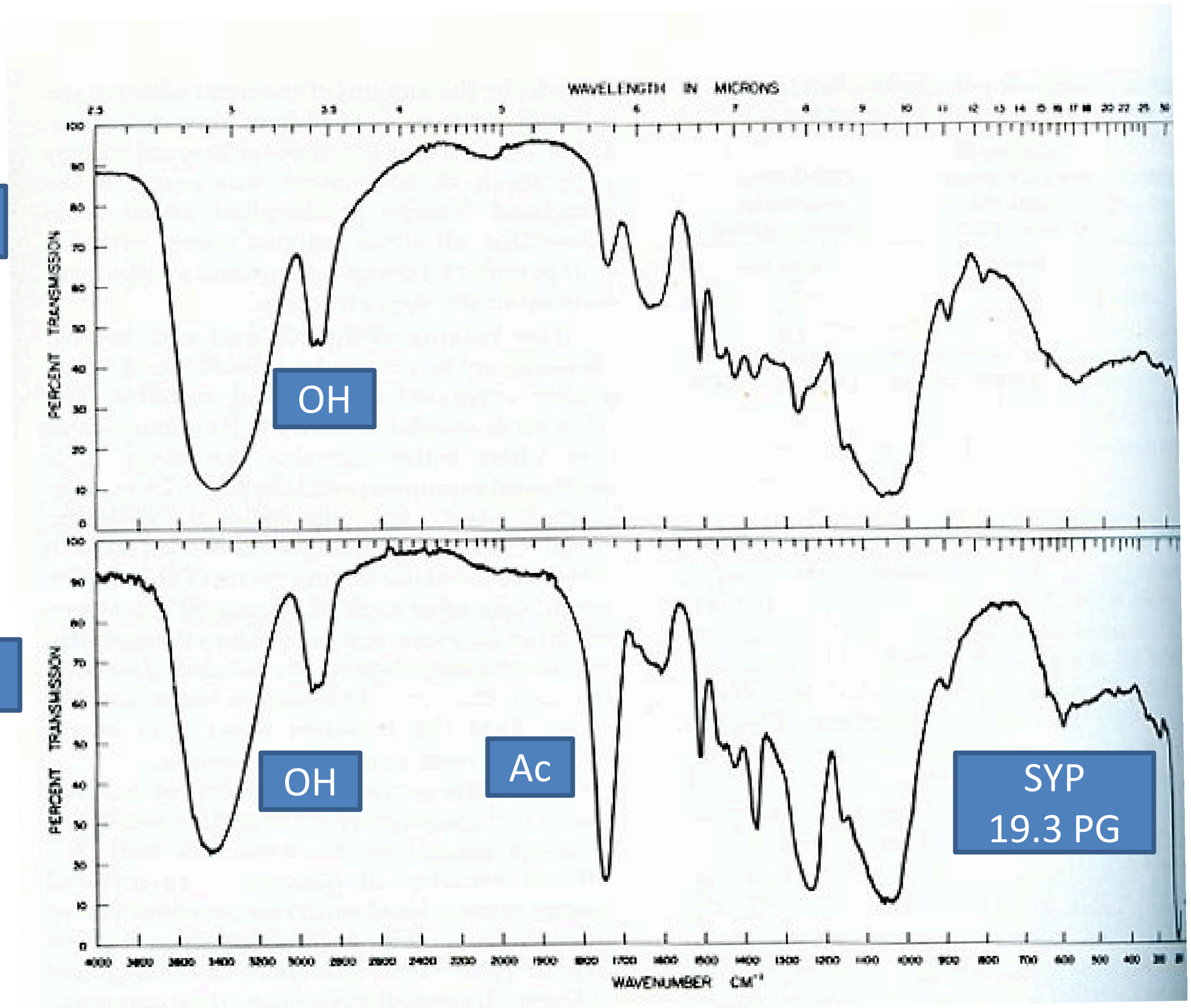
Penetration and Accessibility of Reaction site



Reaction of southern pine with chloroacetic anhydride

Control

Acetylated



-OH 3550 - 3200

Equilibrium moisture content (EMC) of different sizes of wood reacted with acetic anhydride. (1 hr at 120 °C)

Specimen	WPG	EMC at , 90% RH
Solid wood	0	21.3
Solid wood acetylated	17.8	9.3
Large chunks acetylated	18.4	8.2
Flakes acetylated	19.4	5.7
Fiber acetylated	22.4	3.2

Weight gain due to reaction of Scots pine and red oak with acetic anhydride at various reaction times at 120 °C.

Wood Reaction Time (hrs)

	0.25	0.5	1	2	4	24
Scots pine	13.7	15.4	19.5	20.7	24.9	23.7
Red oak	11.9	13.9	17.2	17.8	19.4	18.8

Sugar analysis of Scots pine and red oak.

Wood Percentage in Wood (%)

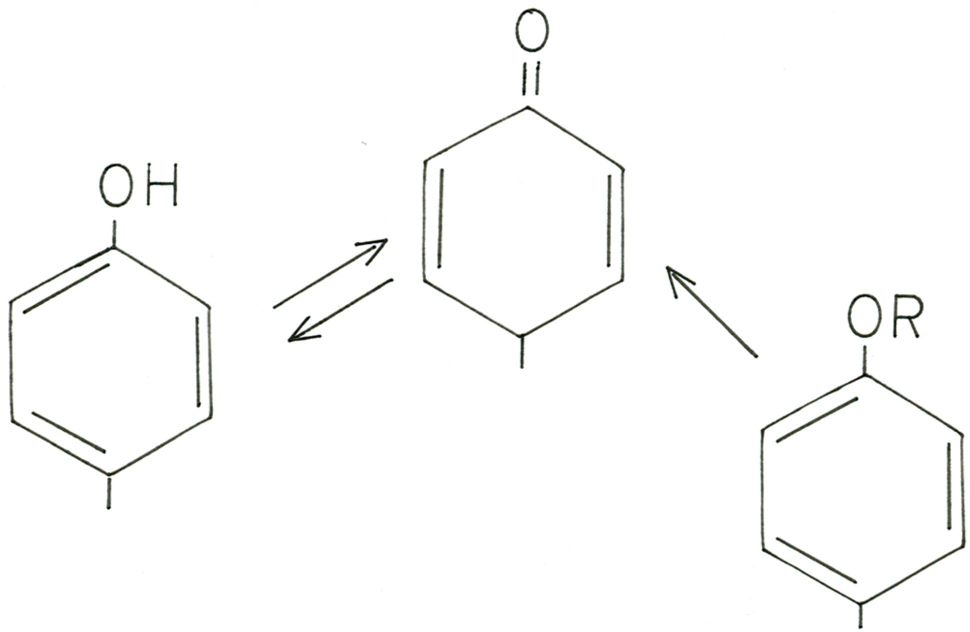
	Glucose	Xylose	Galactose	Arabinose	Mannose
Scots pine	44.0	7.6	3.1	1.6	10.0
Red oak	41.0	19.0	1.2	0.4	2.0

Weight gain of pine wood and isolated cell wall polymers after reaction with acetic anhydride at 120 °C.

Substrate Reaction Time (min)

	15	30	45	60	120	180
Wood	3.8	7.1	11.2	15.0	17.8	18.4
Holocellulose	0.7	1.4	2.0	2.6	6.2	10.3
Hemicellulose	3.8	7.1	15.1	22.2	27.3	30.3
Lignin	9.8	12.7	13.7	14.8	16.7	16.9
Cellulose	0	0	0	0	0	0

Ultra violet protection -
Intermediate quinone-methide that is in a reversible tautomeric equilibrium with the free phenol



Distribution of Acetyl Groups in Southern Yellow Pine

WPG	Total* Accessibility	Limited** Accessibility	DS in Lignin
8.5	0.12	0.28	0.78
18.5	0.19	0.46	1.10
23.6	0.26	0.63	1.15

*Assuming accessibility of all cell wall hydroxyl groups

** Assuming 100% accessibility of hemicelluloses and lignin hydroxyl groups but no accessibility of cellulose hydroxyl groups

Conclusions

- Accessibility of cell wall polymers critical to get reacting chemical to the right place – swelling critical.
- Distribution of bonded chemical critical – especially hemicelluloses (arabinose) for decay resistance and lignin for UV resistance

  (- OH not the site for all bonding, for example – C=C for UV resistance).
- Results of this research may provide information for a better\different cell wall model.
- It has been said that chemical modification of wood is a mature science. I think it is only beginning!