Unité
Sciences du Bois et des Biopolymères

Chemical Functionalization of Lignocellulosic Polymers for the Control of Interfacial Adhesion in Wood and BiofiberPlastic-composites

Dr Gilles SEBE

Assistant Professor - University of Bordeaux

UMR 5103 CNRS-INRA-UBx1, 351 cours de la Libération, F-33405 Talence Cedex

INTRODUCTION

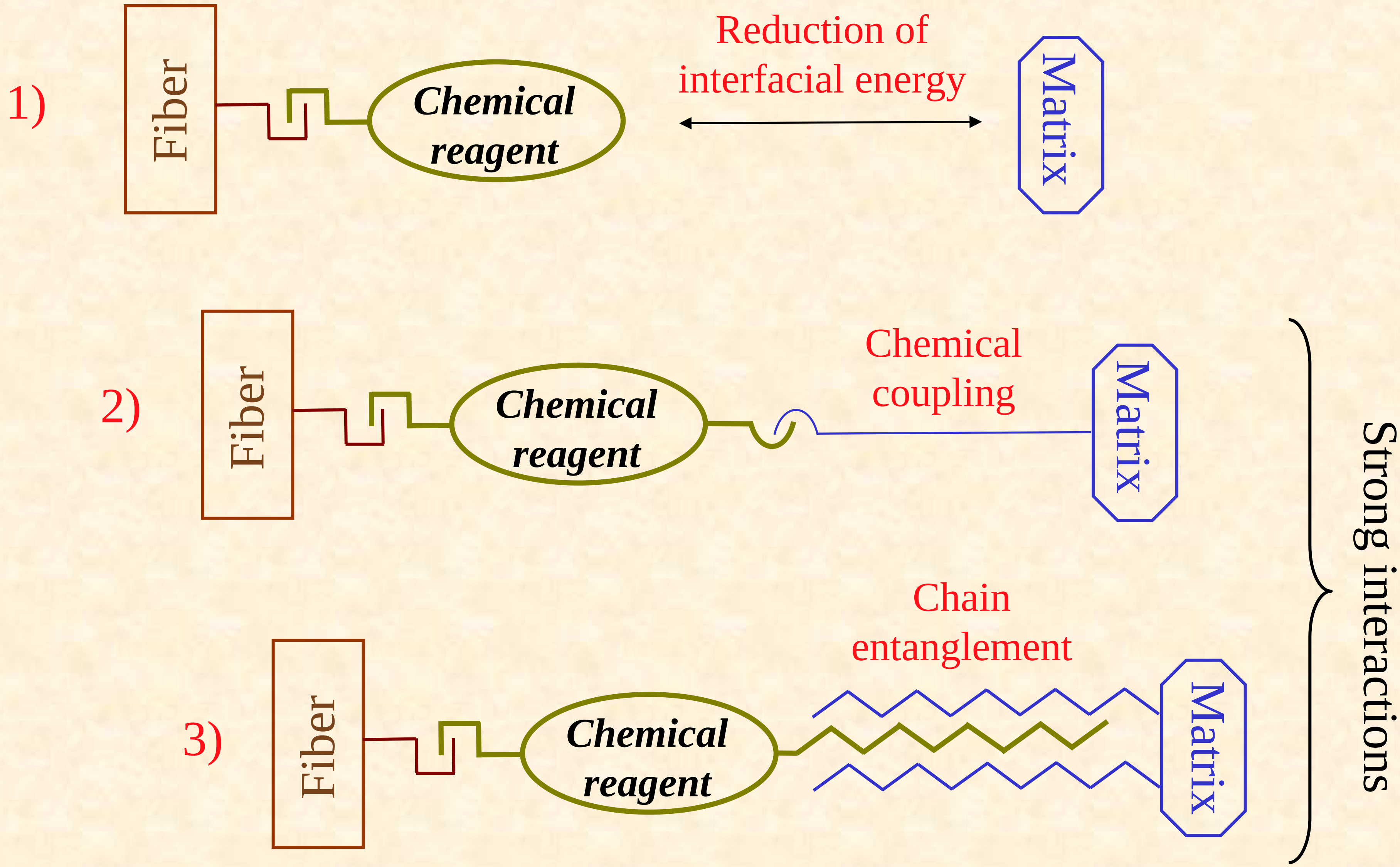
- The mechanical properties of Wood or BiofiberPlastic composites (WPC) are strongly influenced by the quality of the fiber/matrix interface

- The poor adhesion between the hydrophilic lignocellulosic fibers and the hydrophobic polymeric matrix limits the strength performances of the WPC's

However,

- The interfacial adhesion in WPC's can be improved via the chemical functionalization of the lignocellulosic fibers

PRINCIPLE


1)
Fiber
Chemical reagent
Reduction of interfacial energy
Matrix
2)
Fiber
Chemical reagent
Chemical coupling
Matrix
3)
Fiber
Chemical reagent
Chain entanglement
Matrix
Strong interactions

ADDITIONAL IMPROVEMENTS

- The properties of the lignocellulosic fibers can be additionally improved if the functionalization is performed in the bulk:
    - Dimensional stability
    - Decay resistance
    - Photostability
    - Water repellency
    - Thermoplasticity (if the grafted chain is long enough)

OBJECTIVES OF MY RESEARCH

- To develop novel chemical pathways for the functionalization of lignocellulosic materials and to characterize the modifications at a molecular level:

  - Reactions with alkoxysilanes
  - Transesterification reactions

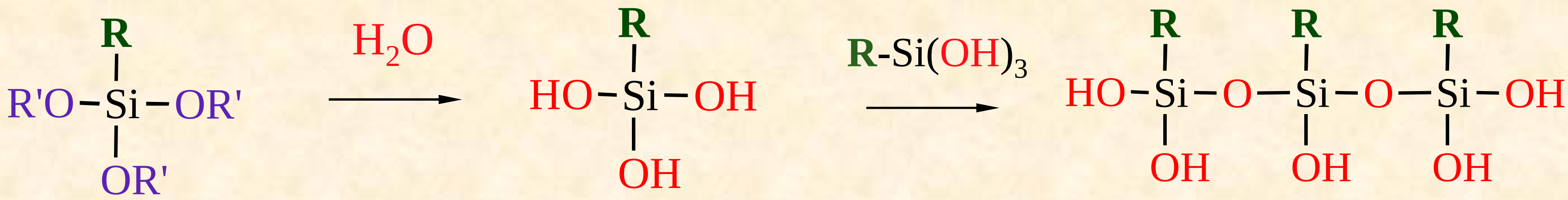
My presentation today

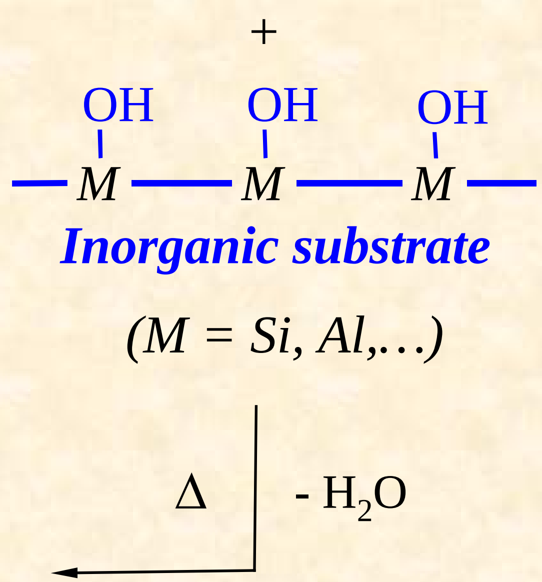
- To study the impact of these modifications on the properties of composites made of wood or plant fibers

- To modelize the mechanisms involved in the interfacial region

REACTION WITH TRIALKOXYSILANES

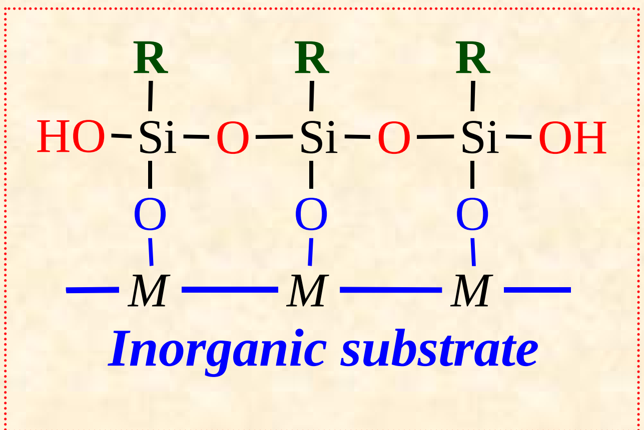
- Trialkoxysilanes are reactive towards most inorganic substrates:





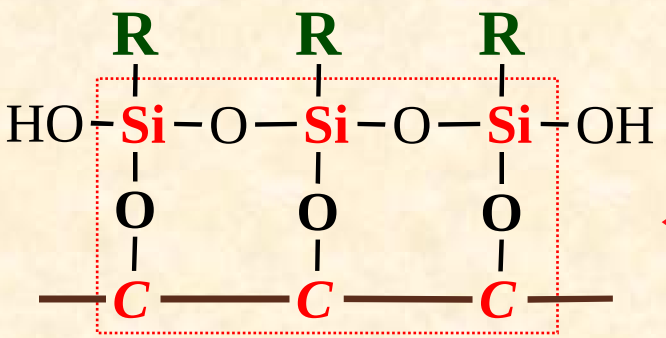
R can be:

- Hydrophilic
- Hydrophobic
- Organoreactive
- UV or heat resistant…



REACTION WITH TRIALKOXYSILANES

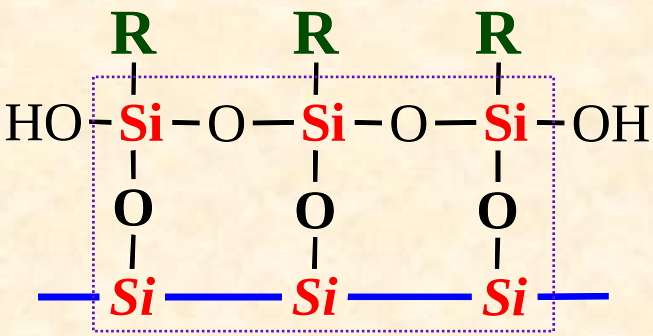
- Similar reactions can be envisaged with lignocellulosic substrates, **but** in that case, the silane bond is **not stable**



Lignocellulosic fibers

Hydrolysis in the presence of water

But **stable** siloxane bonds with siliceous substrates



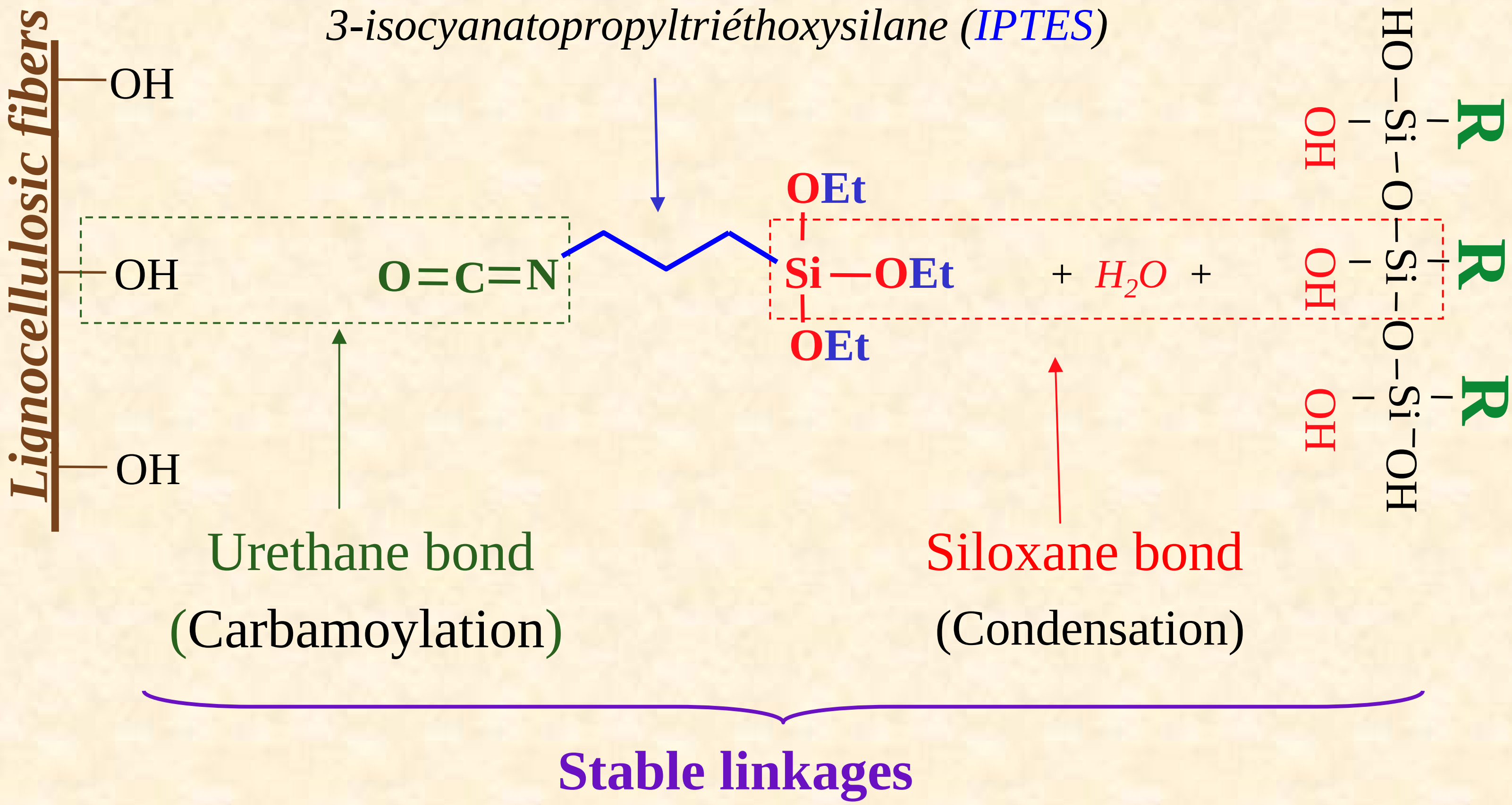
Glass fibers

OUR APPROACH

- Utilization of an organofunctional silane as a coupling agent

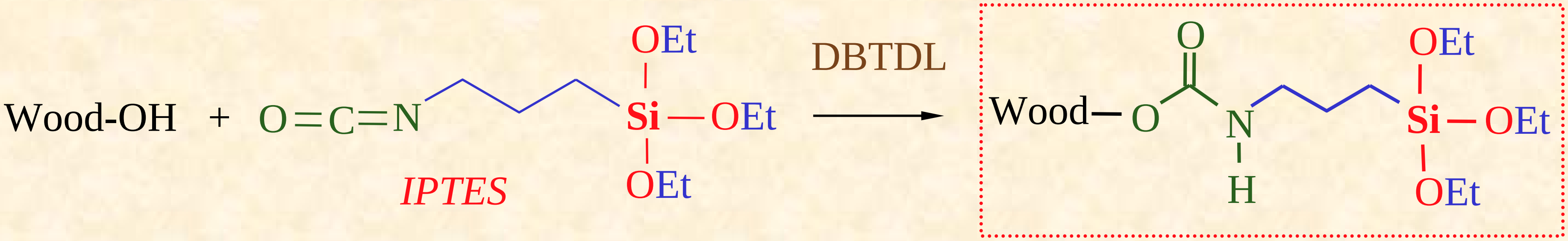
Coupling agent:

3-isocyanatopropyltriéthoxysilane (IPTES)

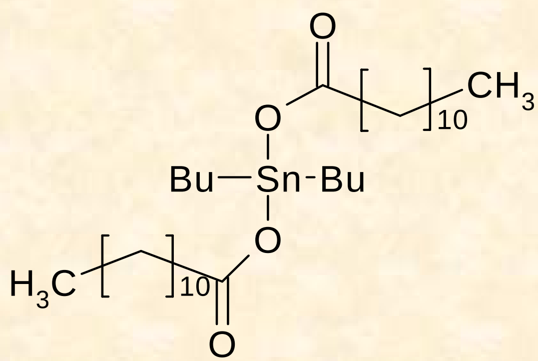


REACTION BETWEEN IPTES AND WOOD

- Reaction



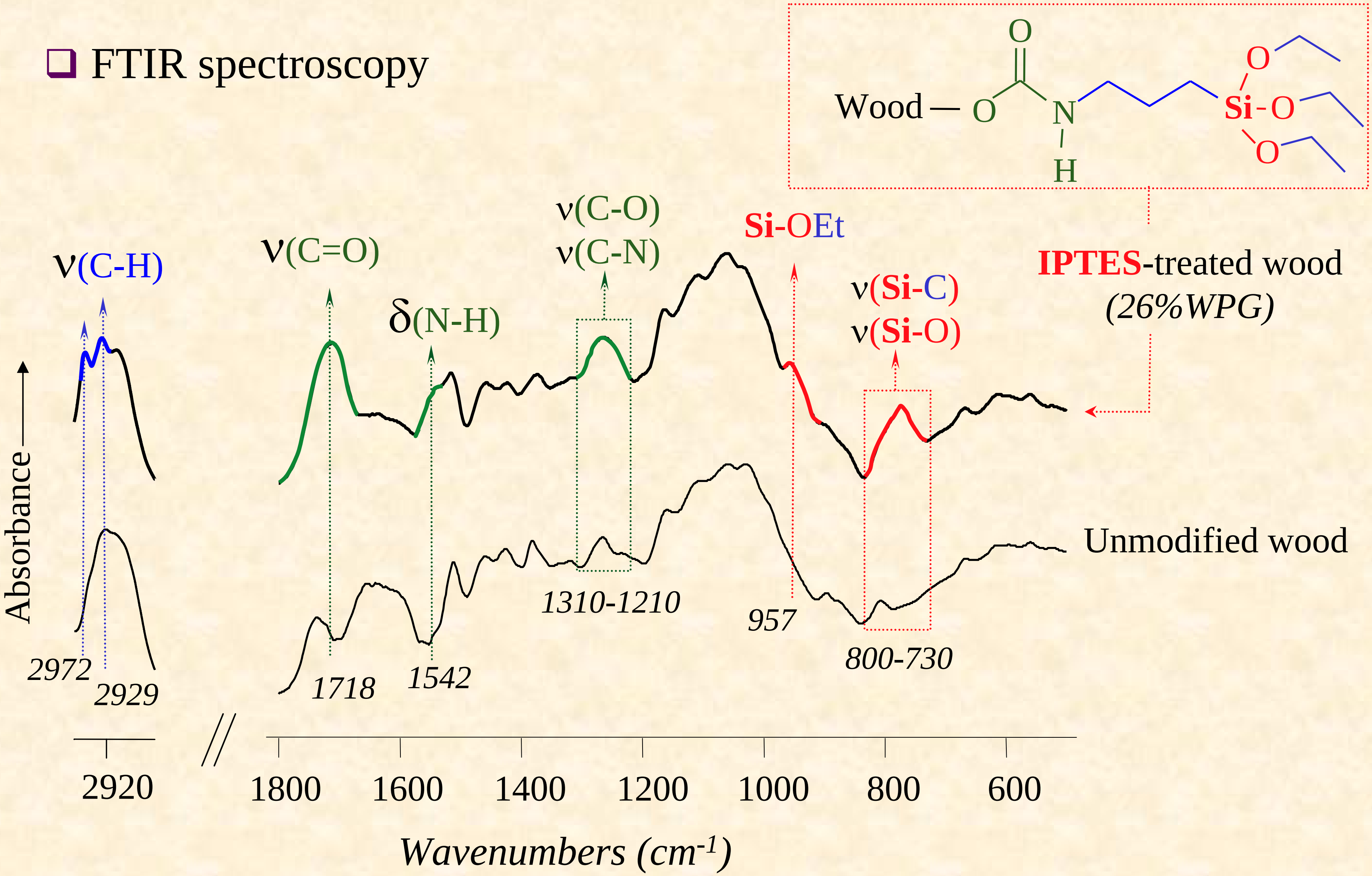
Catalyst = Dibutyltin dilaurate (DBTDL):



- Different modification rates were investigated and characterized by FTIR and solid-state NMR spectroscopy.

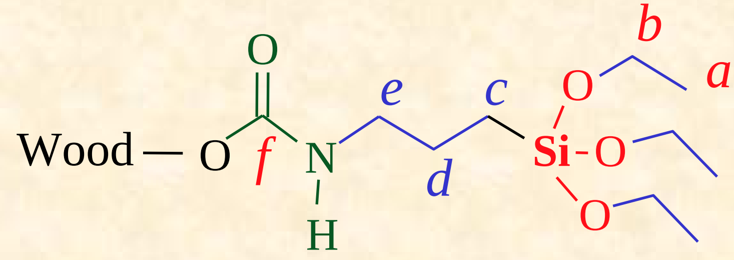
REACTION BETWEEN IPTES AND WOOD

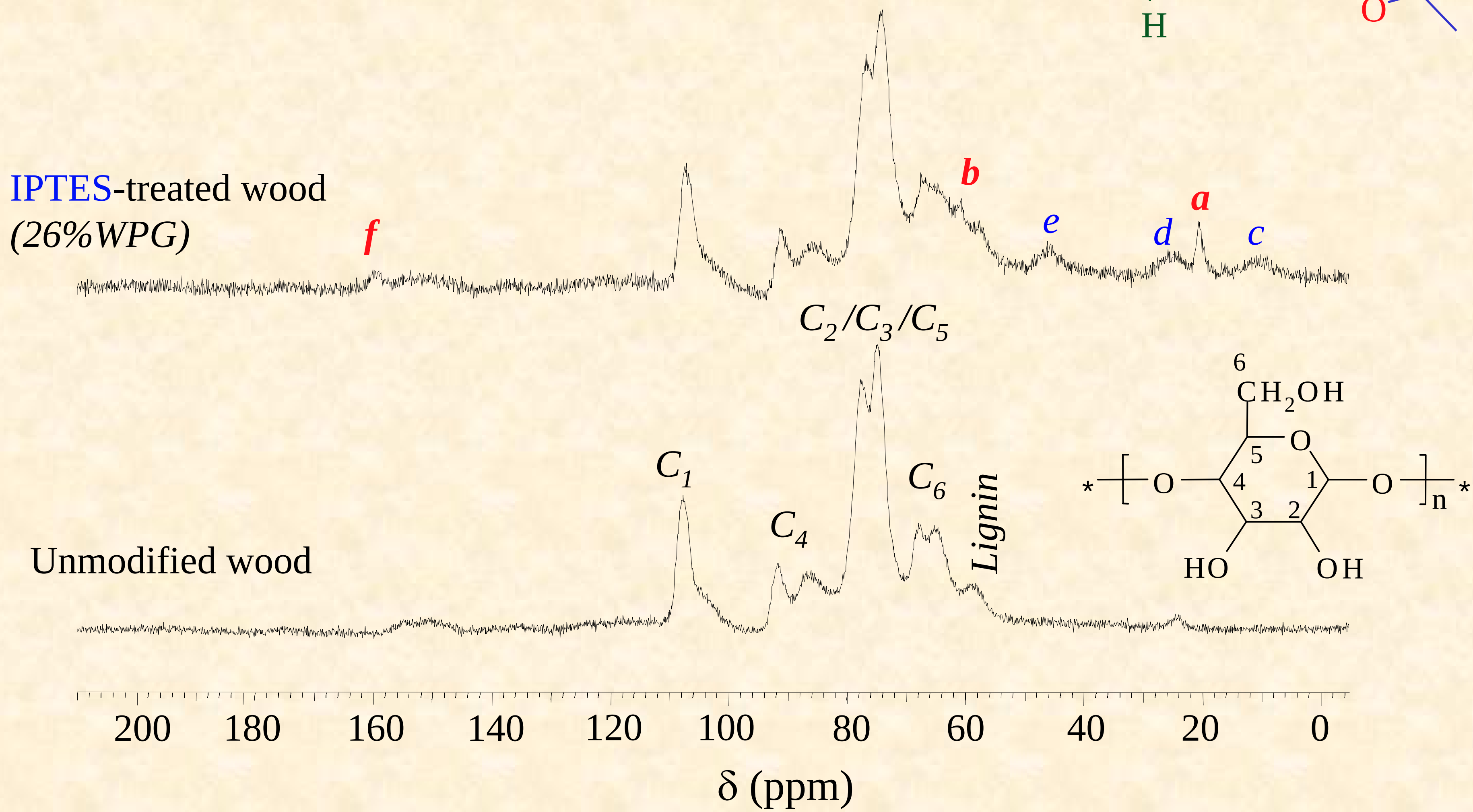
- FTIR spectroscopy



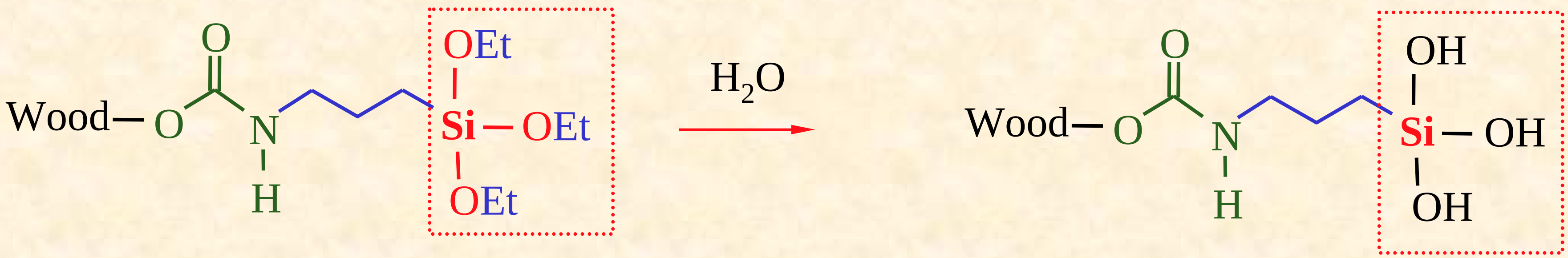
REACTION BETWEEN IPTES AND WOOD

- ^{13}C CP-MAS NMR spectroscopy



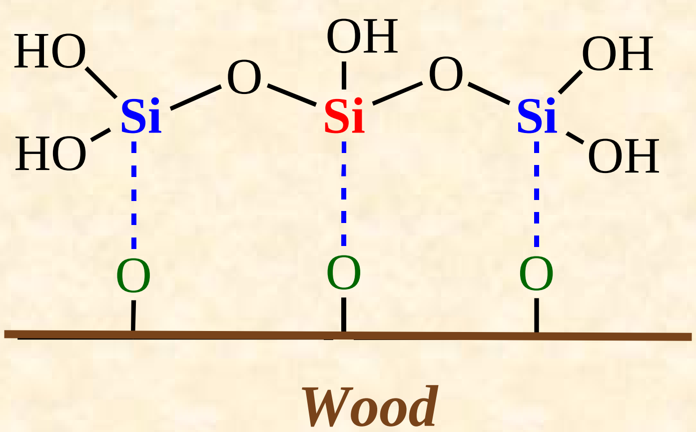


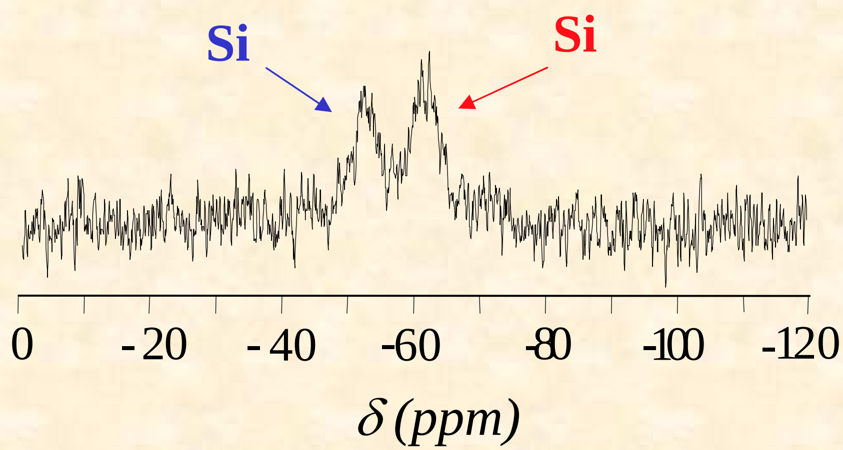
HYDROLYSIS OF IPTES-TREATED WOOD



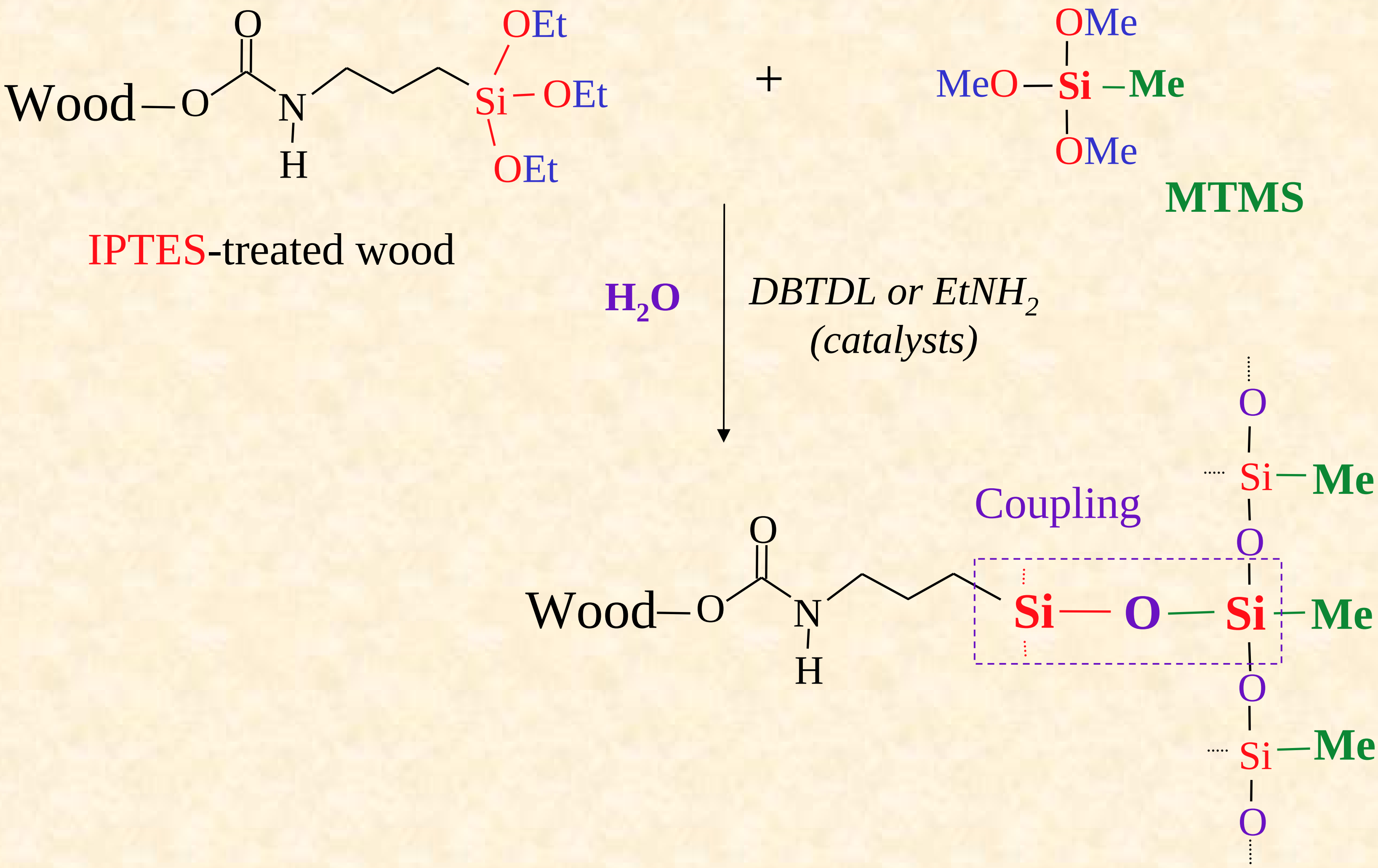
- Cleavage of the **Si-OEt** linkages confirmed by FTIR and ^{13}C NMR

- Partial condensations between neighboring **Si-OH** (^{29}Si NMR)



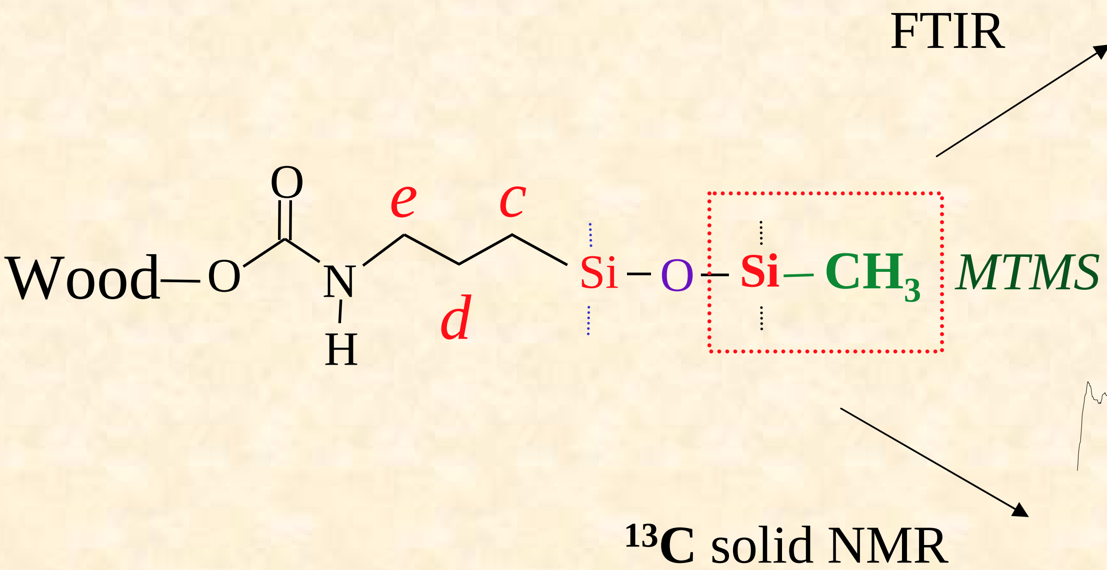


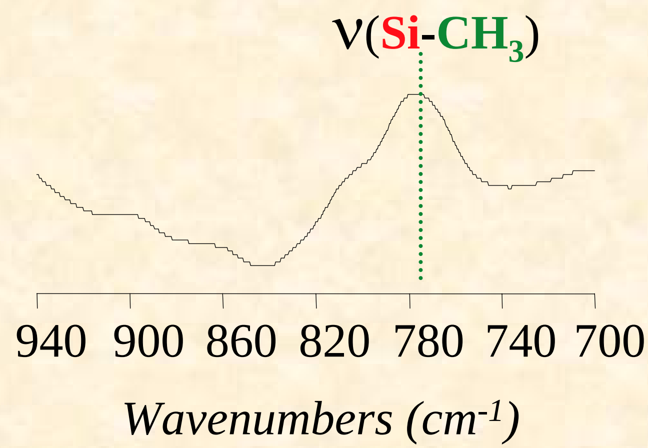
COUPLING WITH METHYLTRIMETHOXYSILANE (MTMS)

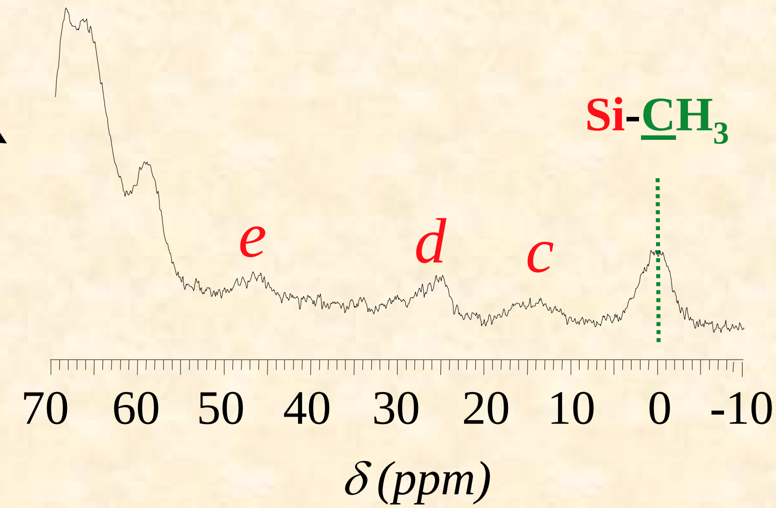


COUPLING WITH MTMS

- Spectroscopic characterizations

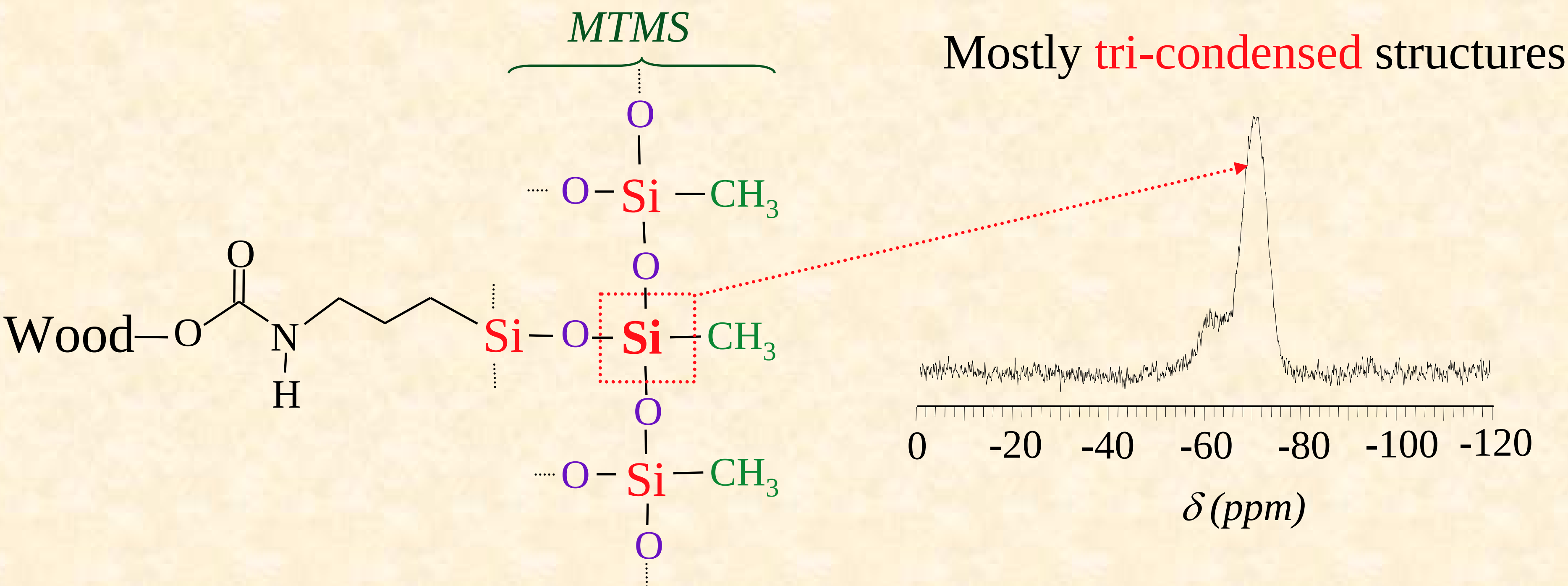






COUPLING WITH MTMS

- ^{29}Si CP-MAS NMR spectroscopy



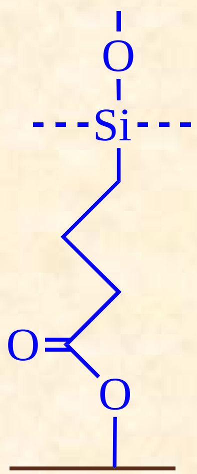
- MTMS grafted in wood in the form of a tri-condensed polysiloxane
- Grafting highly resistant to water leaching

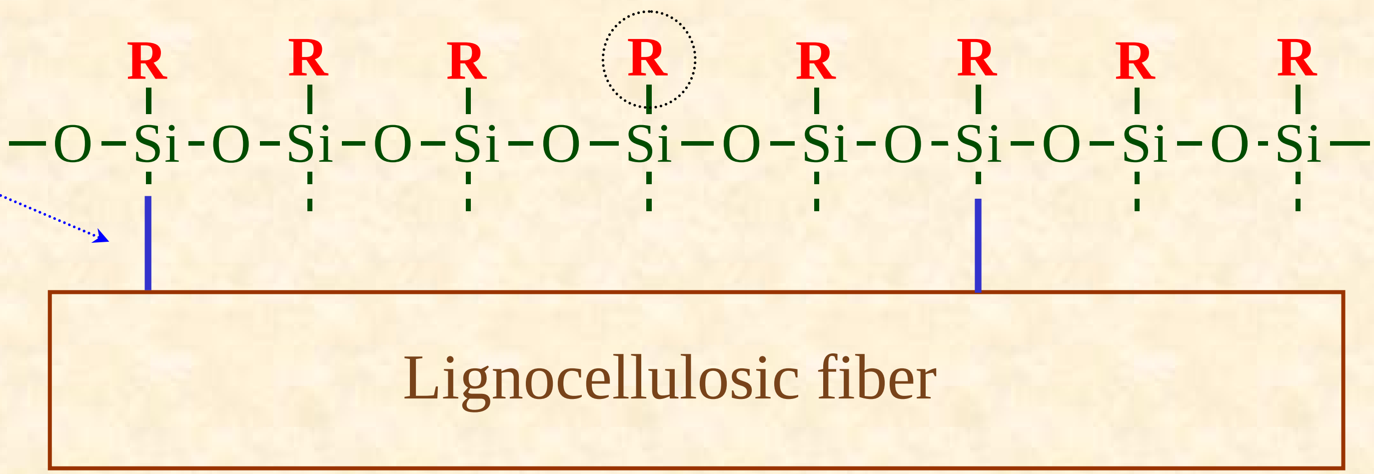
PERSPECTIVES

- Application to WPC's

- Hydrophilic
- Hydrophobic
- Organoreactive
- UV or heat resistant…

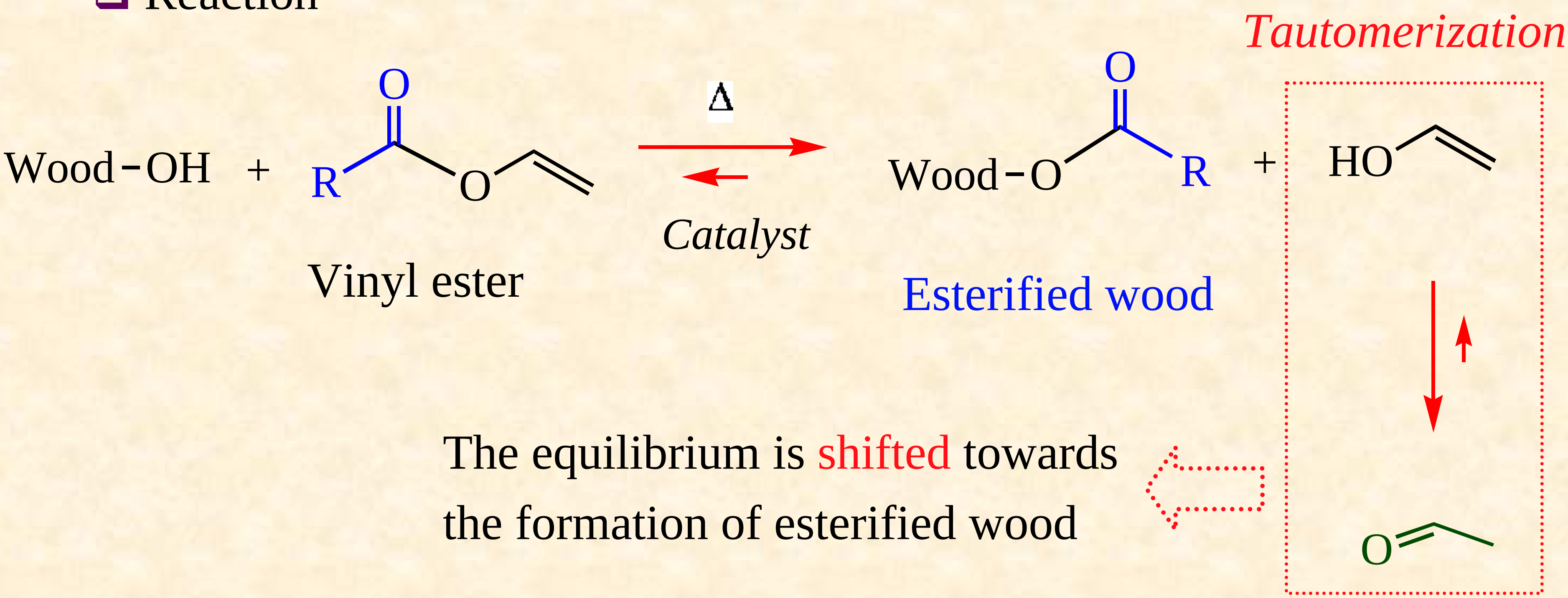
Anchoring site
(coupling agent)





TRANSESTERIFICATION WITH VINYL ESTERS

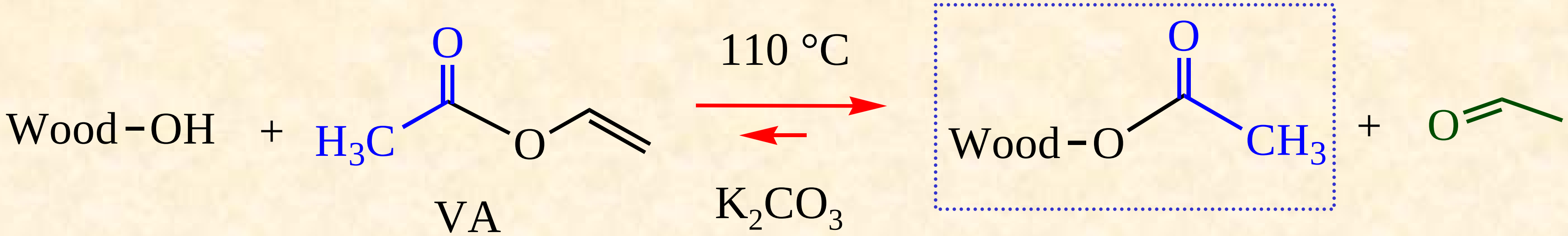
- Reaction



The equilibrium is shifted towards the formation of esterified wood

- The acetaldehyde formed as a by-product can be easily removed after reaction (bp_{760} = 21°C)

REACTION WITH VINYL ACTEATE

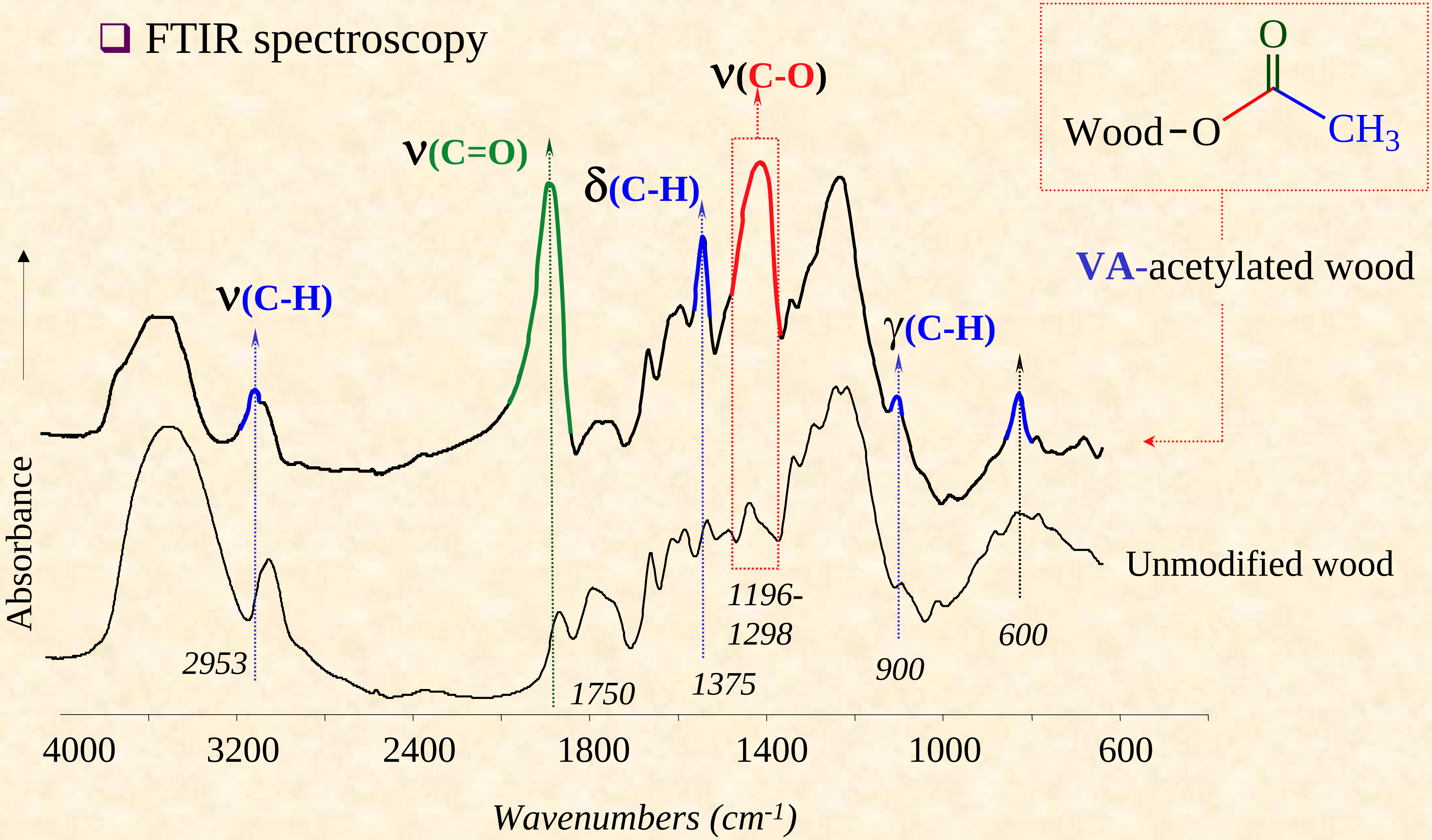


WPG = 26 %

- Preliminary experiments were performed with **sawdust**, under a standard set of conditions:
  - 1.1 mmol K_2CO_3/g wood, as catalyst
  - Dimethylformamide (DMF) as solvent
  - Reaction for 3 hours, at 110 °C

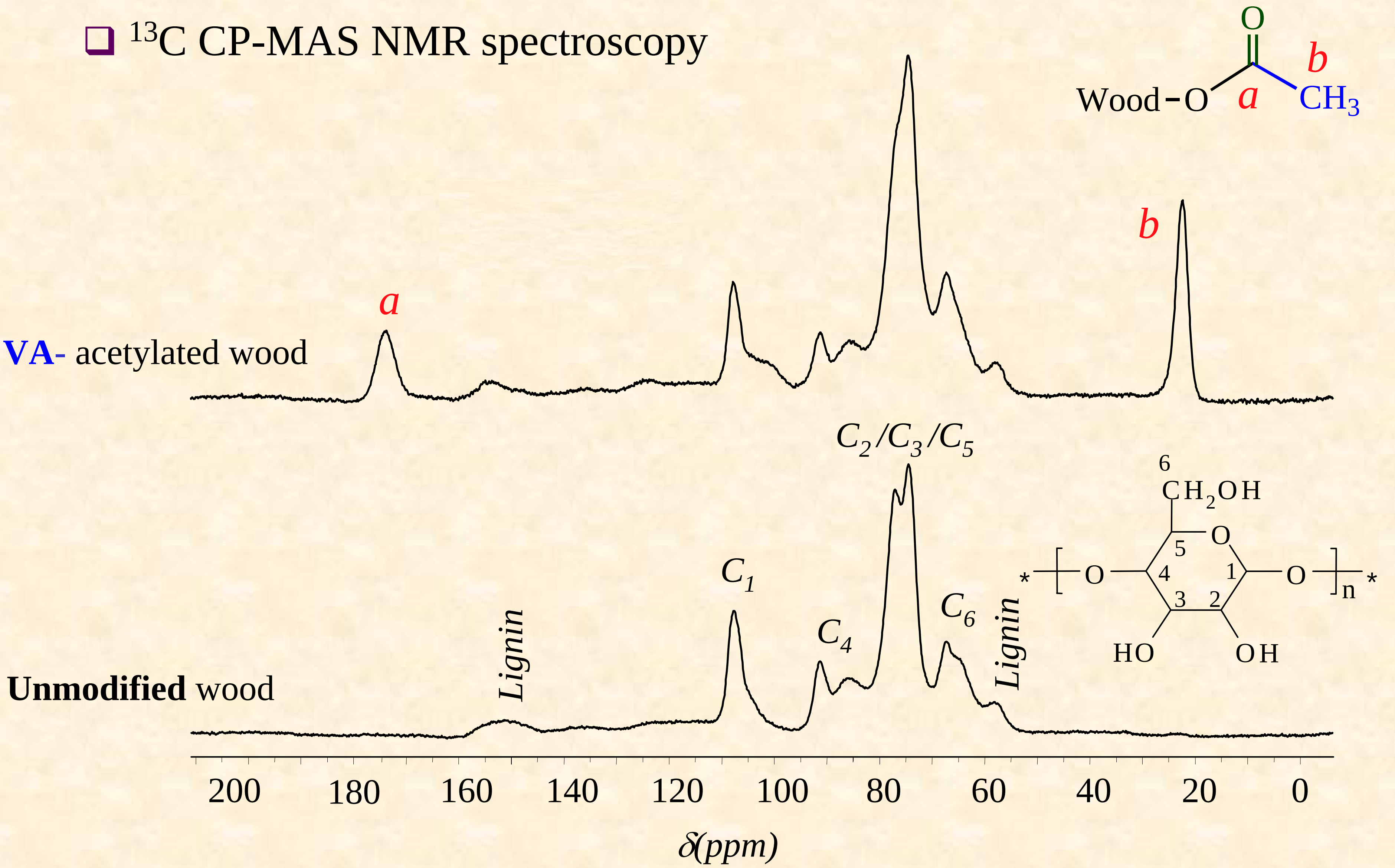
REACTION WITH VINYL ACTEATE

- FTIR spectroscopy



REACTION WITH VINYL ACTEATE

- ^{13}C CP-MAS NMR spectroscopy



REACTION WITH VINYL ACTEATE

Temperature (C)	25	50	**90**	110	130	150
WPG (%)	0.8	9.5	**24.6**	26.2	27.2	27.9

Reaction time = 3 h ; K_2CO_3 = 1.1 mmol/g wood

Reaction time (min)	10	30	60	**180**	360	960
WPG (%)	2.8	7.5	22.3	**24.6**	26.7	25.6

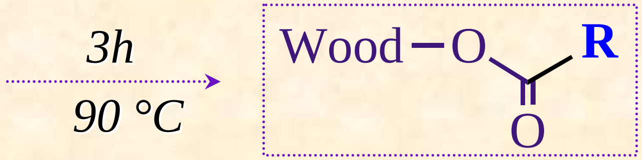
Temperature = 90℃ ; K_2CO_3 = 1.1 mmol/g wood

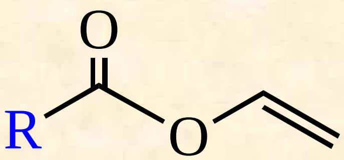
K_2CO_3 (mmol/g wood)	0	0.05	0.1	**1.1**	10.7	21
WPG (%)	0.0	0.05	5.7	**24.6**	24.8	26.9

Reaction time = 3 h ; Temperature = 90℃

REACTION WITH OTHER *VINYL ESTERS*

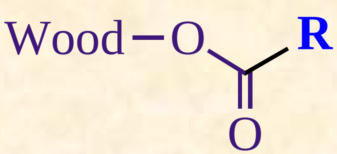
- Saturated vinyl esters

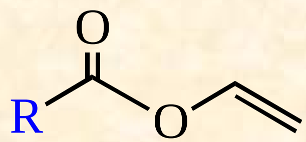
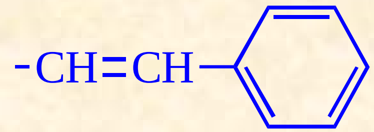
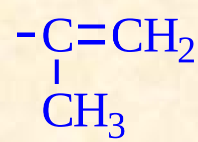
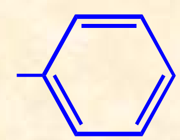


	-R	WPG (%)
Vinyl propionate	$-CH_2-CH_3$	23.6
Vinyl butyrate	$-CH_2-CH_2-CH_3$	30.0
Vinyl pivalate	$-C(CH_3)_3$	15.2
Vinyl dˇcanoate	$-CH_2-(CH_2)_7-CH_3$	49.6
Vinyl stearate	$-CH_2-(CH_2)_{15}-CH_3$	52.2

REACTION WITH OTHER VINYL ESTERS

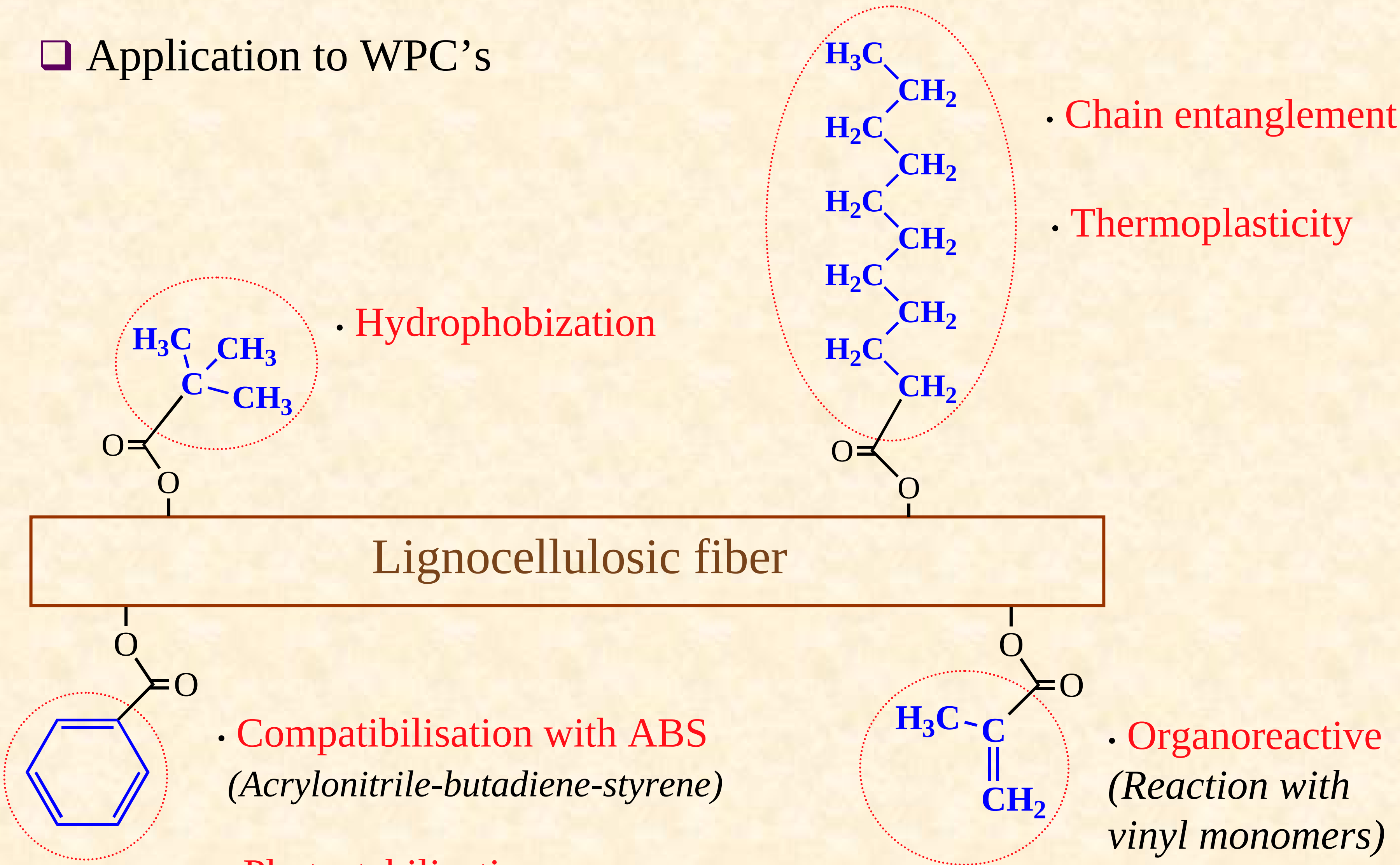
- Unsaturated vinyl esters



	-R	WPG (%)
Vinyl cinnamate		46.3
Vinyl crotonate	$-CH=CH-CH_3$	16.8
Vinyl methacrylate		24.8
Vinyl benzoate		46.5
Vinyl 4-*tert*-butylbenzoate		31.8

PERSPECTIVES

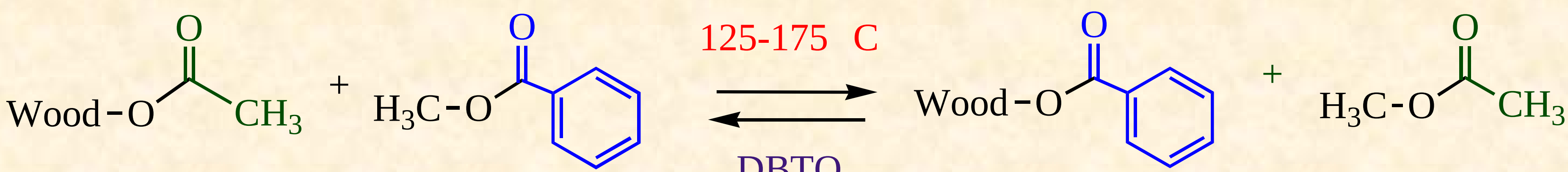
- Application to WPC's



OTHER TRANSESTERIFICATION REACTIONS

- Ester/ester exchange

DBTO = Dibutyltin oxide



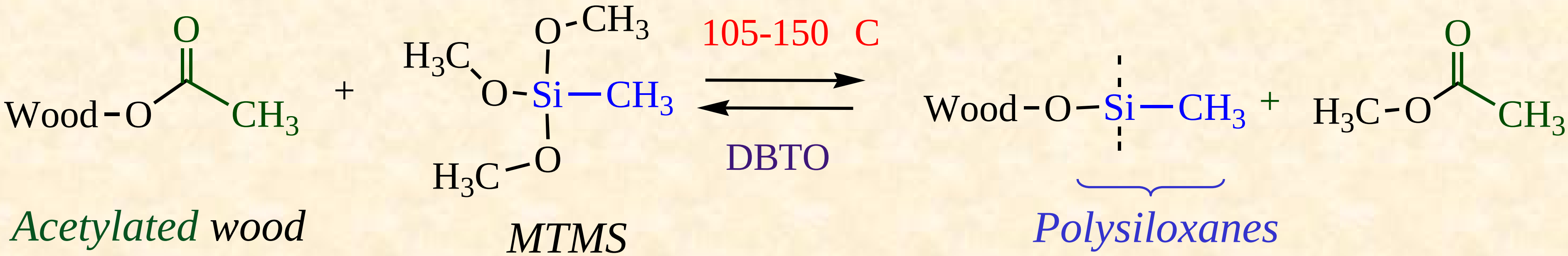
Acetylated wood *Benzoylated wood*

- The interchange reaction has been confirmed by:
  - Infrared spectroscopy (FTIR)
  - ^{13}C solid-state NMR spectroscopy
- No reaction with un-acetylated wood

OTHER TRANSESTERIFICATION REACTIONS

DBTO = Dibutyltin oxide

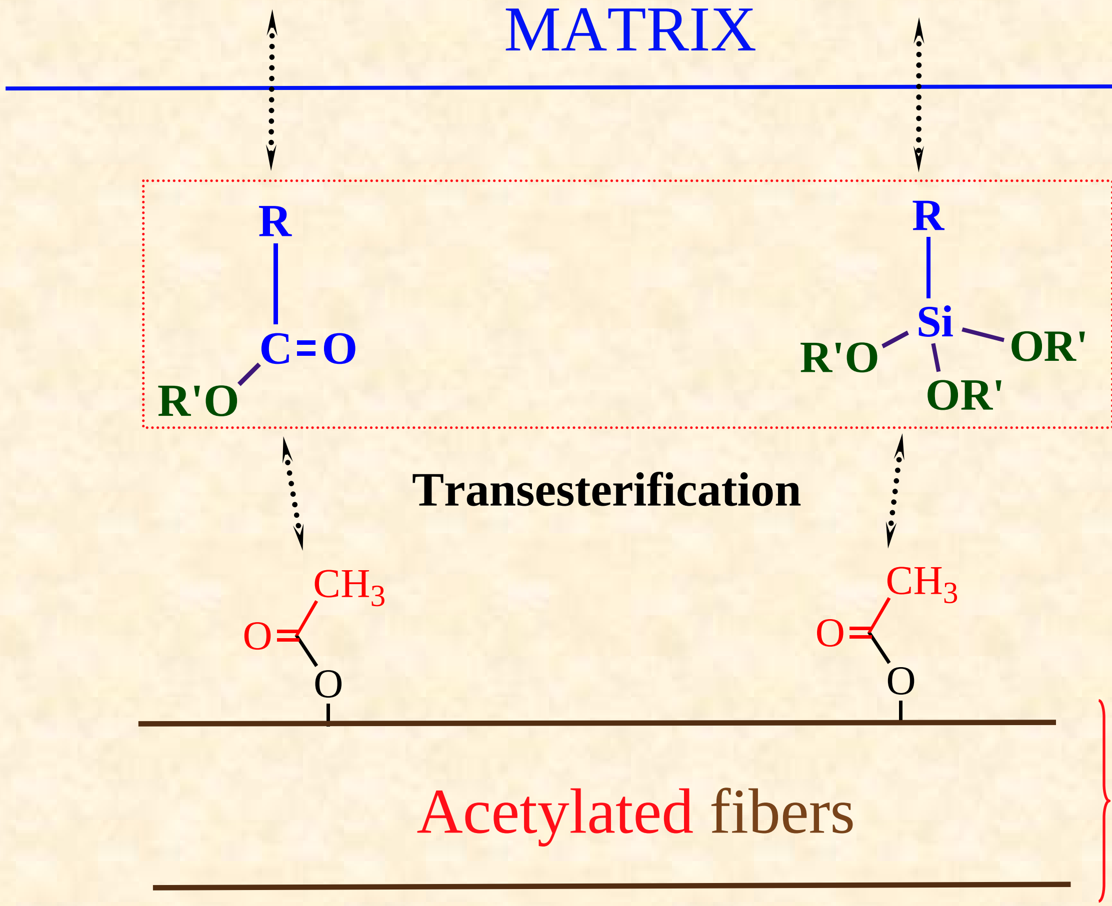
- Ester/alkoxysilane exchange



- The interchange reaction has been confirmed by:
  - Infrared spectroscopy (FTIR)
  - ^{13}C and ^{29}Si solid-state NMR spectroscopy
- No reaction with un-acetylated wood

PERSPECTIVES

- Application to WPC's from acetylated fibers



Coupling agents

- Improved decay resistance
- Dimensional stability

CONCLUSIONS

- Chemical functionnalization of lignocllulosic fibers is a promising route to improve interfacial adhesion in WPC's

- Three novel chemical routes have been proposed to durably graft different functionalities in the fibers or at their surface:

All lignocellulosic materials

- Reaction with **alkoxysilanes** via an anchoring agent
- **Transesterification** with vinyl esters

Acetylated fibers

- **Ester**/**ester** or **alkoxysilane**/**ester** interchange reactions

CONCLUSIONS

- The feasability of these methods has been confirmed by:
  - Weight Percent Gain calculation (WPG)
  - Infrared spectroscopy (FTIR)
  - Solid-state NMR spectroscopy (^{13}C and ^{29}Si CP-MAS)

- These modifications will now be used to prepare model interfaces, at a laboratory scale, and modelize the mechanisms involved in the interfacial region of WPC's

ACKNOWLEDGMENTS

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Thank you for your attention!