CRMR

Centre de recherche sur
les matériaux renouvelables

The Power of Confocal Raman Microscopy in Coating Analysis

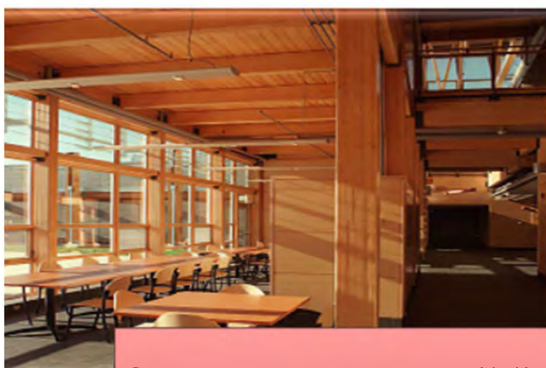
Véronic Landry, Full Professor, Université Laval
September 27
Greensboro, NC
Wood Coatings and Substrates Conference

Coauthors: Dr. Ingrid Calvez, Dr. Jérémy Winninger, Vahideh Akbary, Solène Pellerin, Marie Soula, Dr. Aurélien Hermann, Dr. Juliette Triquet, Rémi Cadieux-Lynch, Assira Keralta

UNIVERSITÉ LAVAL

Wood coatings, adhesives and modification research at UL

Québec City



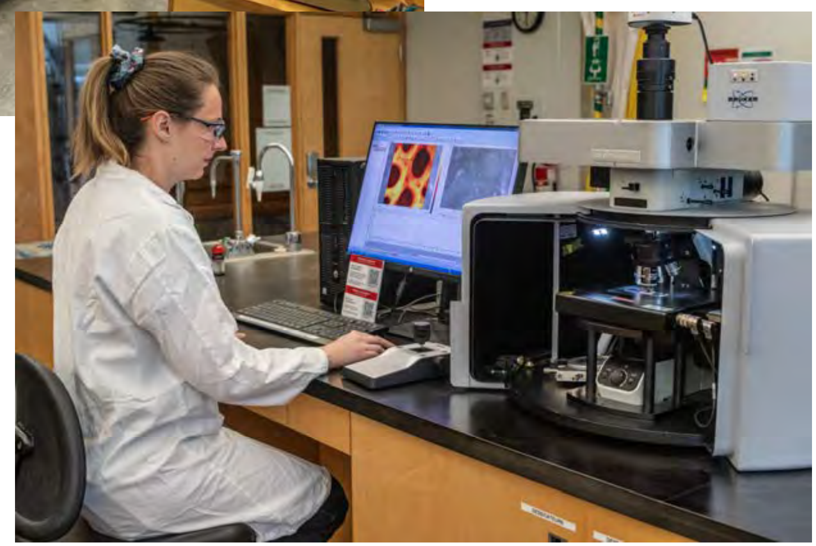
Gene H.- Kruger Building

Landry's research group, september 2024

CRMR
Centre de recherche sur
les matériaux renouvelables

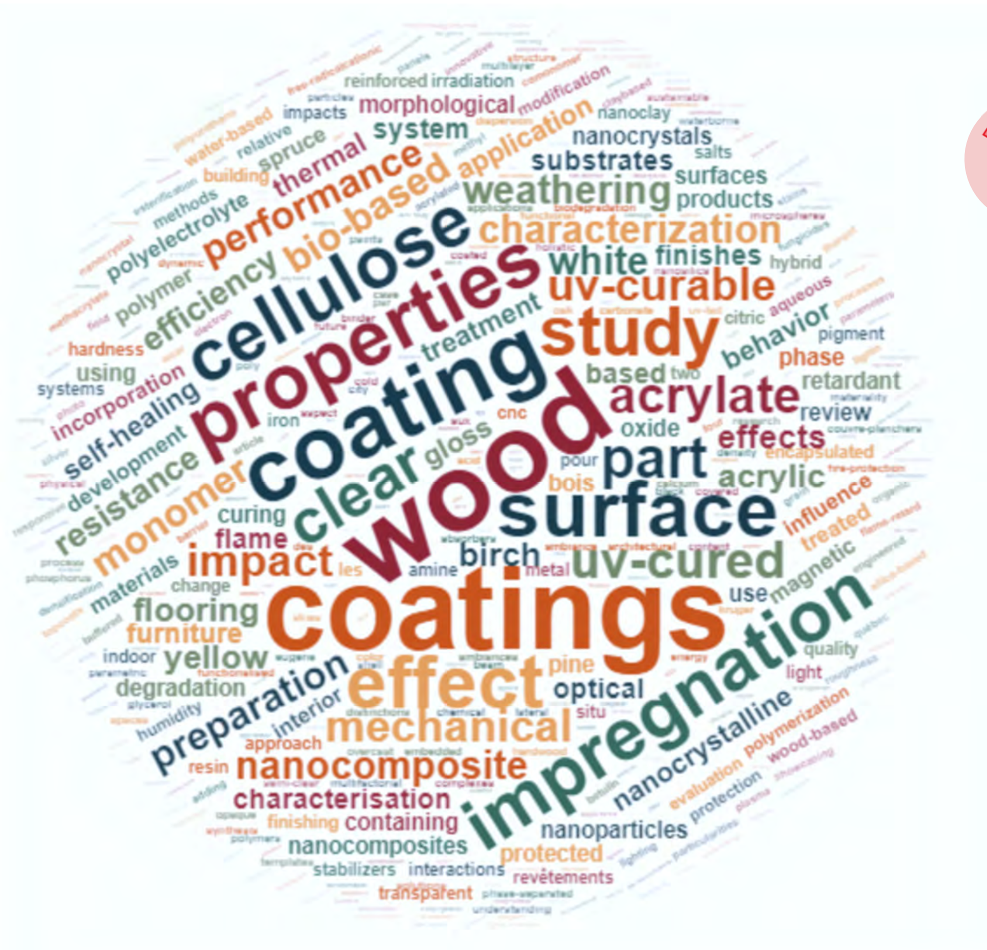
UNIVERSITÉ
LAVAL

Wood coatings, adhesives and modification research



CRMR
Centre de recherche sur
les matériaux renouvelables

Wood coatings, adhesives and modification research at UL



Wood finishing

- Film formation
- Appearance (gloss, etc.)
- Mechanical performance
- Flame retardancy
- Smart coatings

Wood adhesives

- Mechanical performance
- Biobased
- Flame retardancy

Wood modification and impregnation

- Hardening
- Dimensional stability

UNIVERSITÉ LAVAL

Wood coatings, adhesives and modification research at UL

Ongoing Research Projects

Coatings

- Terpene-based latex
- Lignin-based coatings
- Polyelectrolyte complexes for fire retardancy
- Antibacterial coatings
- Anti-fingerprint coatings

Adhesives

- Protein-based adhesive
- Tannin-based adhesives
- Saccharides-based adhesives
- Lignin-based adhesives

Wood modification

- Wood dimensional stabilization using whey ultrafiltration permeate
- Hardening using Michael addition reaction

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

August 2024
Gene H.-Kruger Building

CRMR
Centre de recherche sur
les matériaux renouvelables

Presentation plan

① **Theory on Confocal Raman Microscopy**

② **Confocal Raman Microscopy for Coatings Research**

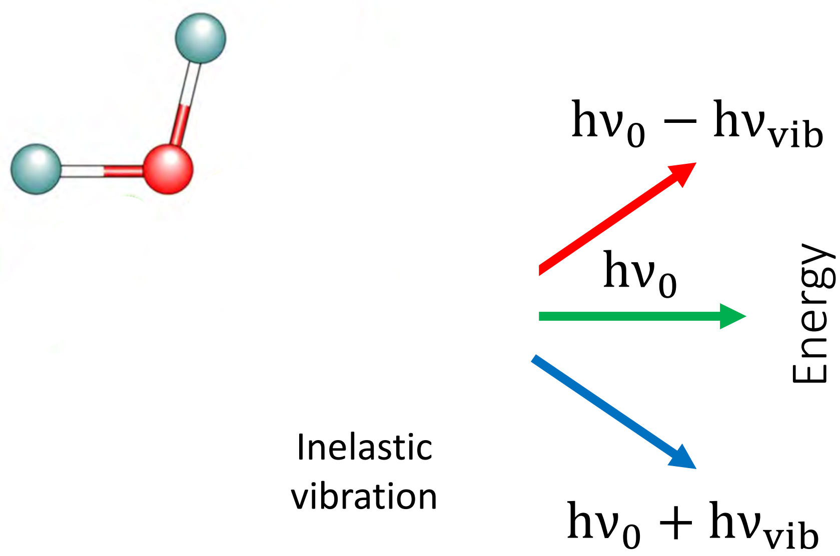
- *Free radical UV-curable coatings*
- *Radical/Cationic UV-curable coatings*

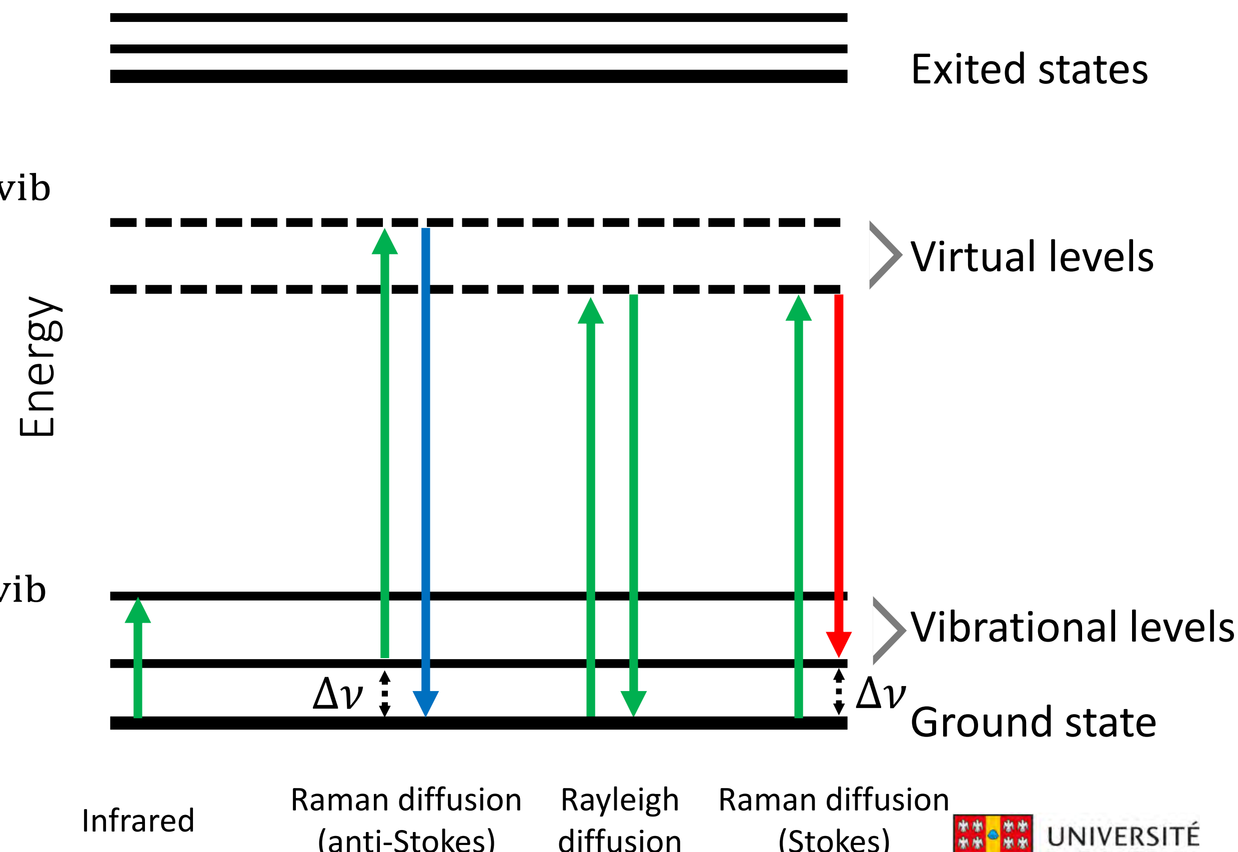
③ **Confocal Raman Microscopy for Wood Modification Research**

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Theory – Raman diffusion (sorry !)

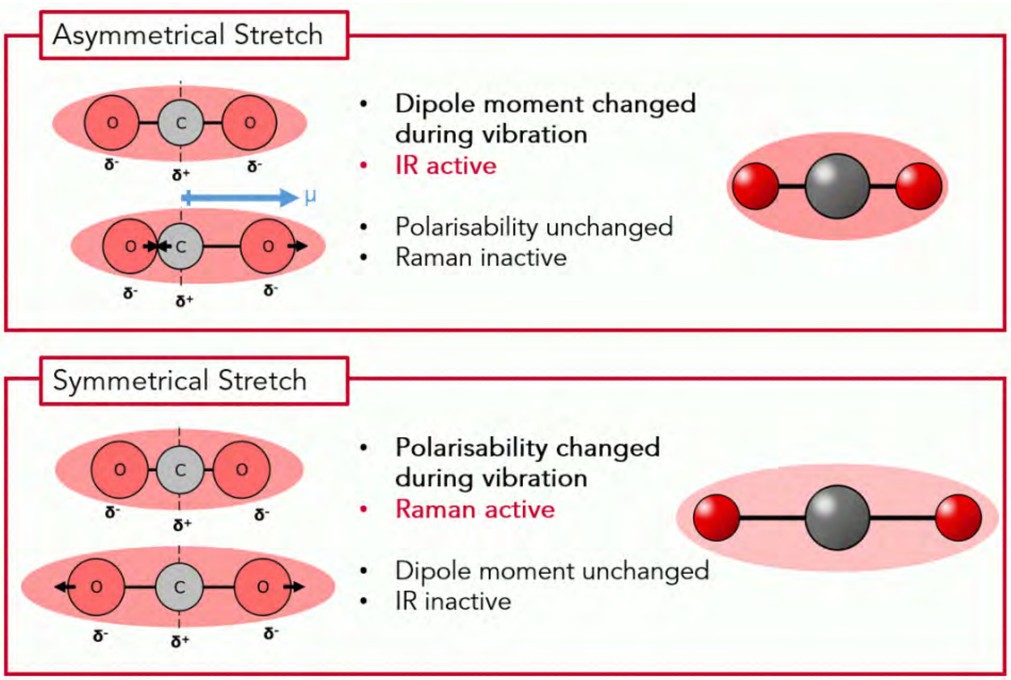




CRMR
Centre de recherche sur les matériaux renouvelables

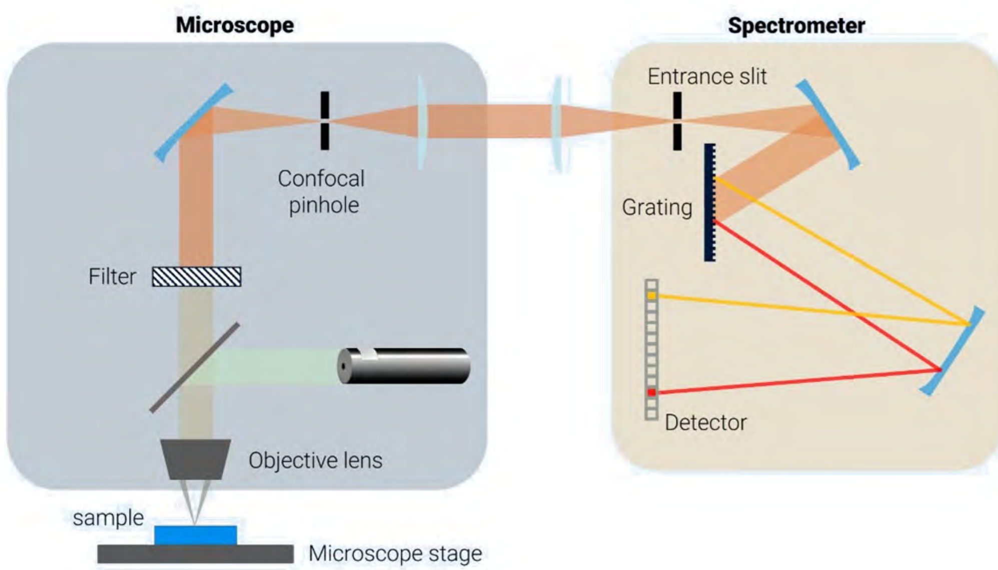
UNIVERSITÉ LAVAL

Theory – Raman vs IR spectroscopy

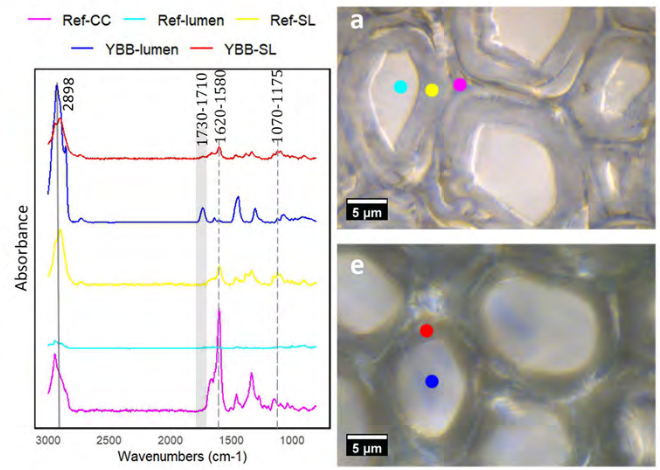


Raman	IR
Analysis of **scattered light** of vibrating molecules	Analysis of **absorption** of the vibrating molecules
Vibration is Raman active if it causes a change in the polarizability	IR active if a change in the dipole moment during the vibration occurs
Water can be used as a solvent	Water cannot be used as a solvent
No need for specific sample preparation	Requires specific sample preparation
Expensive instrumentation	Relatively inexpensive

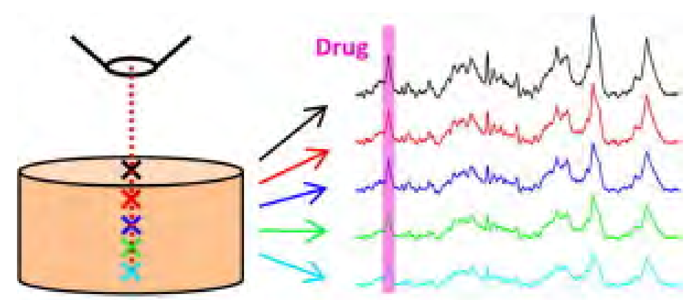
Theory – Raman spectroscopy + Optical Microscopy



Optical Microscopy Coupled with Raman Spectroscopy



Microscopy Coupled with Spectroscopy (X-Y)

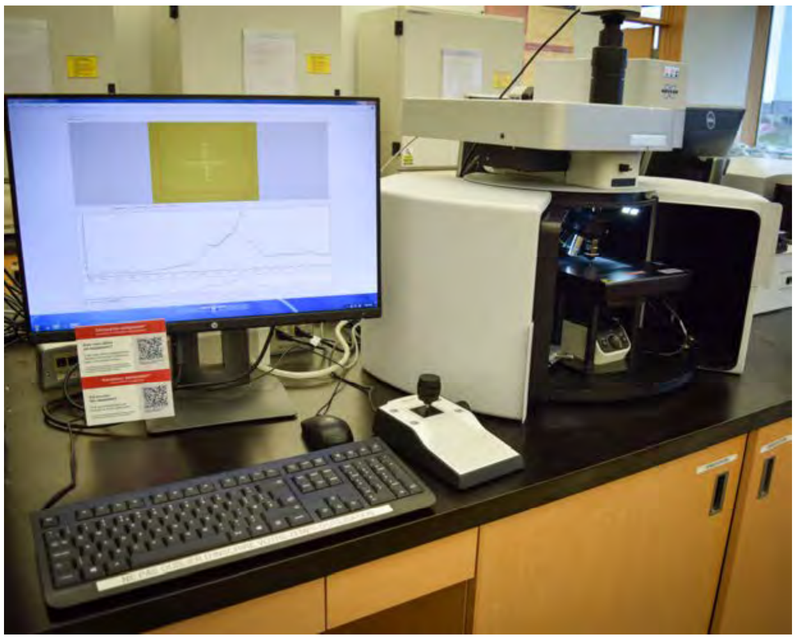


Depth Profiling

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Our system – SENTERRA II (Bruker)



Raman Microscope SENTERRA II (Bruker Optics Inc., Billerica, USA), equipped with a motorized stage and a confocal microscope (with x20, x50, and x100 objectives).

The confocal microscope, coupled with the spectrometer, reduces the analysis area and allows for "microanalysis" conditions (Raman microspectrometry), offering spatial resolution on the order of micrometers (μm).

Lasers available : 532 nm, 633 nm and 785 nm

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Using Raman Confocal for UV-curable coatings

1

Reducing Oxygen Inhibition of UV-curable acrylate coatings (radical polymerization)

2

Hybrid free radical/cationic phase-separated UV-curable system

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Using Raman Confocal for UV-curable coatings

1

Reducing Oxygen Inhibition of UV-curable acrylate coatings (radical polymerization)

2

Hybrid free radical/cationic phase-separated UV-curable system

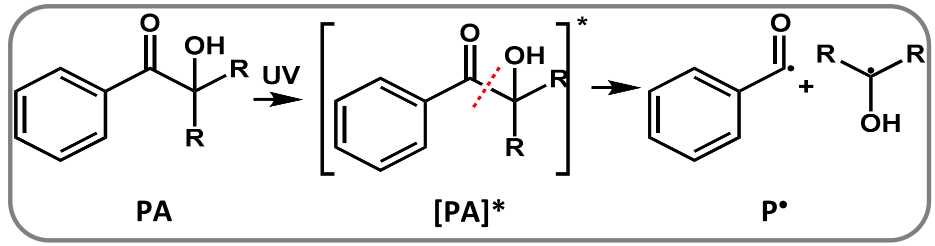
CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

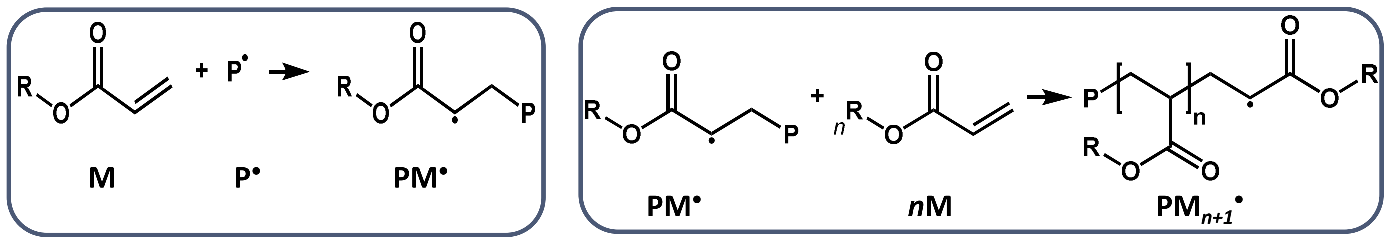
Free radical UV-curable coatings

- UV Irradiation
- Photoinitiator
- Reactive species (radicals, ions)
- Oligomers/ Monomers
- Crosslinked polymer

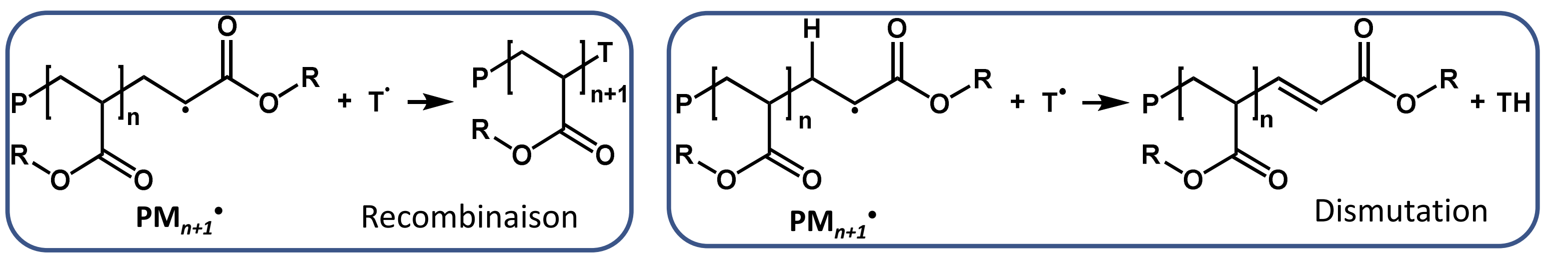
(1) Initiation



(2) Propagation



(3) Terminaison

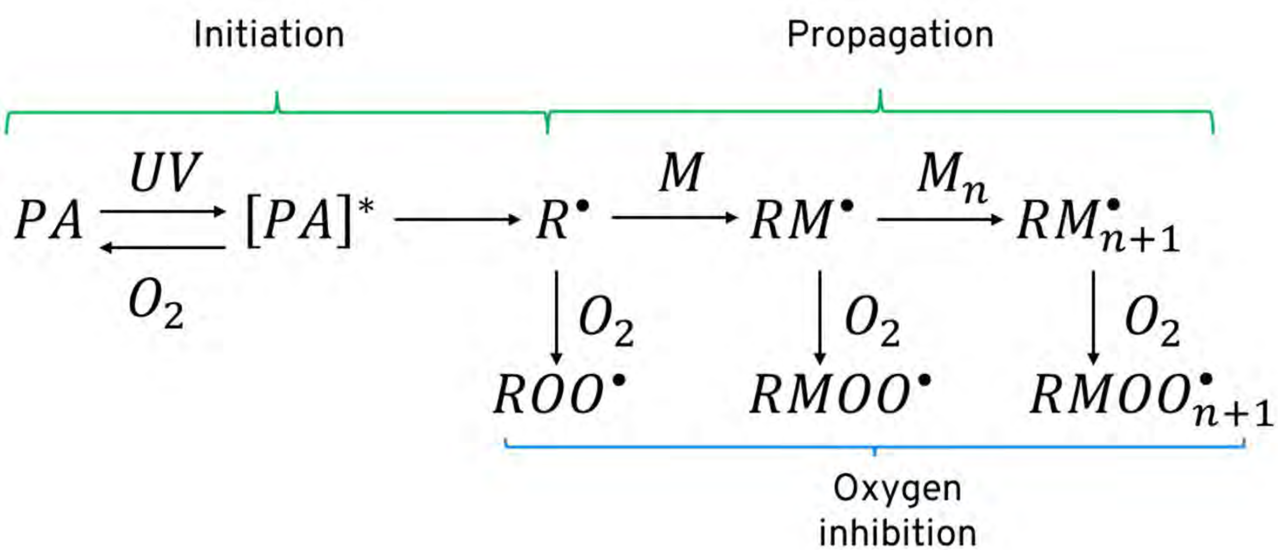


CRMR
Centre de recherche sur
les matériaux renouvelables

UNIVERSITÉ LAVAL

Decker, C. Polymérisation Sous Rayonnement UV : Les Résines Photopolymérisables. Techniques de l'Ingénieur. 2000

Oxygen inhibition of free radical UV-curable coatings



Impact of oxygen inhibition

- Low conversion of acrylates in surface
- Hardness decrease
- Higher residual monomer concentration
- Sticky surfaces
- Possible modification of optical properties

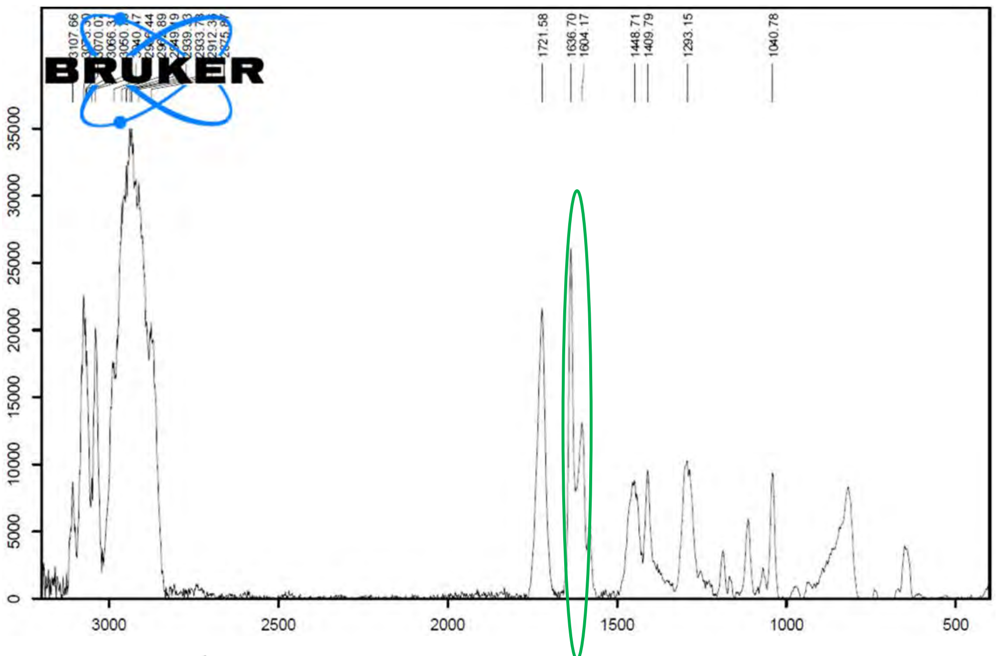
CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Studer, K.; Decker, C.; Beck, E.; Schwalm, R. Overcoming Oxygen Inhibition in UV-Curing of Acrylate Coatings by Carbon Dioxide Inerting, Part I. *Prog. Org. Coat.* **2003, © Aurélien Hermann, 2021**

Using CRM to study oxygen inhibition

Objective in using CRM : Depth profiling of acrylate conversion (double bond conversion, DBC)



Wavenumber (cm^{-1})	Attribution
810	$CH=CH_2$, twisting
1190	C-O, stretching
1405	CH_2, scissor deformation
1636	$CH=CH_2$, stretching
1720	C=O, stretching

$$DBC = \left(1 - \frac{I_z}{I_0}\right) * 100$$

$$Mean\ Raman\ DBC = \frac{1}{n}\sum_{i=1}^{n}(DBC)$$

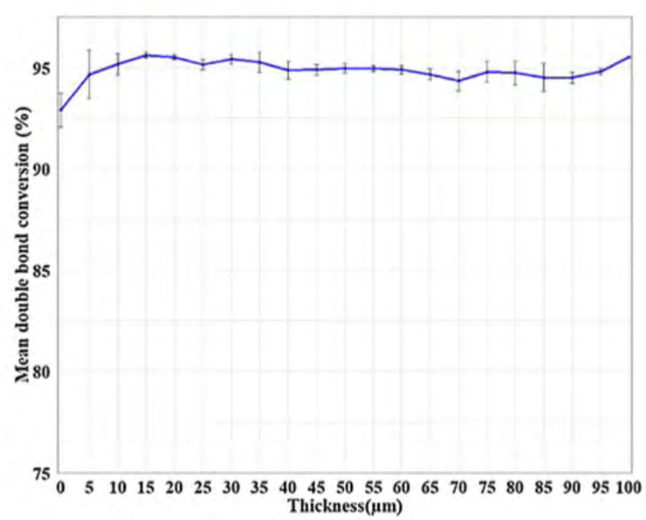
CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Using CRM to study oxygen inhibition

- Distinct analysis of each layer
- Calculation of the average conversion across the thickness

Measurements of the DBC every 5 µm of 100 µm films



Reference formulation – No additive

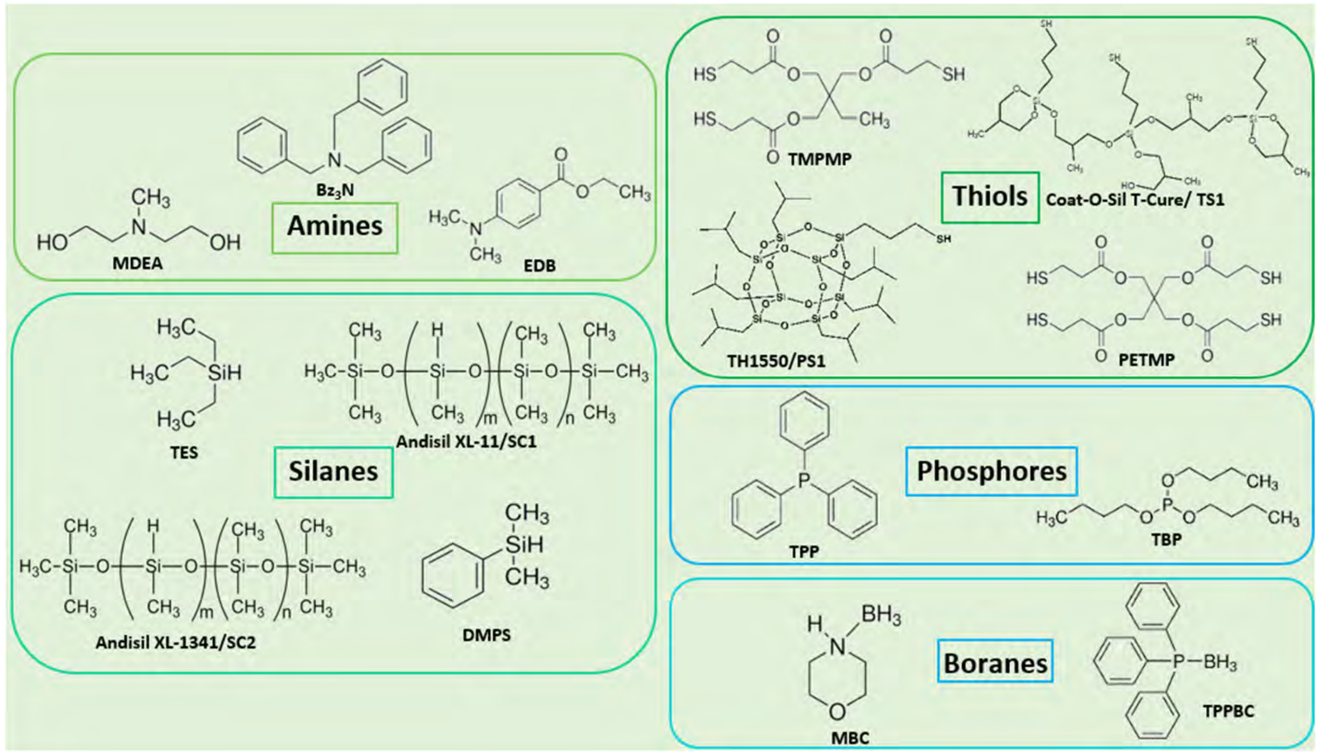
CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

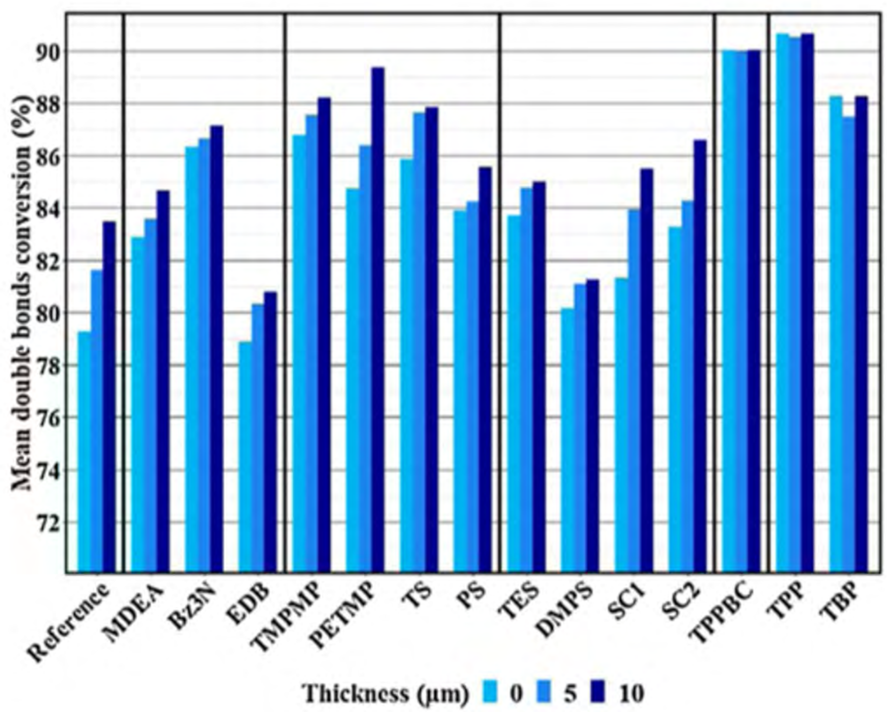
Using CRM to study oxygen inhibition – Additives tested

<u>Hydrogen donors</u>
Amine
Thiols
Silanes

<u>Reducers</u>
Borane
Phosphine
Phosphite



Using CRM to study oxygen inhibition



Double bonds conversion of the first 10 µm for each formulation at 01:02 ratio UV-cured at 5 m/min

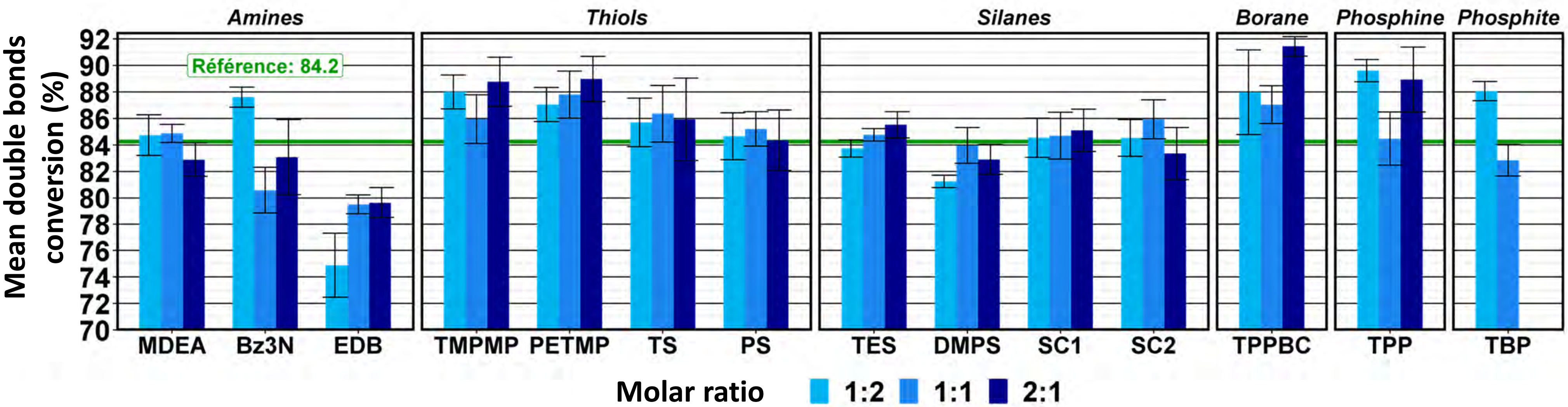
- DBC conversion increase from 0 to 10 µm for most additives
- Phosphorus-based compounds lead to higher DBC.

CRMR
Centre de recherche sur les matériaux renouvelables

A. Hermann, D. Burr, V. Landry, *Comparative study of the impact of additives against oxygen inhibition on pendulum hardness and abrasion resistance for UV-curable wood finishes*, *Prog. Org. Coat.* 148 **2020**

UNIVERSITÉ LAVAL

Using CRM to study oxygen inhibition



Impact of coinitiator addition on conversion at 5 m/min, film thickness: 100 µm

- Borane complex and phosphine give access to good improvements
- Thiols are the product family with the best conversions

CRMR
Centre de recherche sur les matériaux renouvelables

A. Hermann, D. Burr, V. Landry, *Comparative study of the impact of additives against oxygen inhibition on pendulum hardness and abrasion resistance for UV-curable wood finishes*, *Prog. Org. Coat.* 148 **2020**

UNIVERSITÉ LAVAL

Using CRM to study oxygen inhibition

Table 4-6: Impact of the addition of coinitiator summarized

Tests / Coinitiator	Dispersion	Conversion (Photo-DSC)	$T_{induction}$	Maximum photo-polymerization rate	Double bonds conversion	Pendulum Hardness	Abrasion resistance
Reference	/	+	+	+ +	+	+	-
MDEA	+ +	-	+	+	+	-	-
Bz_3N	-	-	-	-	-	-	-
EDB	+ +	-	-	+	-	-	+
TMPMP	+	-	+	+	+ +	- -	+ +
PETMP	+	- -	+	-	+ +	- -	+ +
TS	+	-	+	-	+	- -	-
PS	-	-	+	-	+	+	+
TES	+ +	+	+ +	+	+	-	-

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Using Raman Confocal for UV-curable coatings

1

Reducing Oxygen Inhibition of UV-curable acrylate coatings (radical polymerization)

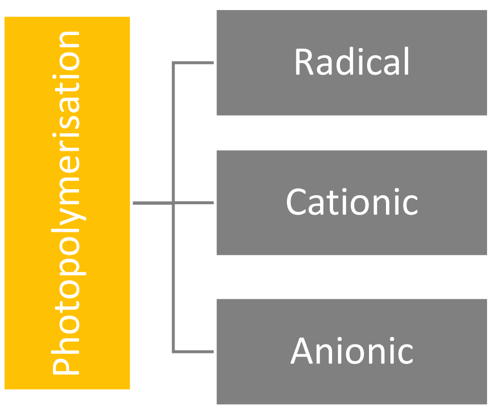
2

Hybrid free radical/cationic phase-separated UV-curable system

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Types of UV-curable coatings chemistry



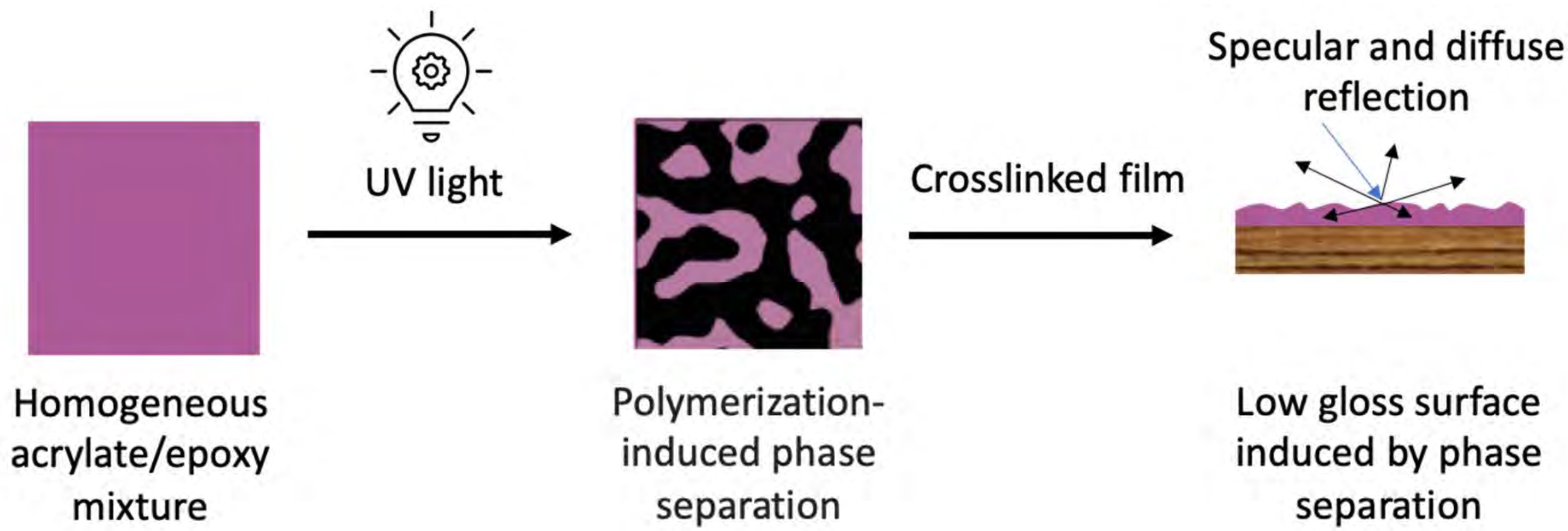
	Free radical system	Cationic system
Lifetimes of reactive species	Short	Long (Dark Cure)
Kinectic speed	Rapid	Moderate to rapid
Humidity/oxygen sensitivity	Humidity: No Oxygen: Yes	Humidity: Yes Oxygen: No
Thermal post-cure	Limited	Yes
Shrinkage	Significant	Not significant
Choice of resins and initiators	Important	Limited

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Free radical/Cationic Hybrid System

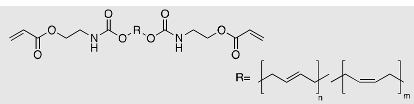
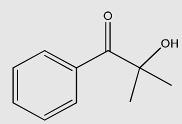
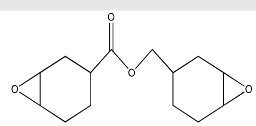
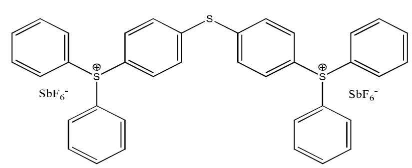
Objective of the project : decreasing gloss without using any additives
Objective in using CRM : depth profiling and phase identification



CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

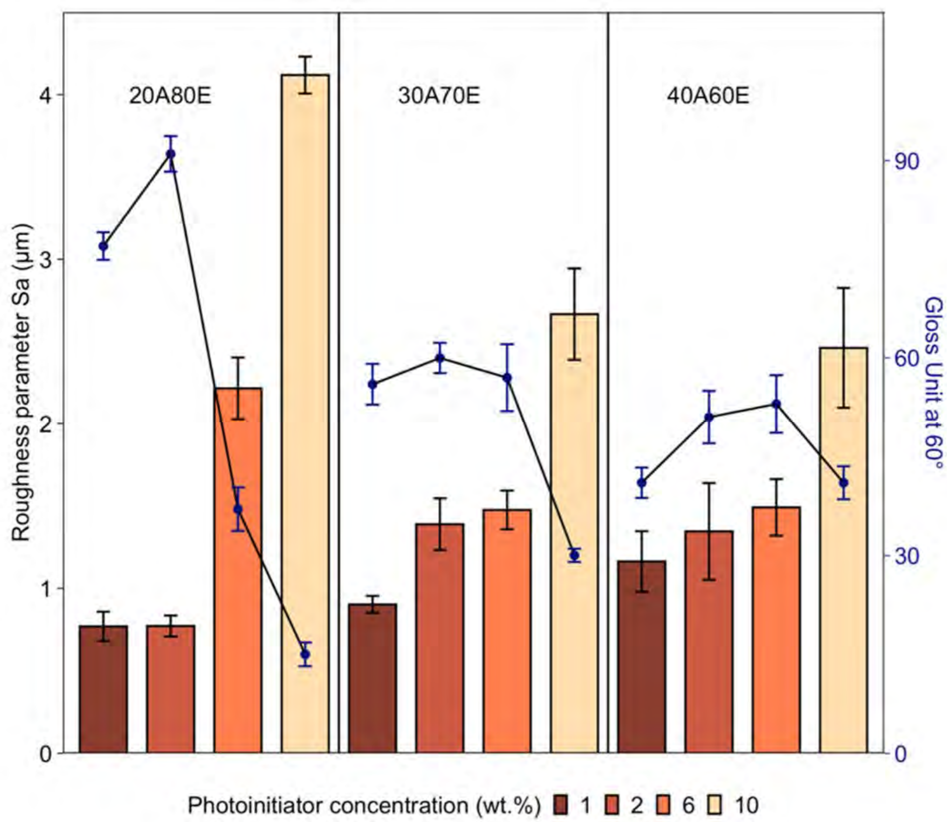
Free radical/Cationic Hybrid System

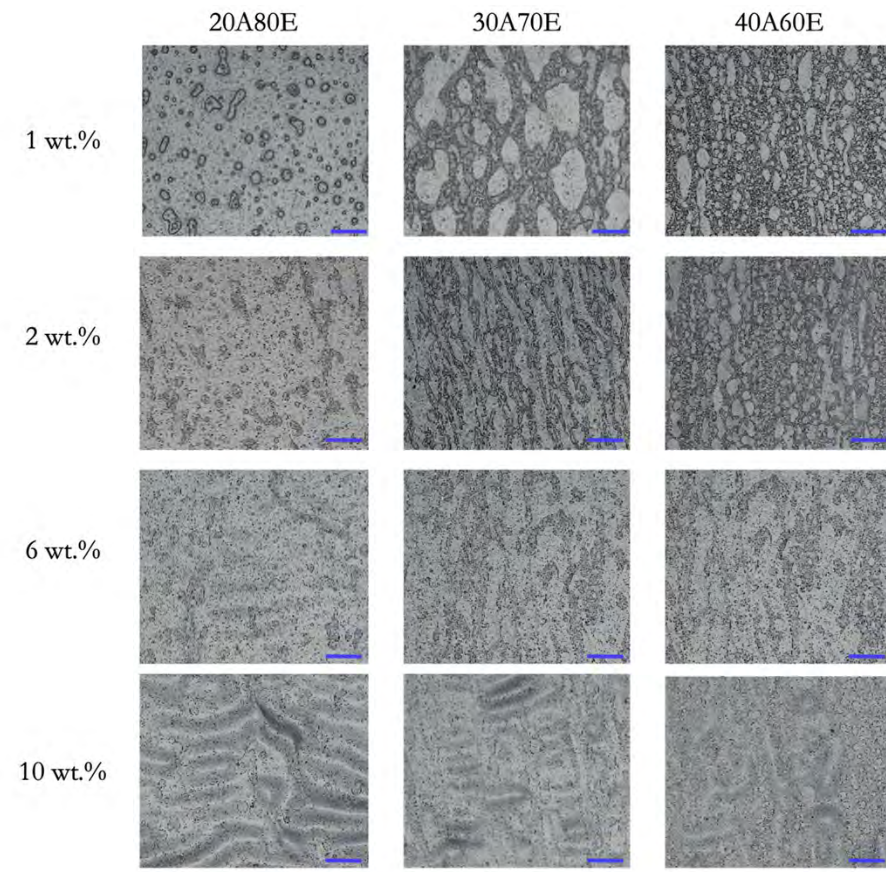
	Chemical name	Commercial name	Chemical structure	Viscosity (mPa.s^{-1})	Tg (°C)
Acrylate part (A)	Aliphatic polybutadiene urethane acrylate	Dymax BR-640D		6000 at 60°C	33
	2-Hydroxy-2-methyl-phenyl-propane-1-one	Darocure 1173 (HMPP)			
Epoxy part (E)	Cycloaliphatic epoxy	Omnilane 1005		220-250 at 25°C	145
	Triarylsulfonium hexafluoroantimonate salts	Omicat 320 TAS			

Mixture	Name	HMPP (%wt)	TAS (%wt)
100A0E	100A0E	1	2
80A20E	80A20E	1	2
50A50E	50A50E	1	2
40A60E	E3005	0,5	1
	E301	1	2
	E303	3	6
	E305	5	10
30A70E	E2005	0,5	1
	E201	1	2
	E203	3	6
	E205	5	10
20A80E	E005	0,5	1
	E01	1	2
	E03	3	6
	E05	5	10
0A100E	0A100E	1	2

Free radical/Cationic Hybrid System

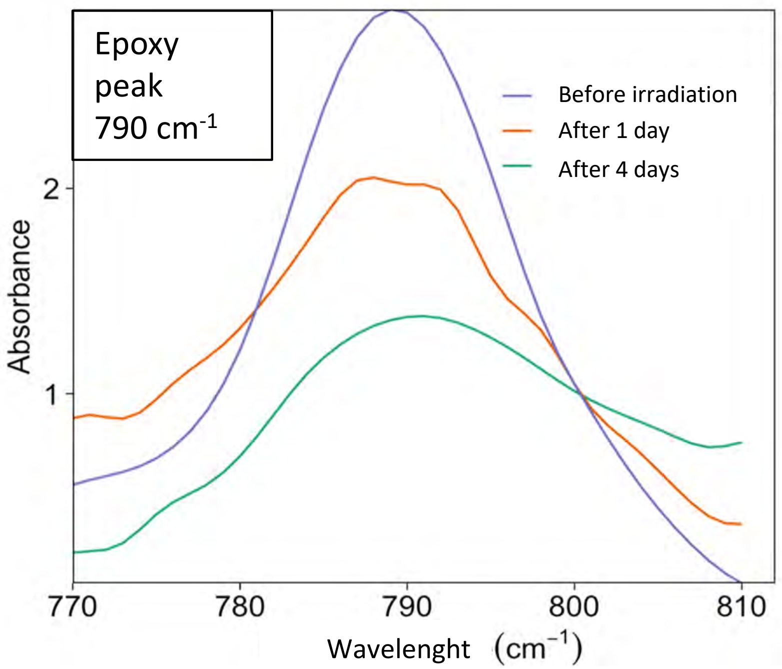
Impact of photoinitiator concentration and acrylate/epoxy ratio on **surface average roughness** (S_a), **gloss** and **morphology** for 20A80E, 30A70E, 40A60E ratios

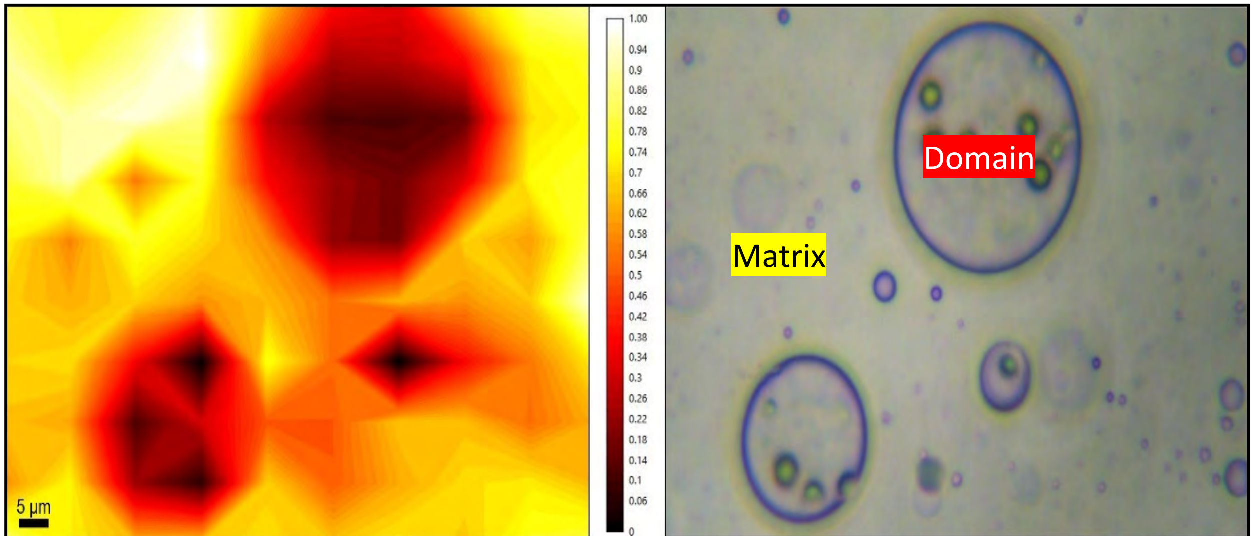




Free radical/Cationic Hybrid System – *Impact of photoinitiator*

Monitoring of cationic polymerization after 1 day and 4 days (dark polymerization).





Monitoring of the intensity of the epoxy peak at 790 cm^{-1} in function of the zone (yellow = epoxy rich, red = acrylate rich).

-Film thickness: 50 µm on alumimum panels.
-UV light intensity : 500 mW/cm^2 at 5 m/min.

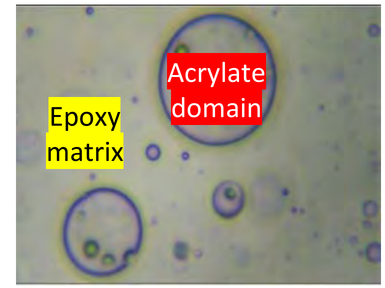
CRMR
Centre de recherche sur
les matériaux renouvelables

UNIVERSITÉ LAVAL

Calvez, I., Szczepanski, C. R., & Landry, V. (2022). Hybrid free-radical/cationic phase-separated UV-curable system: impact of photoinitiator content and monomer fraction on surface morphologies and gloss appearance. *Macromolecules*, *55*(8), 3129-3139.

Free radical/Cationic Hybrid System – *Impact of photoinitiator*

		EPOXY PART				ACRYLATE PART	
		Day 1		Day 4		Day 1	
		Domain	Matrix	Domain	Matrix	Domain	Matrix
20A80E	E005	37 ± 1	50 ± 1	54 ± 0	58 ± 0	93 ± 2	96 ± 3
	E01	42 ± 2	55 ± 1	59 ± 2	69 ± 1	95 ± 1	96 ± 1
	E03	50 ± 1	57 ± 1	63 ± 3	77 ± 5	90 ± 2	96 ± 1
	E05	62 ± 1	64 ± 2	71 ± 0	78 ± 1	91 ± 2	96 ± 1
30A70E	E2005	41 ± 1	44 ± 1	53 ± 1	54 ± 1	95 ± 3	96 ± 2
	E201	42 ± 3	49 ± 1	59 ± 2	69 ± 2	92 ± 2	95± 2
	E203	58 ± 3	65 ± 1	74 ± 2	82 ± 3	93 ± 2	98 ± 1
	E205	67 ± 1	70 ± 1	78 ± 1	90 ± 5	92 ± 3	95 ± 2
40A60E	E3005	27 ± 1	34 ± 1	39 ± 1	43 ± 1	95 ± 3	98 ± 2
	E301	37 ± 3	44 ± 1	61 ± 1	70 ± 1	94 ± 1	98 ± 1
	E303	55 ± 1	59 ± 1	71 ± 3	74 ± 2	94 ± 2	96 ± 3
	E305	69 ± 1	74 ± 1	79 ± 1	89 ± 1	92 ± 3	96 ± 2

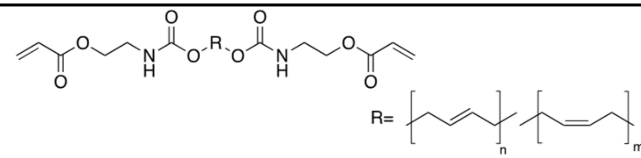
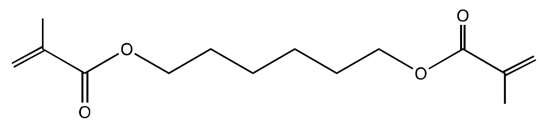
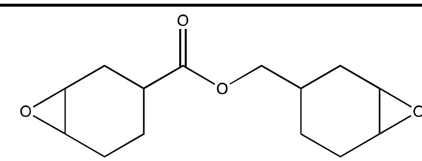
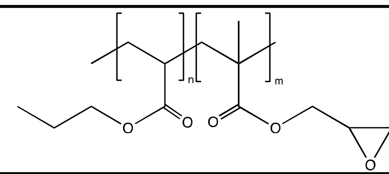


After polymerization (Day 1), the conversions for both the acrylate and epoxy parts were higher in the matrix than in the domain → **The viscosity of the acrylate component limited the diffusion of reactive species.**

The conversion increased with photoinitiator content for both the epoxy and acrylate parts.

For the epoxy part, conversion continued to increase after 4 days of dark polymerization.

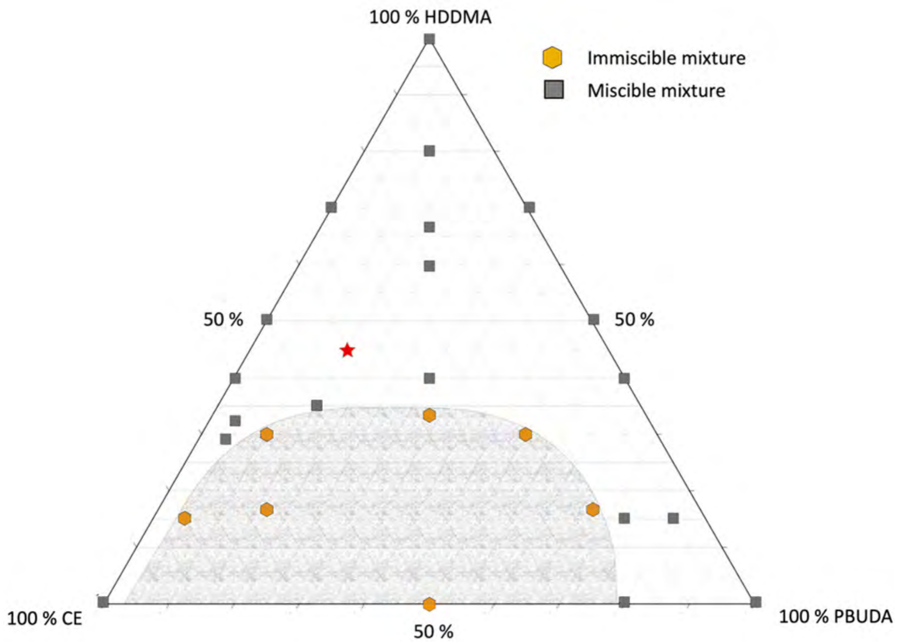
Free radical/Cationic Hybrid System

Chemical and commercial name	Chemical structure
Polybutadiene urethane diacrylate (PBUDA) - Dymax BR-640D	
1,6-hexanediol dimethacrylate (HDDMA) - Miwon Miramer M201	
Epoxycyclohexylmethyl *3,4*-epoxycyclohexanecarboxylate (CE) - Omnilane 1005	
Poly(butyl acrylate-co-glycidyl methacrylate) (PBGMA)	

CRMR
Centre de recherche sur
les matériaux renouvelables

UNIVERSITÉ
LAVAL

Free radical/Cationic Hybrid System



Terniary phase diagram of CE/PBUDA/HDDMA in a liquid state at 25^{o}C, The shaded region indicates immiscibility, and **the star represents the experimental composition selected for further analysis in this study**.

	Reference (★) *			Mixture						
	Part E	Part A	HDDMA	PBGMA						
Composition (%wt)	40	15	45	0	1	2	3	5	7	10
Viscosity (cP) at 25 °C	180-450	6000 at 60 °C	1-10	51 ± 2	59 ± 1	76 ± 5	104 ± 6	139 ± 3	207 ± 4	234 ± 5

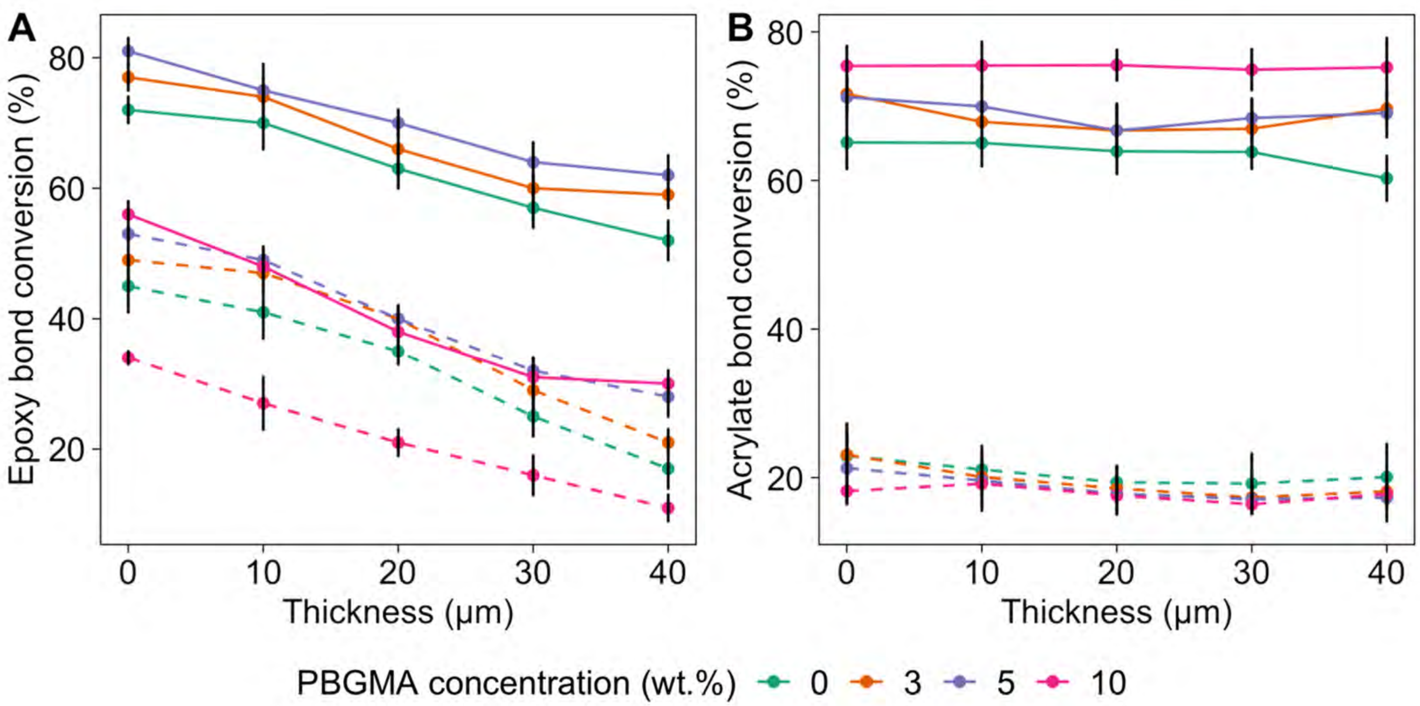
* With 1%m HMPP and 3%m iodonium salt.

CRMR
Centre de recherche sur les matériaux renouvelables

Calvez, I., Szczepanski, C. R., & Landry, V. (2022). Effect of copolymer on the wrinkle structure formation and gloss of a phase-separated ternary free-radical/cationic hybrid system for the application of self-matting coatings. Polymers, 14(12), 2371.

UNIVERSITÉ LAVAL

Free radical/Cationic Hybrid System



Conversion of (A) the epoxy part and (B) the acrylate part as a function of depth and PBGMA concentration.

Raman spectra were recorded every 10 µm in depth.

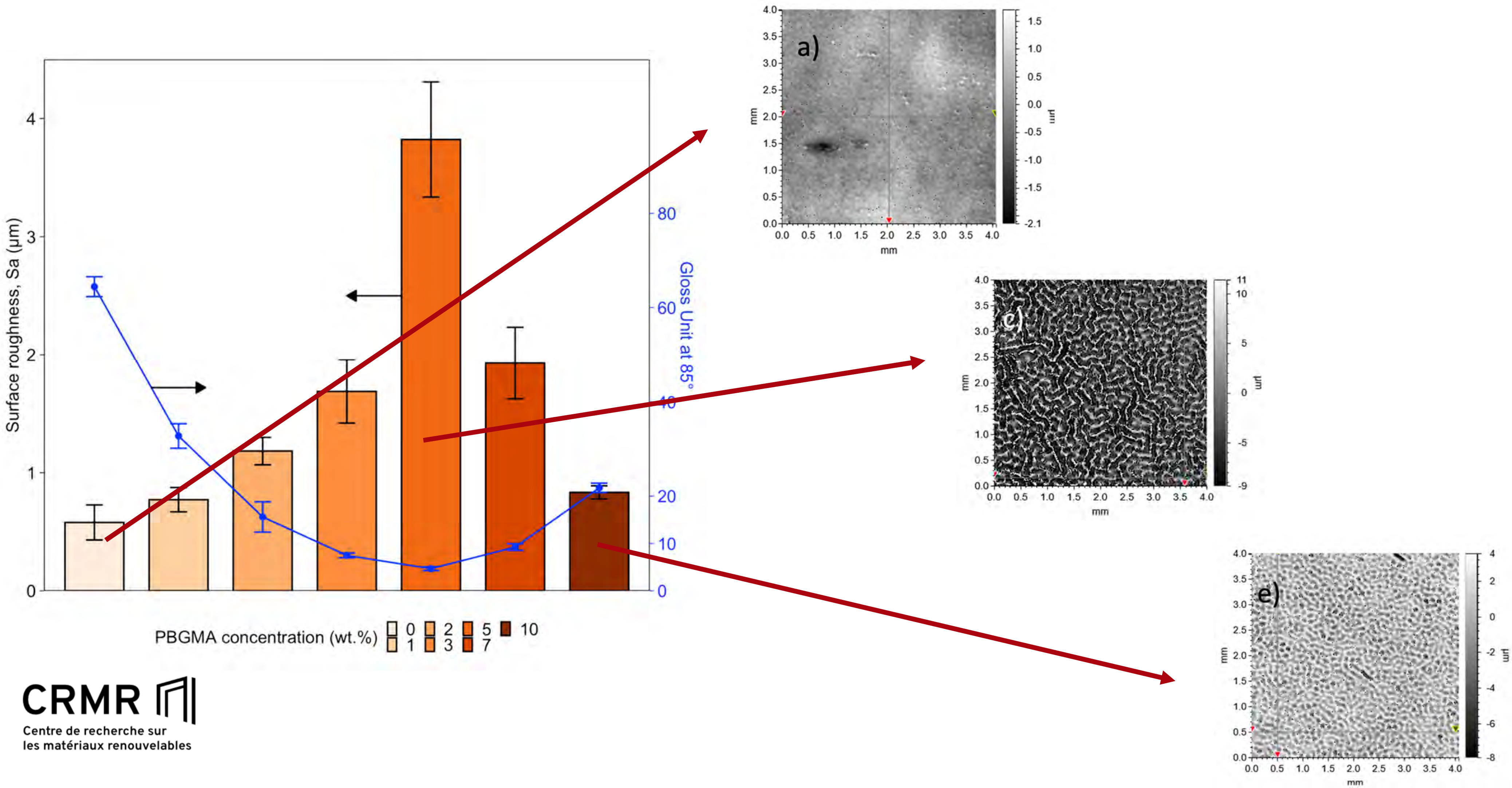
The dash lines correspond to the conversion after a first pass under UV light at 800 $mWcm^{-2}$ and the solid lines to the conversion after a second pass under UV light at 1200 $mWcm^{-2}$.

CRMR
Centre de recherche sur les matériaux renouvelables

Calvez, I., Szczepanski, C. R., & Landry, V. (2022). Effect of copolymer on the wrinkle structure formation and gloss of a phase-separated ternary free-radical/cationic hybrid system for the application of self-matting coatings. Polymers, 14(12), 2371.

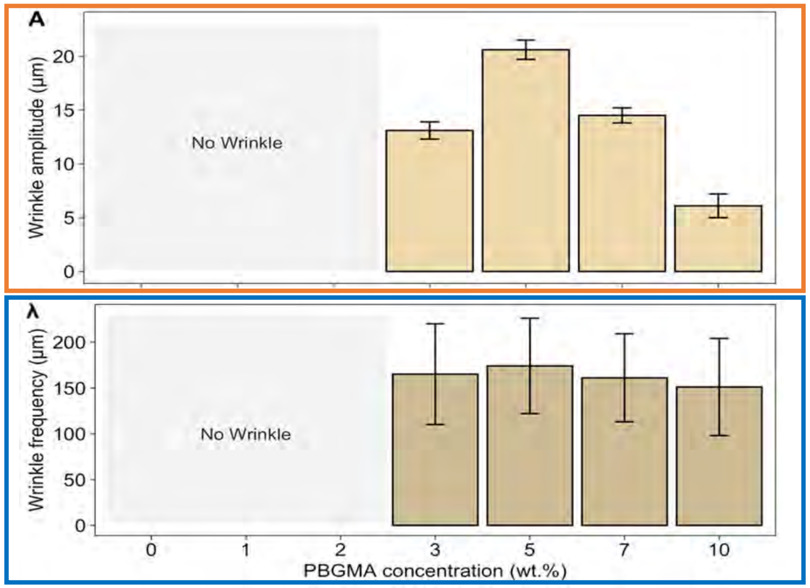
UNIVERSITÉ LAVAL

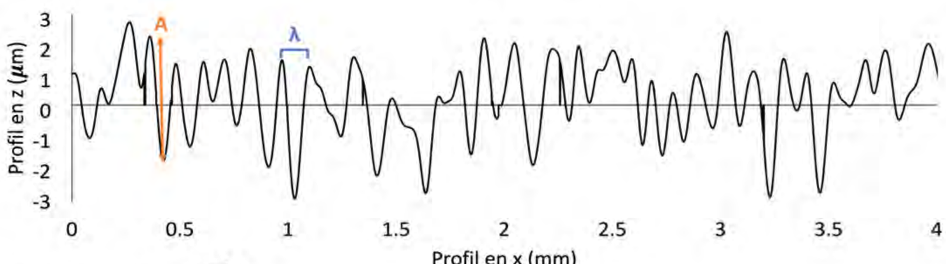
Free radical/Cationic Hybrid System

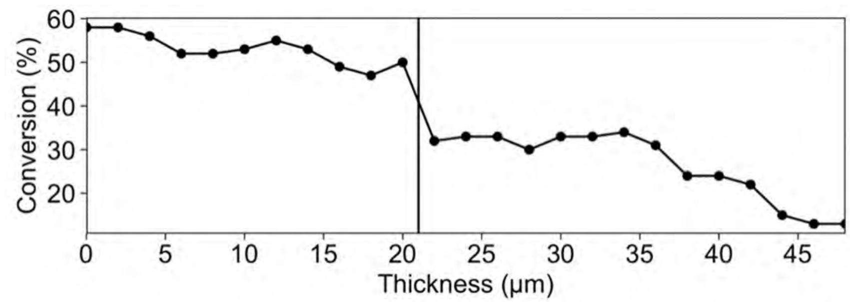


CRMR
Centre de recherche sur
les matériaux renouvelables

Free radical/Cationic Hybrid System





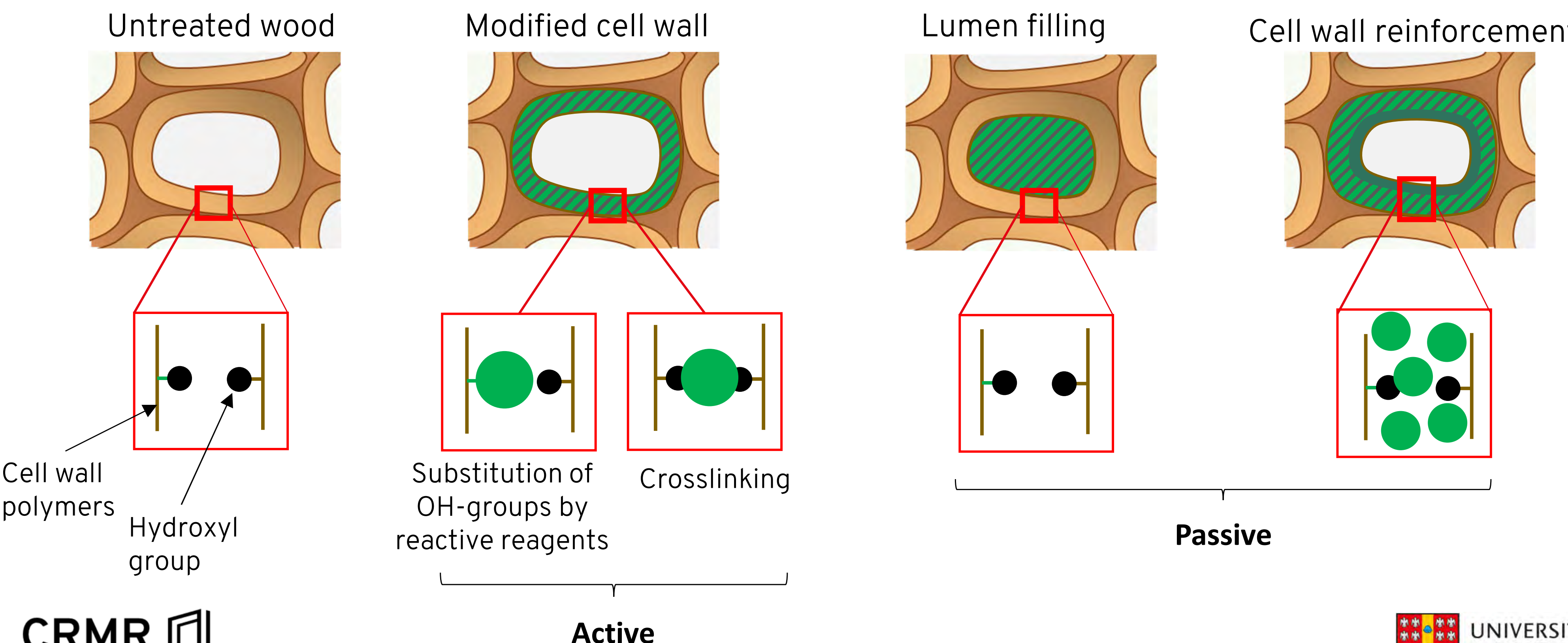


CRM analysis of conversion as a function of depth for 5 wt.% PBGMA system
→ This technique allows to obtain the thickness of the cured film by measuring the conversion in function of the thickness, and incremental measurements of 2 µm were made.

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Types of wood modification



CRMR
Centre de recherche sur les matériaux renouvelables

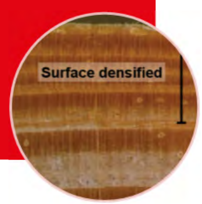
UNIVERSITÉ LAVAL

Ermeydan MA (2014) Wood cell wall modification with hydrophobic molecules. PhD thesis, University of Potsdam, Potsdam

Projects on wood modification

- Free radical polymerization of acrylates using electron beam
- Using Michael addition reaction for wood hardening

Wood hardening



- Impregnation and polymerization of phosphorylated acrylates in North American Wood Species

Fire retardancy

- Valorization of whey ultrafiltration permetate for wood stabilization

Wood stabilization

J Mater Sci (2022) 57:6656–6668

Composites & nanocomposites

Chemical surface densification of hardwood through lateral monomer impregnation and in situ EB polymerization, Part II: effect of irradiation dose on hardness, wood chemistry and polymer conversion

Juliette Triquet[1,2], Pierre Blanchet[1,2,3], and Véronic Landry[1,2,3,*]

Wood Science and Technology (2024) 58:1199–1225
https://doi.org/10.1007/s00226-024-01564-z

ORIGINAL

Chemical surface densification of sugar maple through Michael addition reaction

Vahideh Akbari[1,2] · Stéphanie Vanslambrouck[3] · Véronic Landry[1,2]

ELSEVIER

Journal of Materials Research and Technology

Volume 29, March–April 2024, Pages 1911-1922

From waste to building material: How whey ultrafiltration permeate can increase wood stability

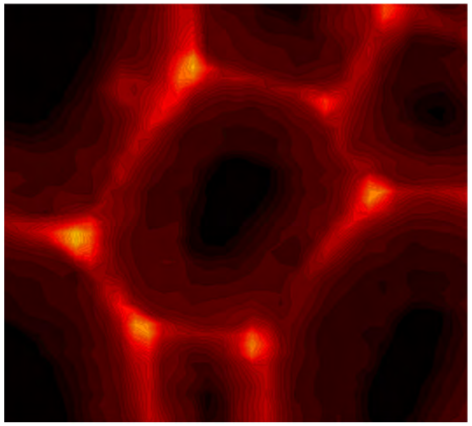
Rémi Cadieux-Lynch [a], Emma Leroux [a], Aurélien Hermann [a], Solène Pellerin [a], Assira Keralta [a], Maude Blouin [d], Jules Larouche [d], Jacopo Profili [b c], Julien Chamberland [d], Véronic Landry [a]

Using CRM to study wood modification

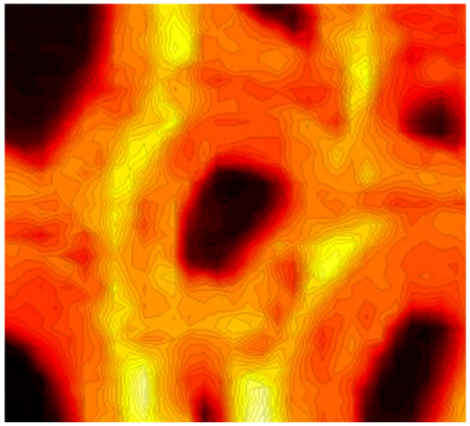
Wood regions are distinguished by characteristic peaks of cellulose (**1175–1070 cm^{-1}**) and lignin (**1620–1580 cm^{-1}**).

Acrylic polymers can be identified by specific peaks related to the C=C bond, detected at **1636 cm^{-1}**, 1420 cm^{-1}, and 810 cm^{-1}. These markers allow for the analysis of wood components and polymers.

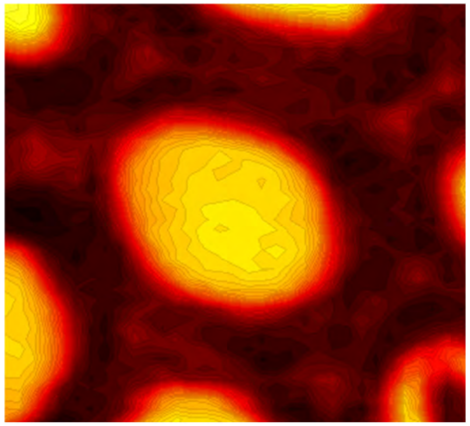
Lignin



Cellulose



C=C of acrylic groups



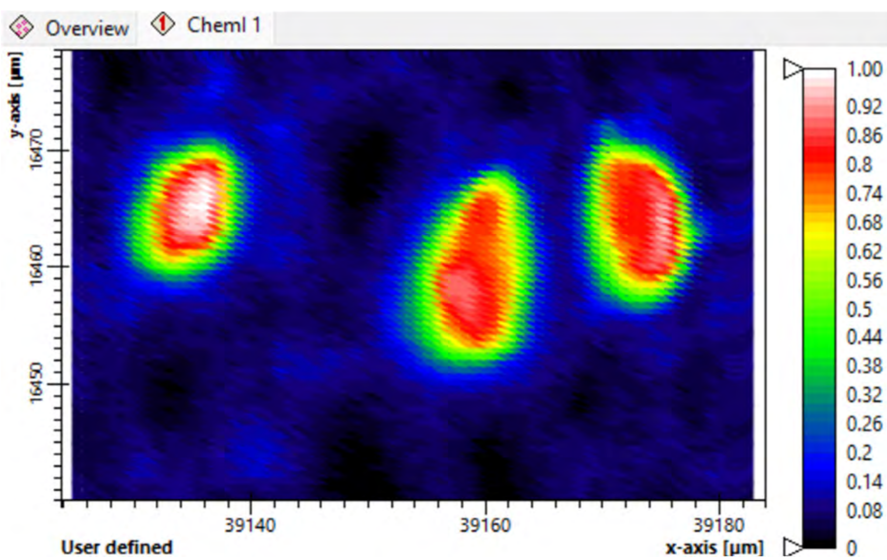
CRMR Centre de recherche sur les matériaux renouvelables

Université Laval

Akbari *et al*, Chemical surface densification of sugar maple through Michael addition reaction. 2024

Using CRM to study wood modification

To detect the presence of chemicals in wood, **chemical mapping** can be used.



Chemical mapping allows for visualizing the spatial distribution of the chemical composition of a sample by collecting Raman spectra at each point during analysis.

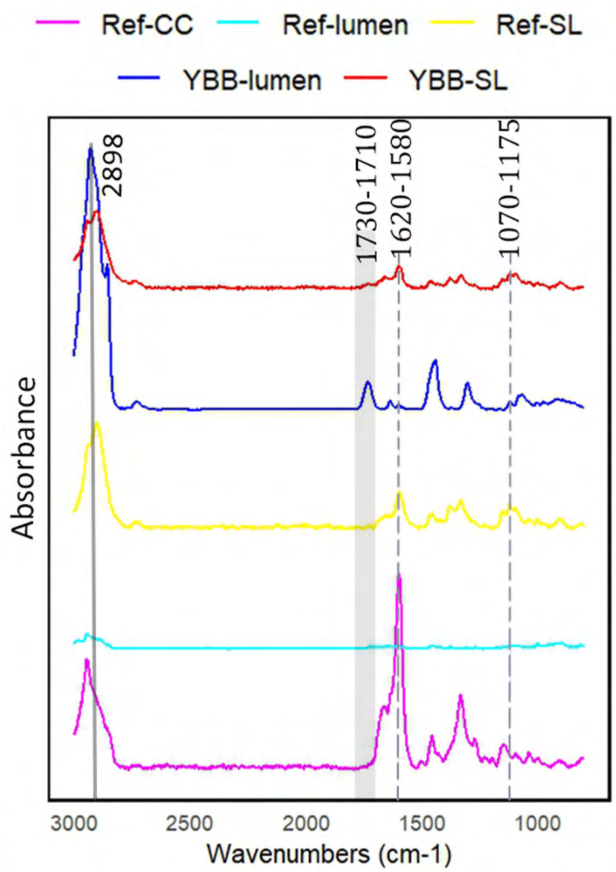
By analyzing specific Raman peaks, the technique generates a map showing the distribution of different chemical species or functional groups within the sample.

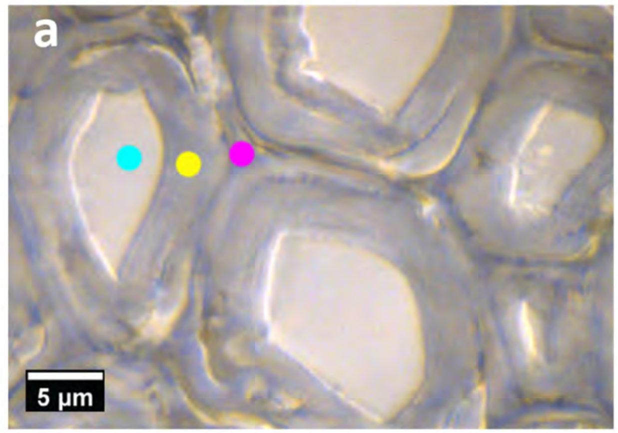
CRMR
Centre de recherche sur les matériaux renouvelables

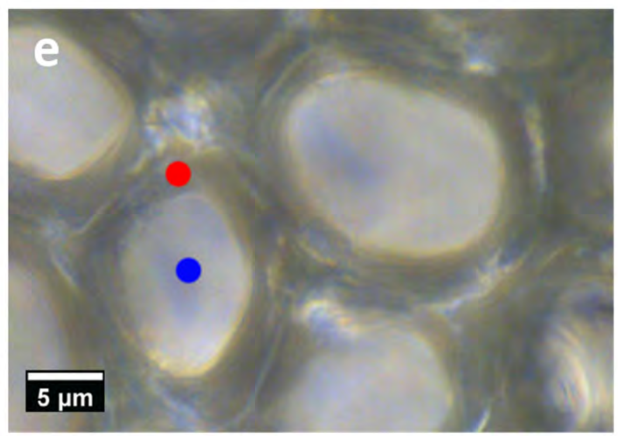
UNIVERSITÉ LAVAL

Chemical densification – Passive modification (lumen)

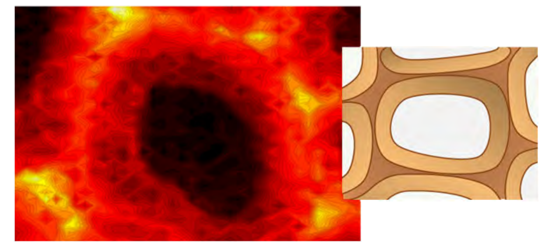
Surface impregnation of yellow birch by acrylate monomers polymerized by electron beam



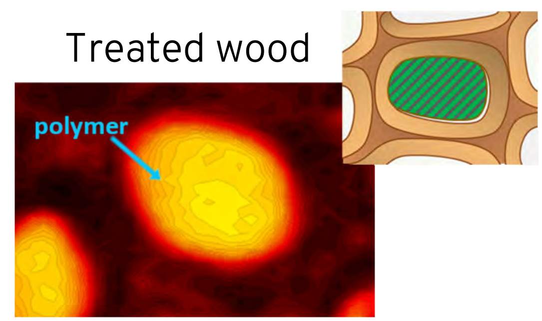




Untreated wood



Treated wood

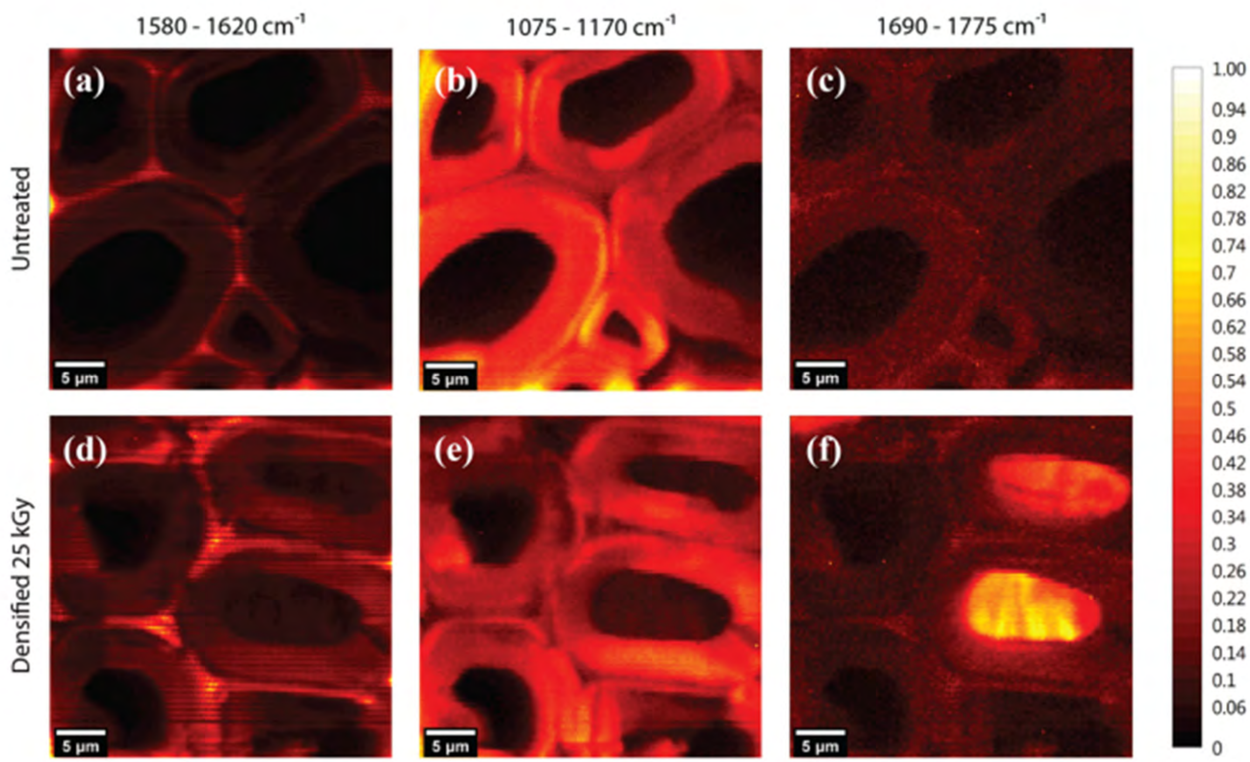


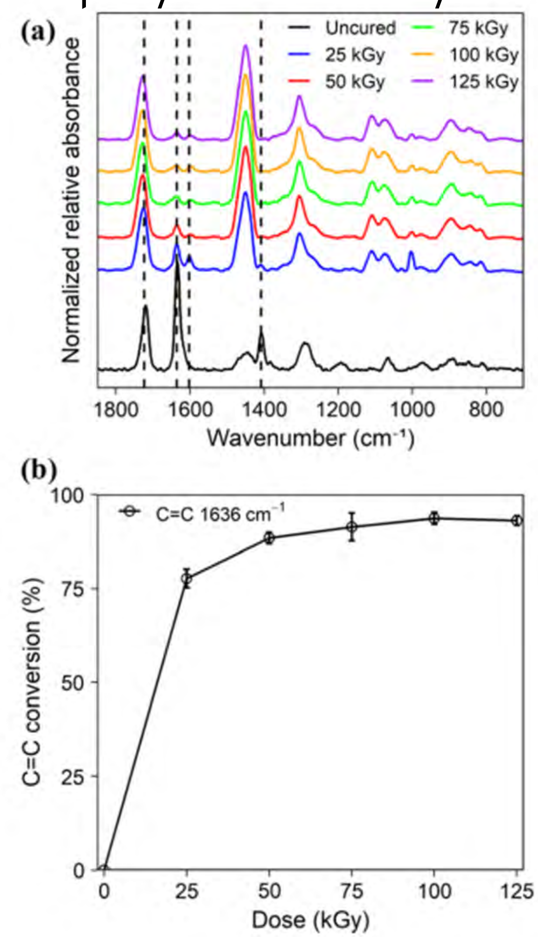
CRMR | Centre de recherche su les matériaux renouvelables

UNIVERSITÉ LAVAL

Chemical densification – Passive modification (lumen)

Surface impregnation of yellow birch by acrylate monomers polymerized by electron beam (25, 50, 75, 100, 125 kGy)





Chemical densification – Passive modification (lumen)

- **Michael addition** reaction between malonate and acrylate;
- **With and without photopolymerization**

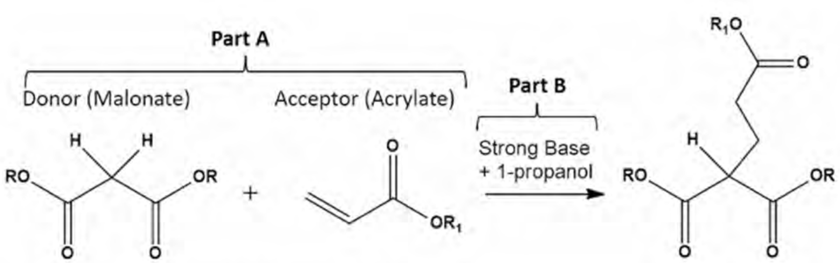
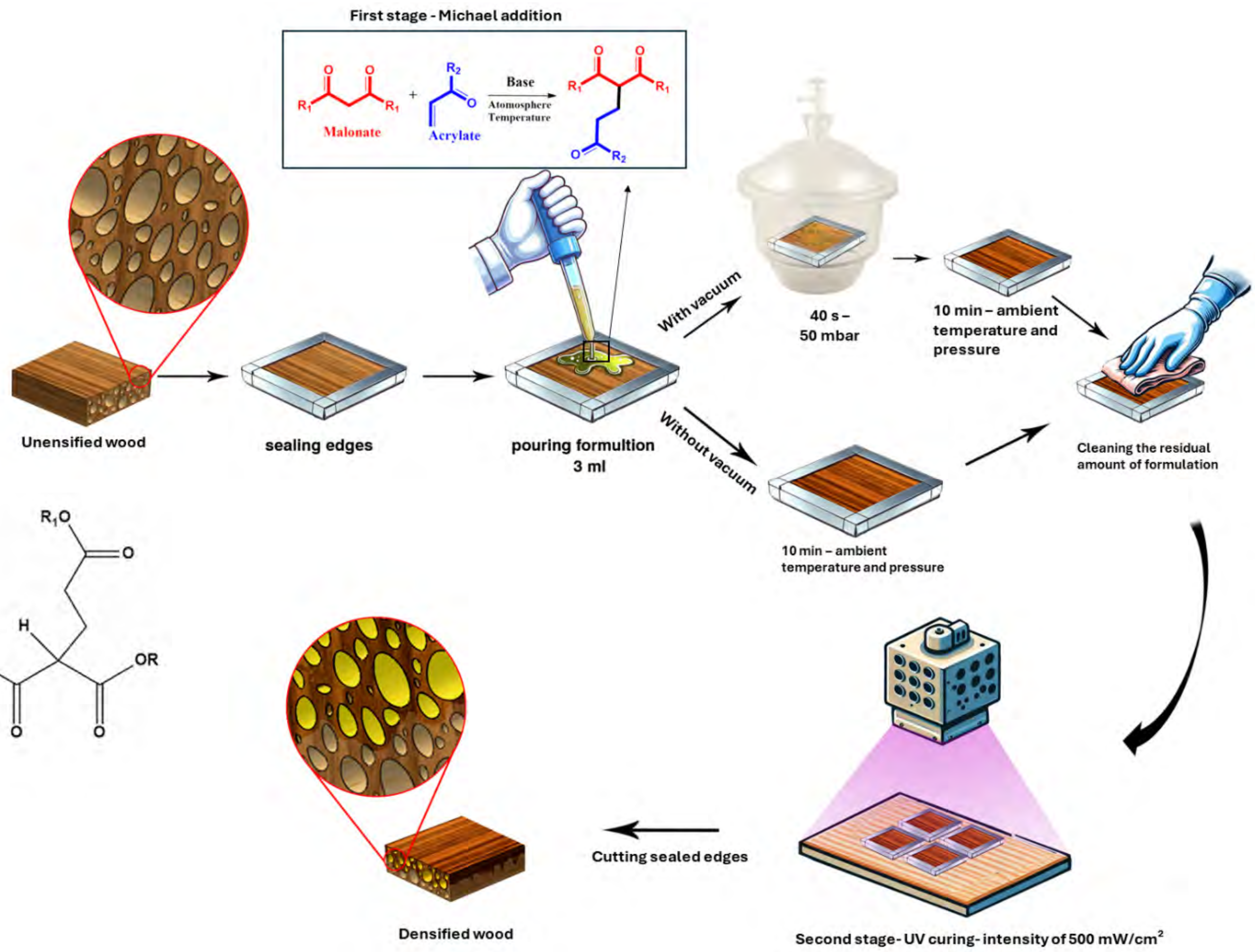


Fig. 1 Michael addition reaction between malonate and acrylate



CRMR
Centre de recherche sur
les matériaux renouvelables

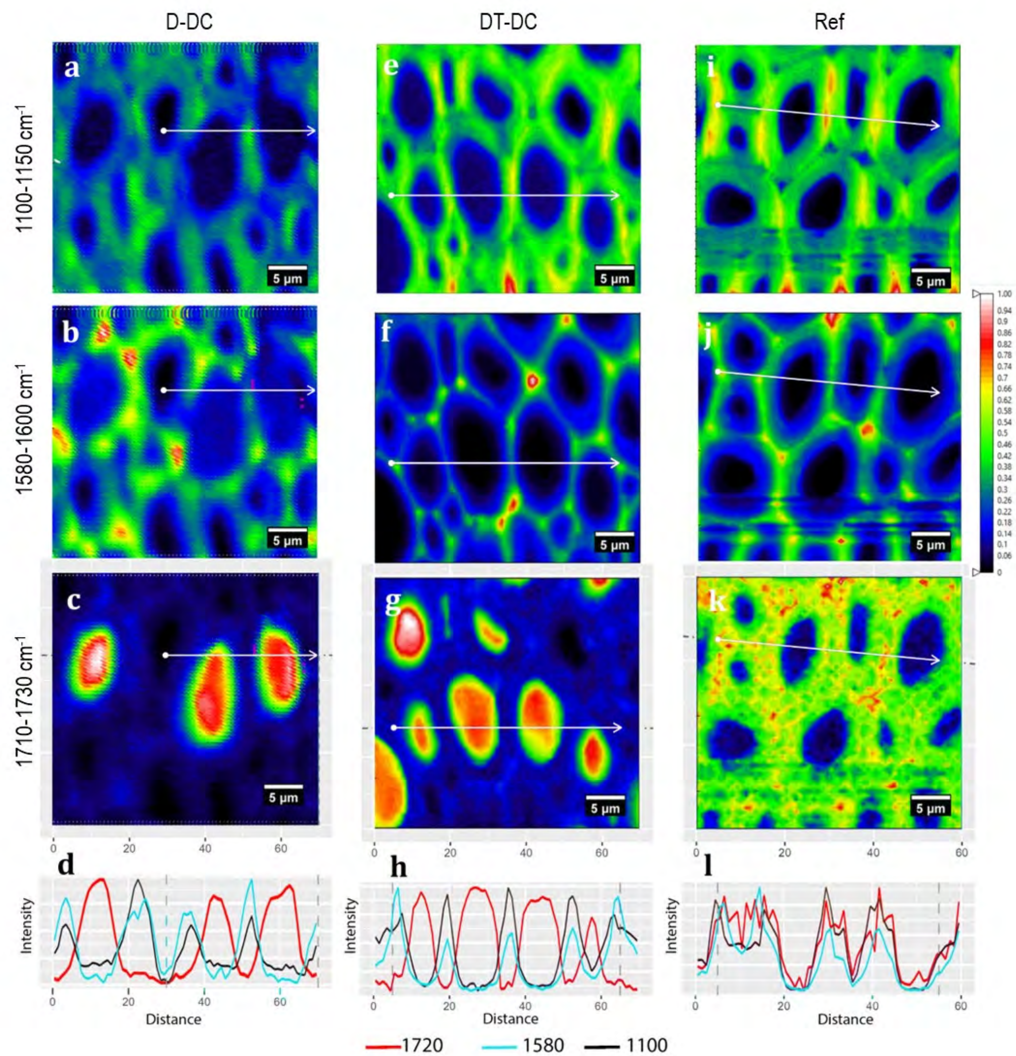
Chemical densification – Passive modification (lumen)

D-DC : single cure (Michael addition)

DT-DC : dual-cure (Michael addition and photopolymerization)

The images show chemical mapping based on cellulose (1075–1170 cm^{-1}: a, e, i), lignin (1580–1620 cm^{-1}: b, f, j), and carbonyls (1690–1775 cm^{-1}: c, g, k).

The intensity plots (d, h, l) represent the distribution along the measured distance, corresponding to the arrows indicated on each sample.



Chemical densification – Active modification (cell wall)

1 000 kg of whole milk

→ **Cheese production** →

120 kg

880 kg of whey

→ **Ultrafiltration Diafiltration** →

22 kg

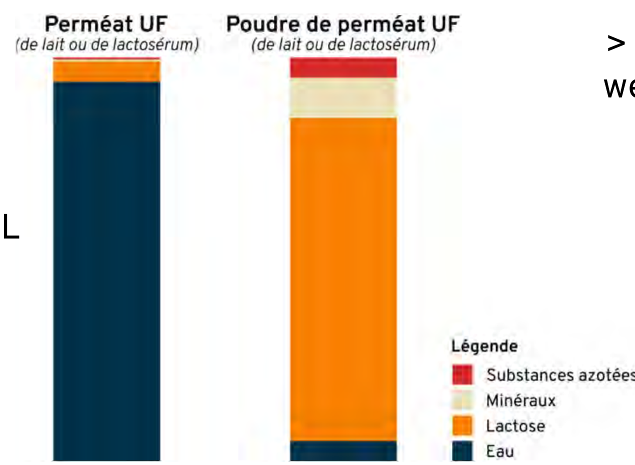
→ **PUL**

858 kg

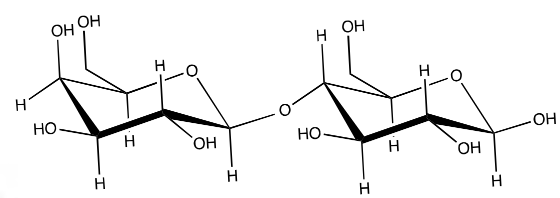
- Animal feed
- Lactose powder
- Platform molecules
- Mineral salts

→ **Expensive treatments**

A solid content of ~5%
Chemical Oxygen Demand ~ 80 g/L
Biochemical Oxygen Demand ~ 50 g/L
Pollution potential



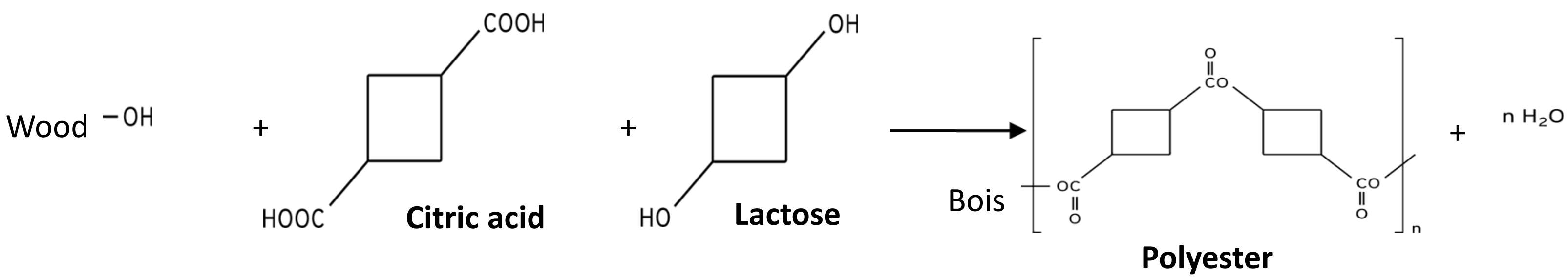
> 88% of lactose (on a dry weight basis), a saccharide

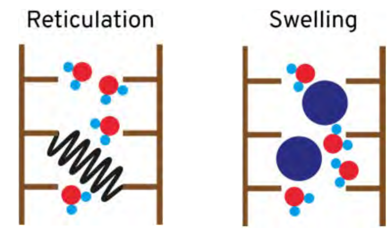


CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Chemical densification – Active modification (cell wall)





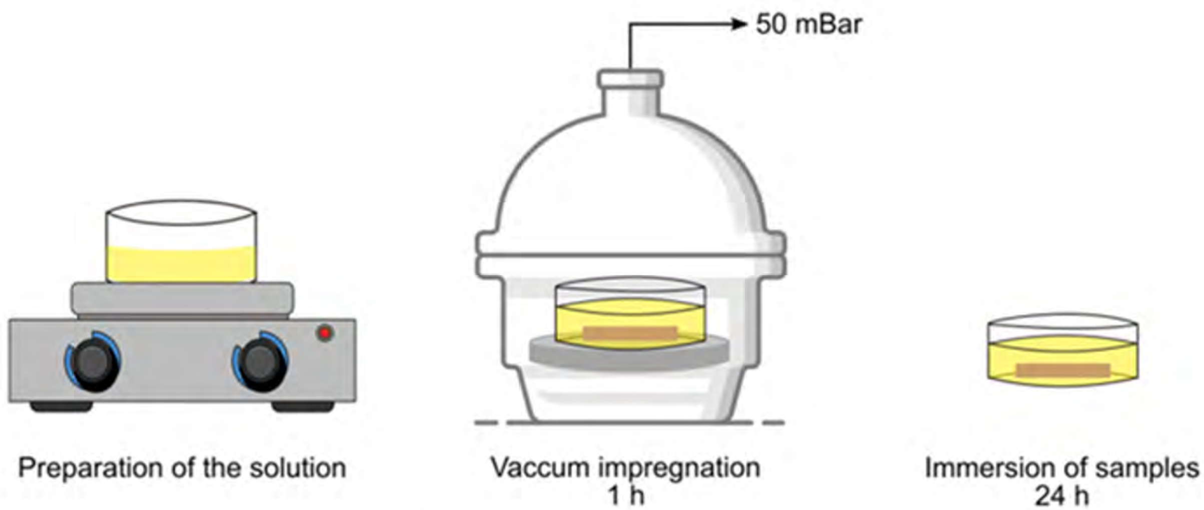
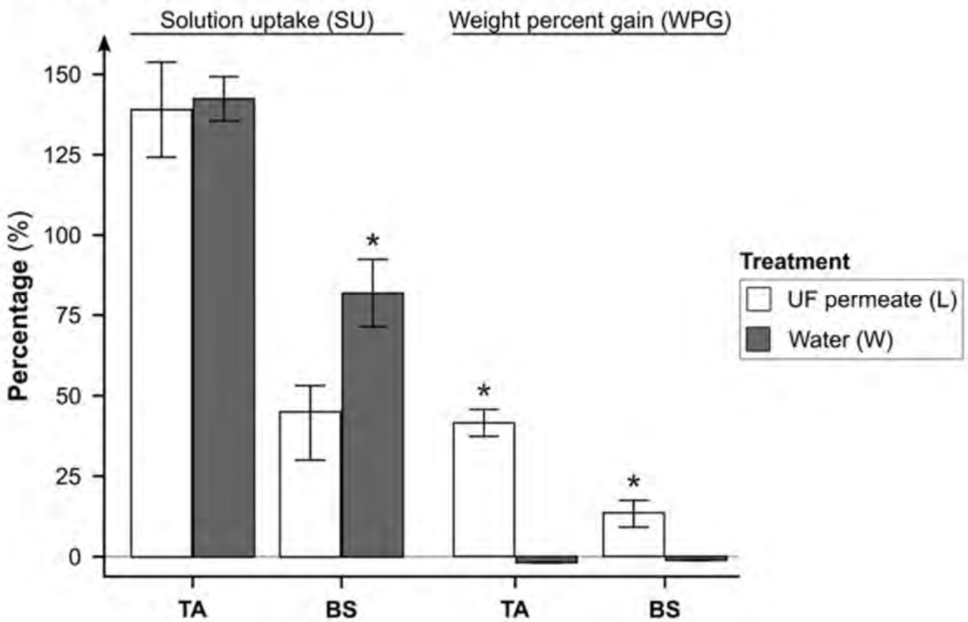


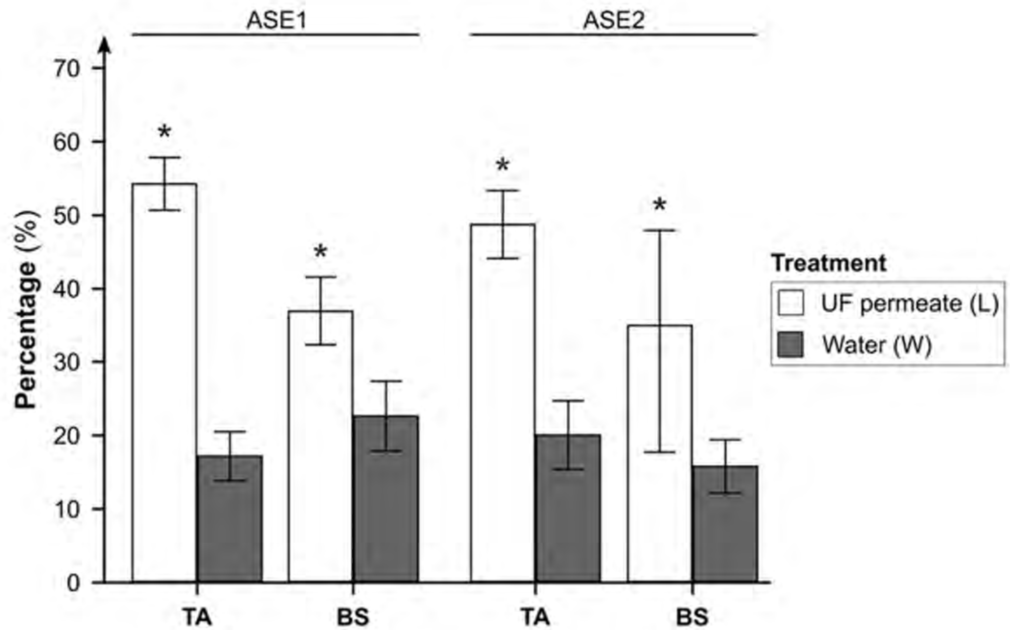
Fig. 2. Wood impregnation process.

CRMR
Centre de recherche sur
les matériaux renouvelables

UNIVERSITÉ
LAVAL

Chemical densification – Active modification (cell wall)





The **ASE** was calculated from the volumetric swelling coefficient (S(%)) of untreated (Su) and treated samples (St)

CRMR
Centre de recherche sur les matériaux renouvelables

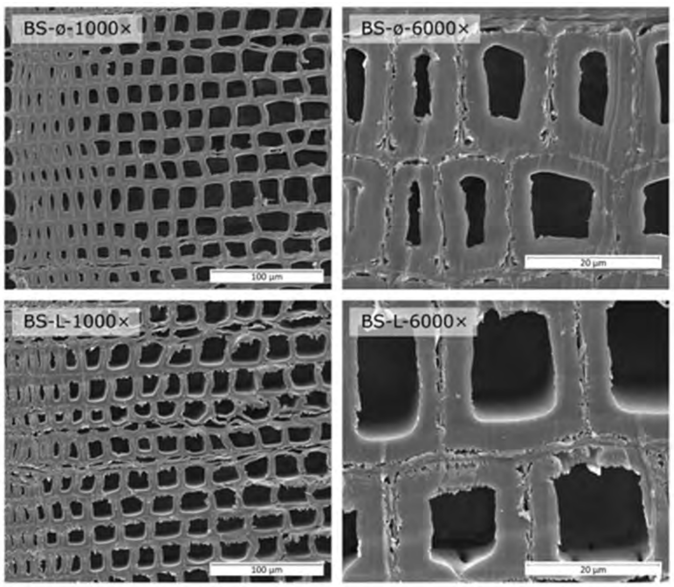
$$ASE(\%) = \frac{S_u - S_t}{S_u} \times 100$$

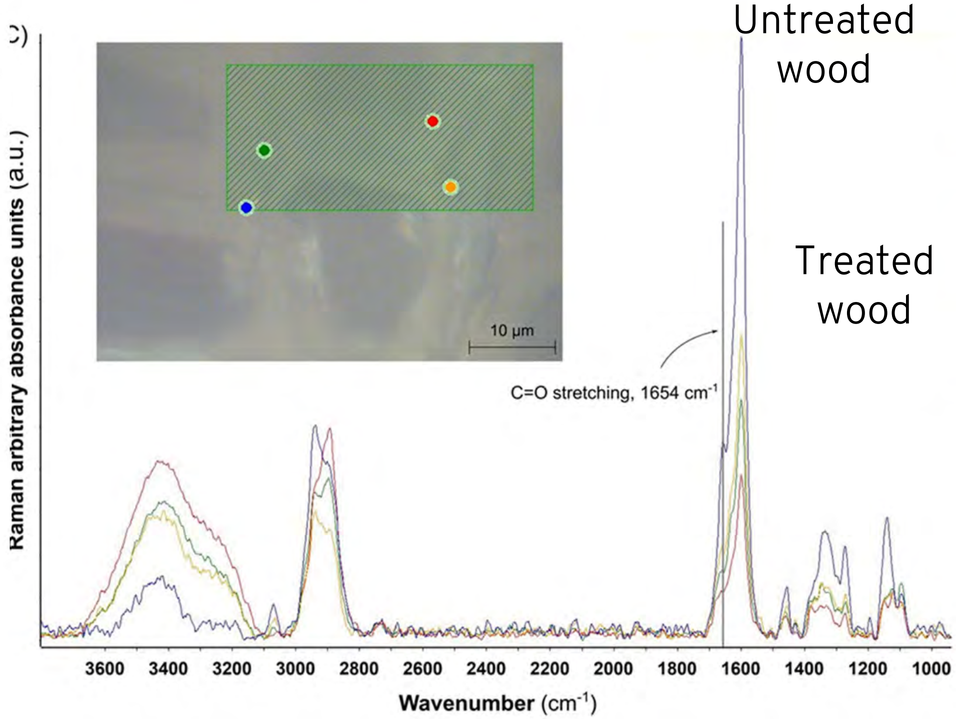
$$S(\%) = \frac{V_f - V_i}{V_i} \times 100$$

UNIVERSITÉ LAVAL

Chemical densification – Active modification (cell wall)

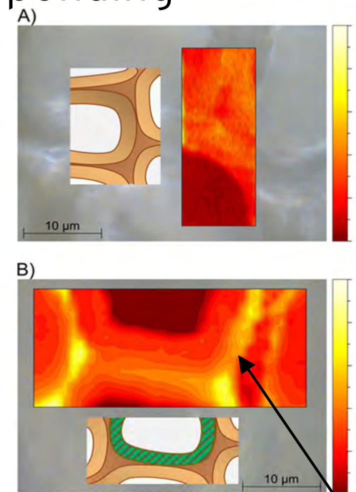
Chemical mapping, focused on the intensity in the 1610-1590 cm^{-1} range, corresponding to the C=O stretching vibration peak of the ester





Untreated wood

Treated wood



Cell wall penetration

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

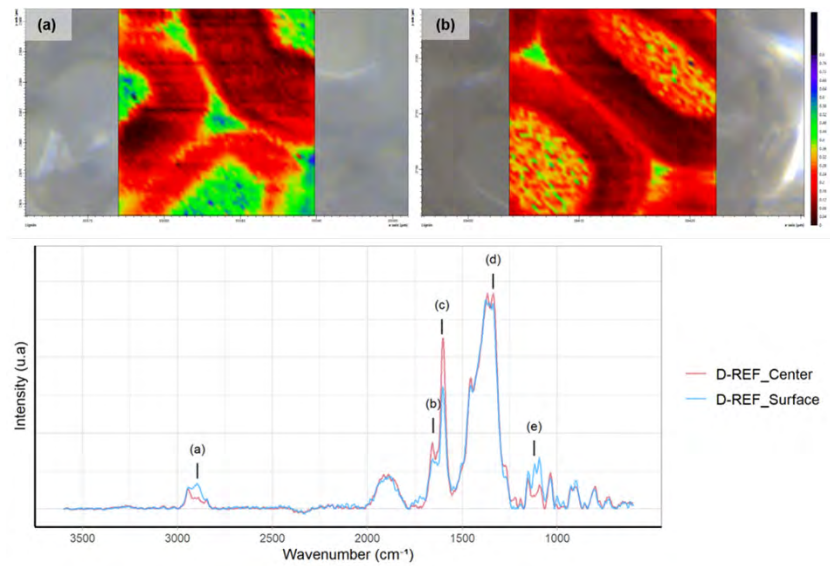
Cadieux-Lynch *et al*, From waste to building material: How whey ultrafiltration permeate can increase wood stability . 2024

Conclusions

- Confocal Raman microscopy is a powerful tool **for studying various gradients**.

- Its ability to combine **chemical composition** analysis with **high-resolution X-Y microscopy, as well as depth profiling in the Z-axis**, provides a comprehensive understanding of materials at the microscopic level.

- The versatility of this technique opens the door to a wide range of applications



Ex. : Wood delignification

CRMR
Centre de recherche sur les matériaux renouvelables

UNIVERSITÉ LAVAL

Thank you !

veronic.landry@sbf.ulaval.ca

CRMR Centre de recherche sur les matériaux renouvelables
NSERC CRSNG
Fonds de recherche Nature et technologies Québec
CRIF
CIRCERB INDUSTRIAL RESEARCH CHAIR ON ECO-RESPONSIBLE WOOD CONSTRUCTION
UNIVERSITÉ LAVAL