Presentation on the 4th of October 2022, JEPO

Cellulose nanocrystals modification by « grafting from » ring opening polymerization of a cyclic carbonate

Lille – Leuven Collaboration

Michaël Lalanne-Tisné

Supervisors: Pr. P. Zinck and Pr. W. Thielemans

Co-supervisor: Dr. A. Favrelle-Huret

Overview

I. Context and Aim
  - Cellulose
  - Cellulose nanocrystals
  - Cellulose nanocrystals modification

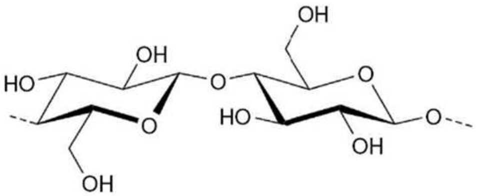
II. Polycarbonate Grafting
  - Catalyst comparison
  - Analysis

III. Conclusion

I. Context and Aim

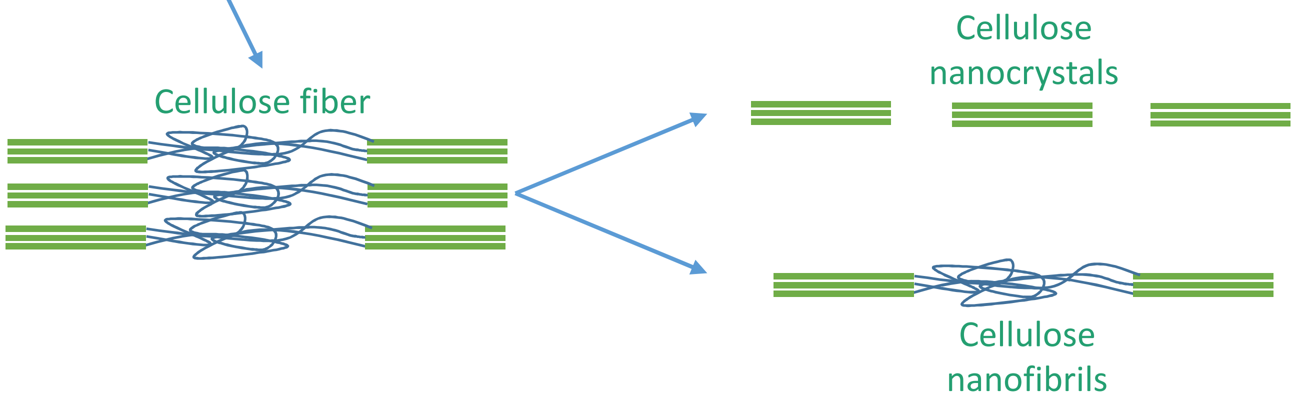
Cellulose

- Polysaccharide



- Most common biopolymer on the planet (annual production >10^{10} tons)

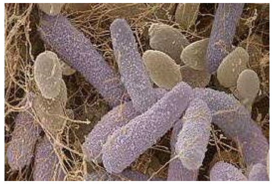
Different sources of cellulose: (1) wood, (2) tunicate, (3) Acetobacter xylinum



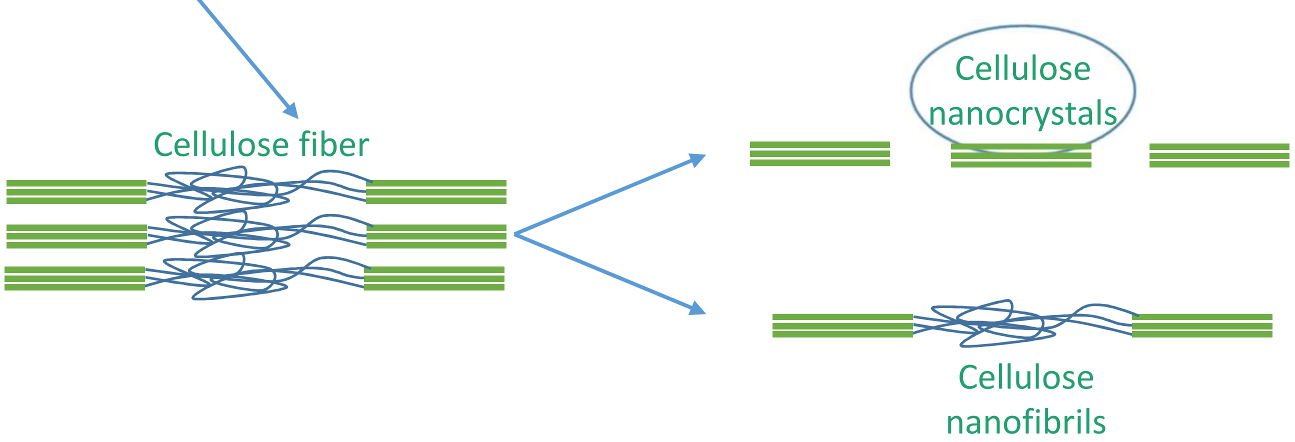
Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479–3500
S. Eyley, C. Schütz and W. Thielemans, in *Cellulose Science and Technology*, eds. T. Rosenau, A. Potthast and J. Hell, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2018, pp. 223–252

I. Context and Aim

Cellulose nanocrystals

Different sources of cellulose: (1) wood, (2) tunicate, (3) Acetobacter xylinum

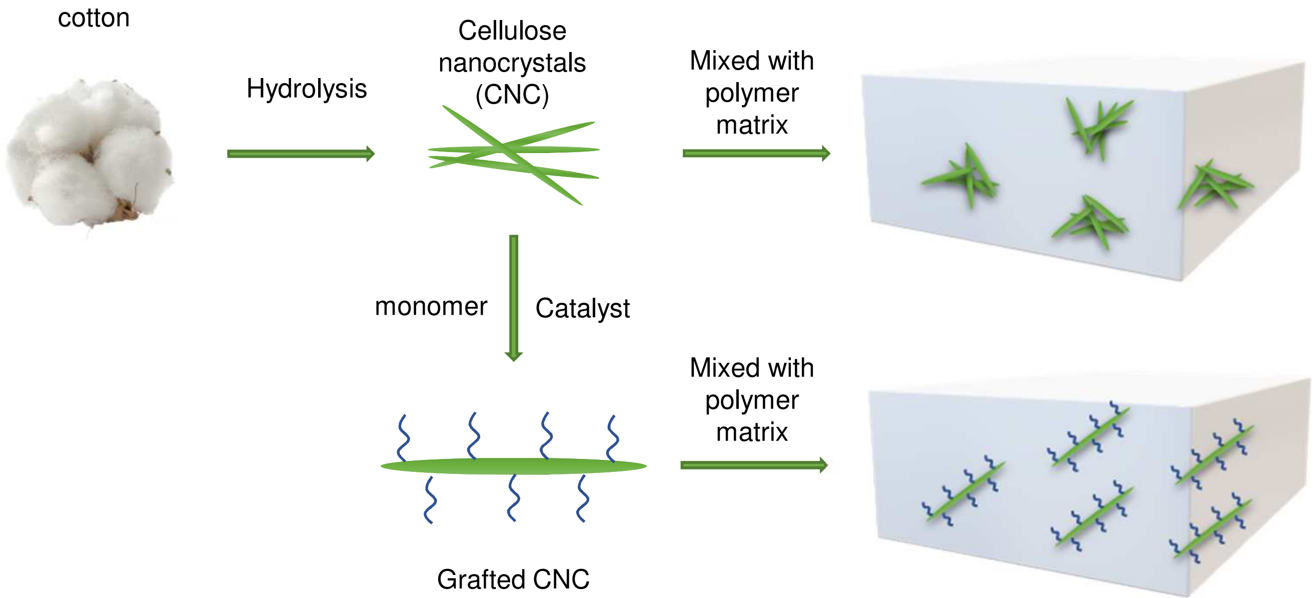


- Very stiff (> 110 GPa) rod-like material (4-20nm x 50+nm)
- Nanocellulose produced at industrial scale
- Lot of functionalisations possible, lot of applications
- Good candidate as reinforcement

G. Siqueira, J. Bras and A. Dufresne, *Polymers*, 2010, **2**, 728–765
D. Bondeson, A. Mathew and K. Oksman, *Cellulose*, 2006, **13**, 171–180
S. J. Eichhorn., A. Dufresne, M. Aranguren & al, *J Mater Sci*, 2010, **45**, 1–33

I. Context and Aim

Cellulose nanocrystals modification



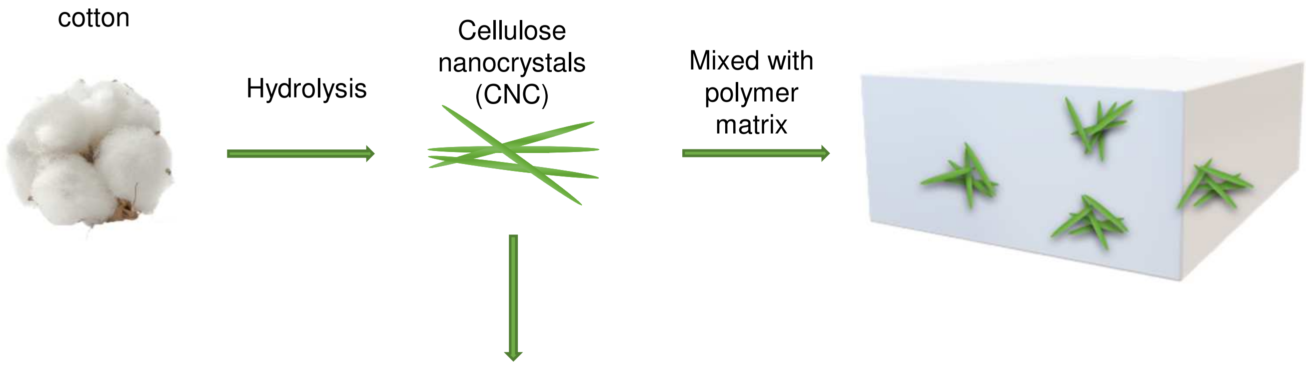
- Fiber clusters
- Weak physical properties

- Good fiber dispersion
- Enhanced properties

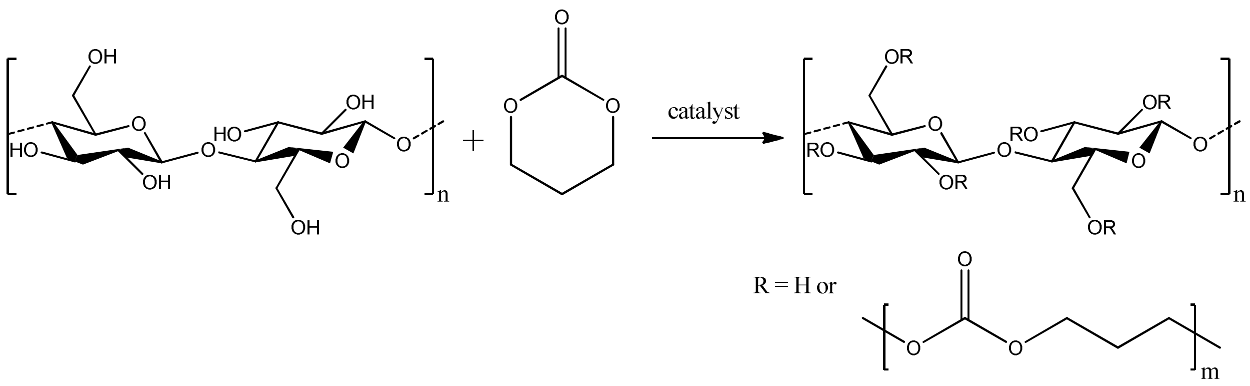
J.-C. Liu, R. J. Moon, A. Rudie and J. P. Youngblood, *Holzforschung*, 2014, **68**, 283–290.
Y. Habibi, *Chem. Soc. Rev.*, 2014, **43**, 1519–1542.
S. Eyley and W. Thielemans, *Nanoscale*, 2014, **6**, 7764–7779.
Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479–3500.

I. Context and Aim

Cellulose nanocrystals modification



- ❖ Fiber clusters
- ❖ Weak physical properties

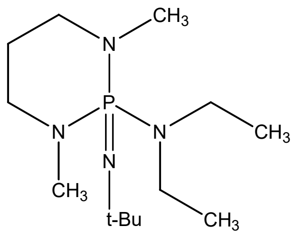


- CNC-OH as co-initiator

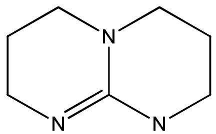
J.-C. Liu, R. J. Moon, A. Rudie and J. P. Youngblood, *Holzforschung*, 2014, **68**, 283–290.
Y. Habibi, *Chem. Soc. Rev.*, 2014, **43**, 1519–1542.
S. Eyley and W. Thielemans, *Nanoscale*, 2014, **6**, 7764–7779.
Y. Habibi, L. A. Lucia and O. J. Rojas, *Chem. Rev.*, 2010, **110**, 3479–3500.

II. Polycarbonate Grafting

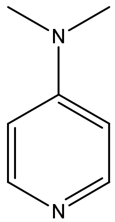
Catalysts comparison



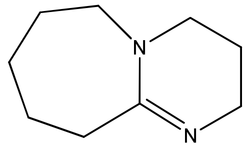
BEMP



TBD



DMAP



DBU

Reactions performed at 25°C over 5h in THF, TMC/cat/OH ratio of 500/1/50

Catalyst	Conversion	%w grafts*	grafting efficiency	Mn homopolymer	D
BEMP	0.48	**35**	8.5%	38000	1.8
TBD	0.99	**51**	16.7%	20600	1.9
DMAP	0.44	**25**	5.2%	40400	1.7
DBU	0.06	**12**	2.2%		

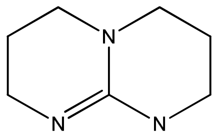
*similar reactions for lactide yield 20% grafts and less than 5% grafting yield

- Only TBD leads to full conversion of monomer
- DMAP, BEMP and DBU do not fully convert TMC even for longer reaction time

M. Stepanova, I. Averianov, I. Gofman, O. Solomahka, Y. Nashchekina, V. Korzhikov-Vlakh, M. Helou, O. Miserque, J.-M. Brusson, J.-F. Carpentier and S. M. Guillaume, *Chem. Eur. J.*, 2010, **16**, 13805–13813

II. Polycarbonate Grafting

Catalysts comparison



TBD

Reactions performed at 25°C over 5h in THF

TMC/TBD/OH	Conversion	%w grafts	grafting efficiency	Mn homopolymer	D
500/0.25/50	0.70	**64**	28.231%	13000	1.6
500/0.5/50	0.99	**73**	42.935%	16000	1.8
500/1/50	0.99	**51**	16.528%	20000	1.9
500/2/50	0.99	**9**	1.571%	30400	1.8
500/5/50	0.99	**9**	1.571%	3800	1.2

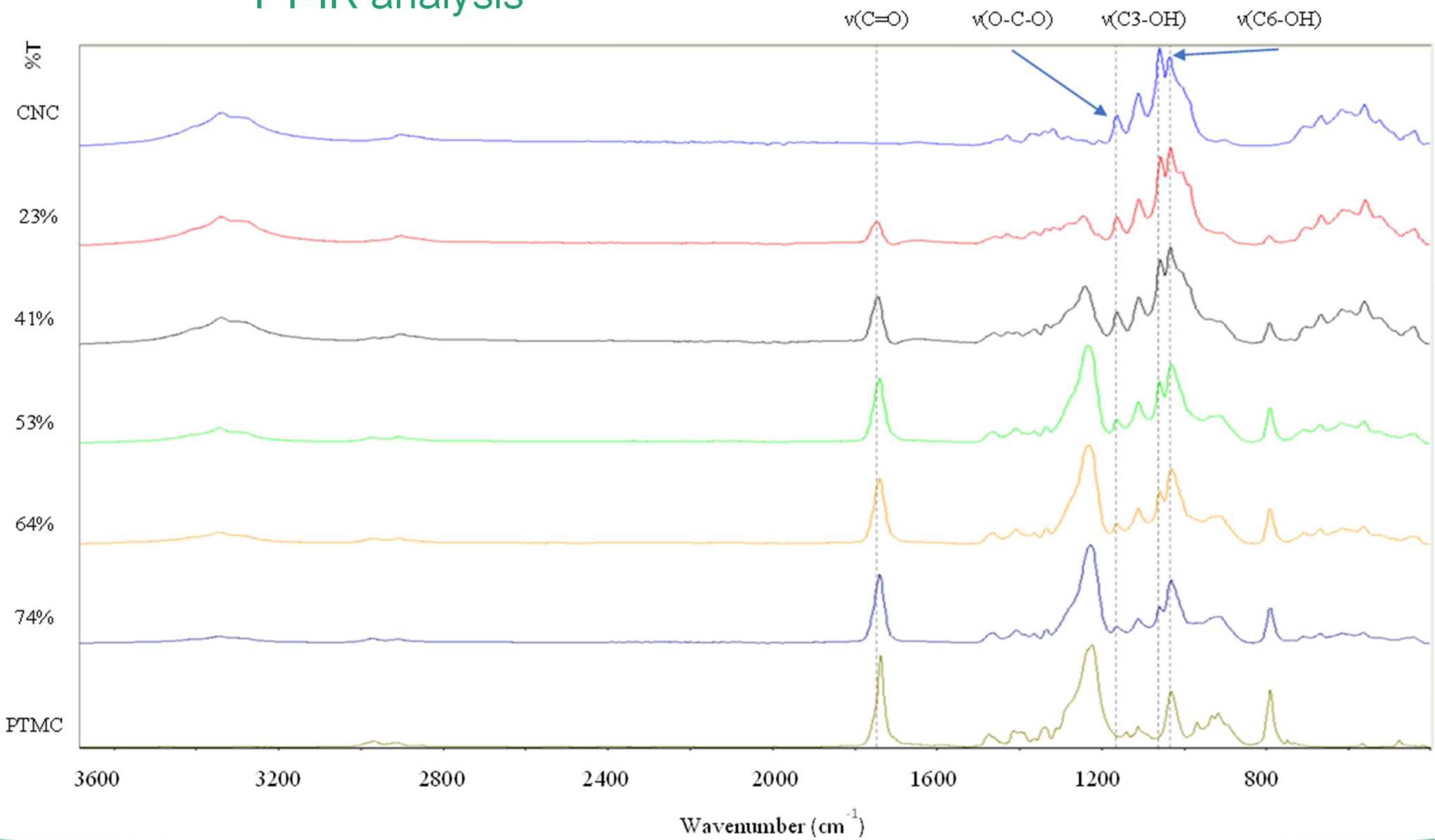
*similar reactions for lactide yield 20% grafts and less than 5% grafting yield

- Best values of grafting reached for 0.5eq of TBD
- Grafting as high as 73%, meaning a product that is ¾ PTMC, ¼ CNC

M. Stepanova, I. Averianov, I. Gofman, O. Solomahka, Y. Nashchekina, V. Korzhikov-Vlakh, M. Helou, O. Miserque, J.-M. Brusson, J.-F. Carpentier and S. M. Guillaume, *Chem. Eur. J.*, 2010, **16**, 13805–13813

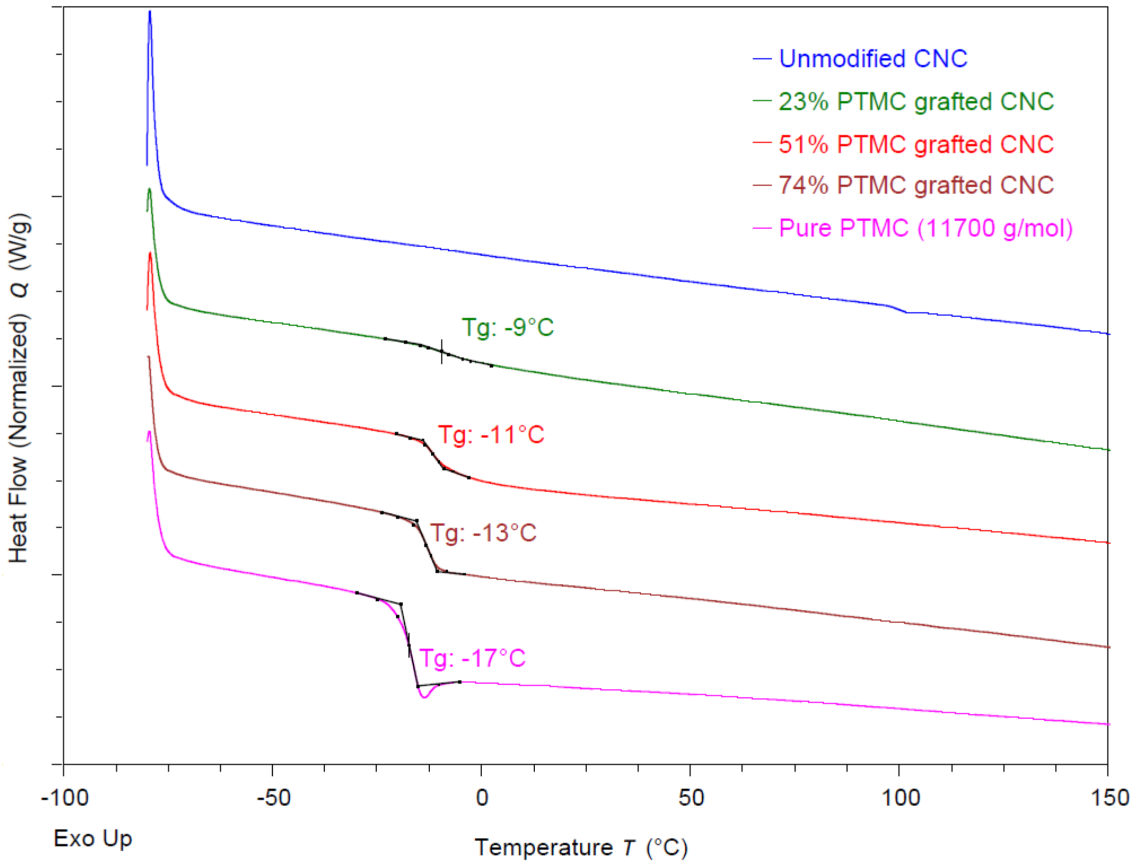
II. Polycarbonate Grafting

FT-IR analysis



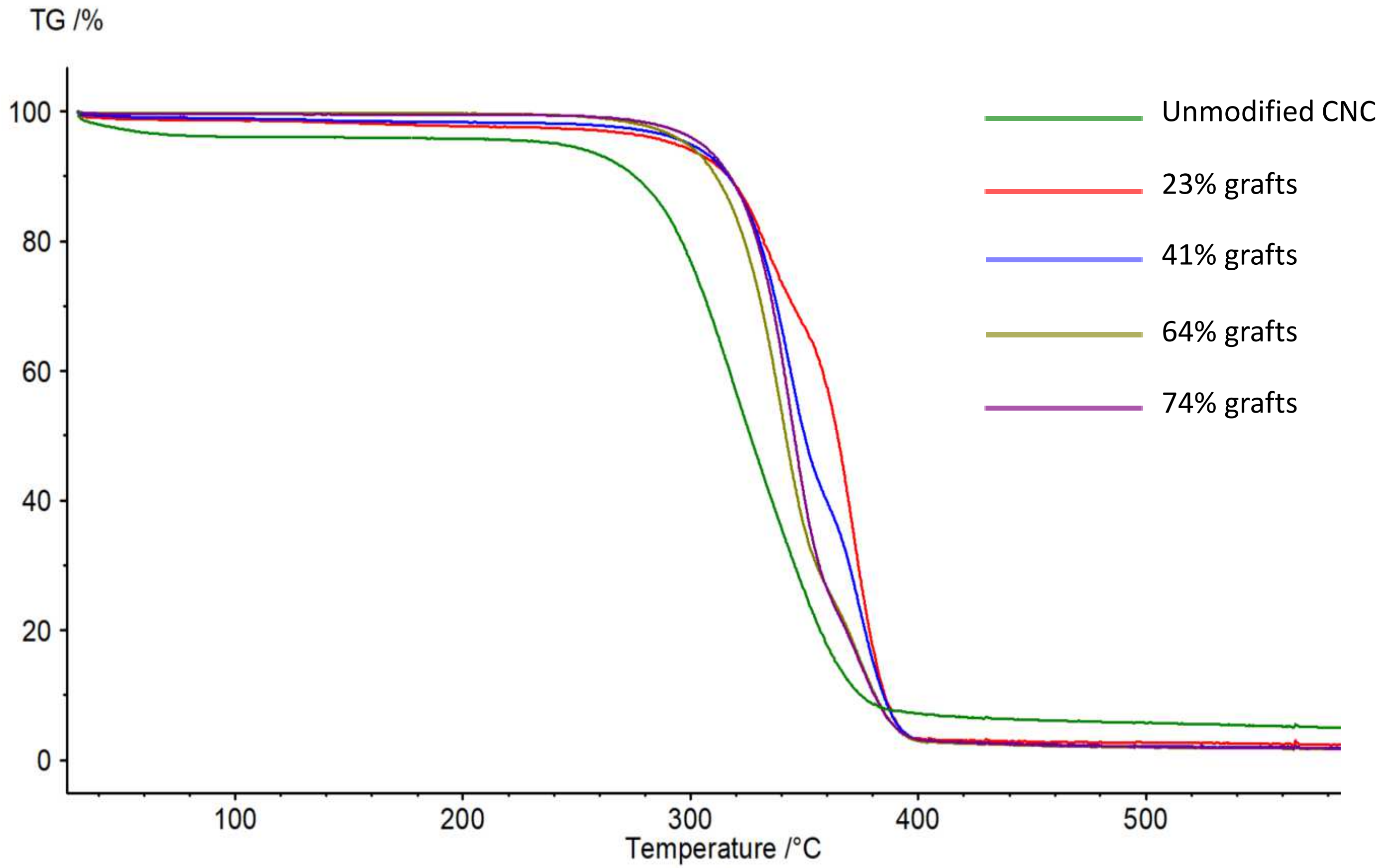
II. Polycarbonate Grafting

DSC analysis



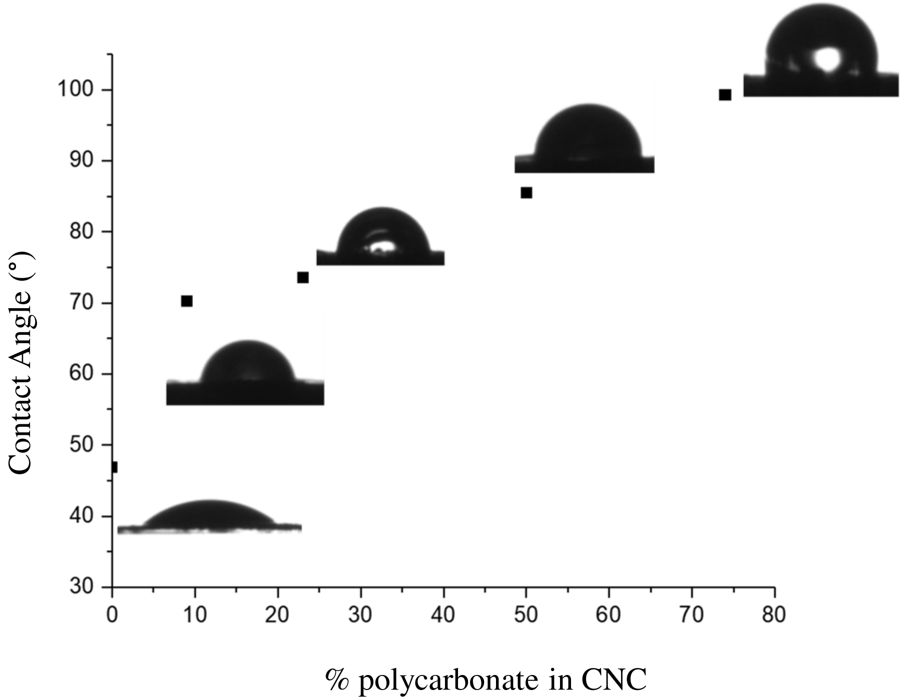
II. Polycarbonate Grafting

TGA



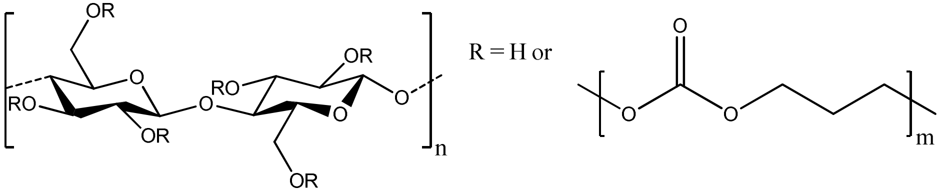
II. Polycarbonate Grafting

Contact angle



- Small amount of grafting already increase hydrophobicity
- Angle increases proportionally to grafting

Conclusion



- Grafting of polycarbonate on CNC can be done with organic catalysts and was reported for the first time
- Results were better than similar studies for cyclic esters (up to 73% grafts)
- Wide range of grafting % possible with optimized parameters
- DSC shows grafts long enough to have a Tg
- No loss of properties of CNCs

M. Stepanova, I. Averianov, I. Gofman, O. Solomahka, Y. Nashchekina, V. Korzhikov-Vlakh, V.
M. Lalanne-Tisné, M. A. Mees, S. Eyley, P. Zinck and W. Thielemans, *Carbohydrate Polymers*, 2020, **250**, 116974.
M. Labet and W. Thielemans, *Polym. Chem.*, 2012, **3**, 679.

THANK YOU FOR YOUR ATTENTION

Aknowledgement:
My supervisors W. Thielemans and P. Zinck for their support
All my colleagues at Ku Leuven and Ulille
In particalar Samuel Eyley for his help with analysis

Initiatives for Science, Innovation, Territories and Economy (I-SITE) Lille Nord – Europe

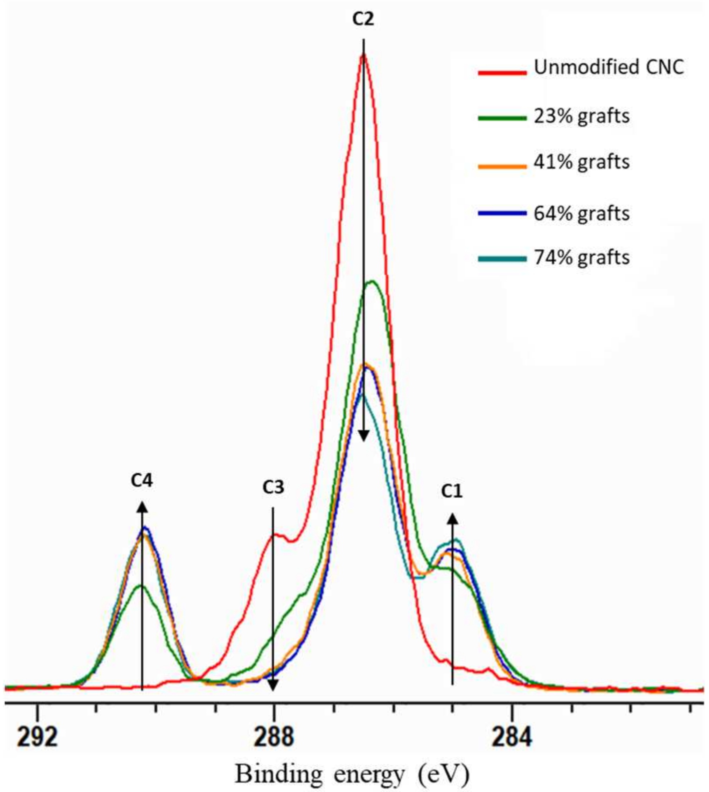
Additionnal information

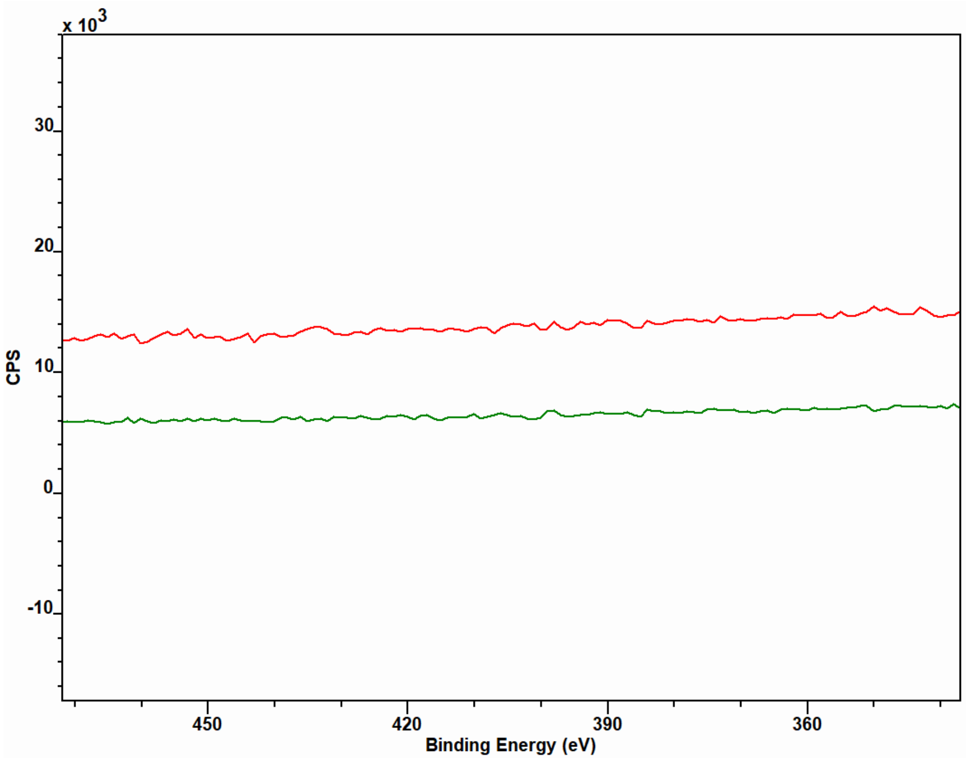
SWAX

Sample	$\chi_{c,\ sample}$	$\Delta\chi_{c,\ sample}$	φ_{PTMC}	$\Delta\chi_{c,\ cellulose}$
Unmodified CNC	0.99	-	0	0
23% PTMC-g-CNC	0.68	-0.31	0.27	-0.04
41% PTMC-g-CNC	0.56	-0.43	0.46	0.03
51% PTMC-g-CNC	0.37	-0.62	0.56	-0.06
64% PTMC-g-CNC	0.26	-0.73	0.69	-0.04
74% PTMC-g-CNC	0.14	-0.85	0.78	-0.07

Additionnal information

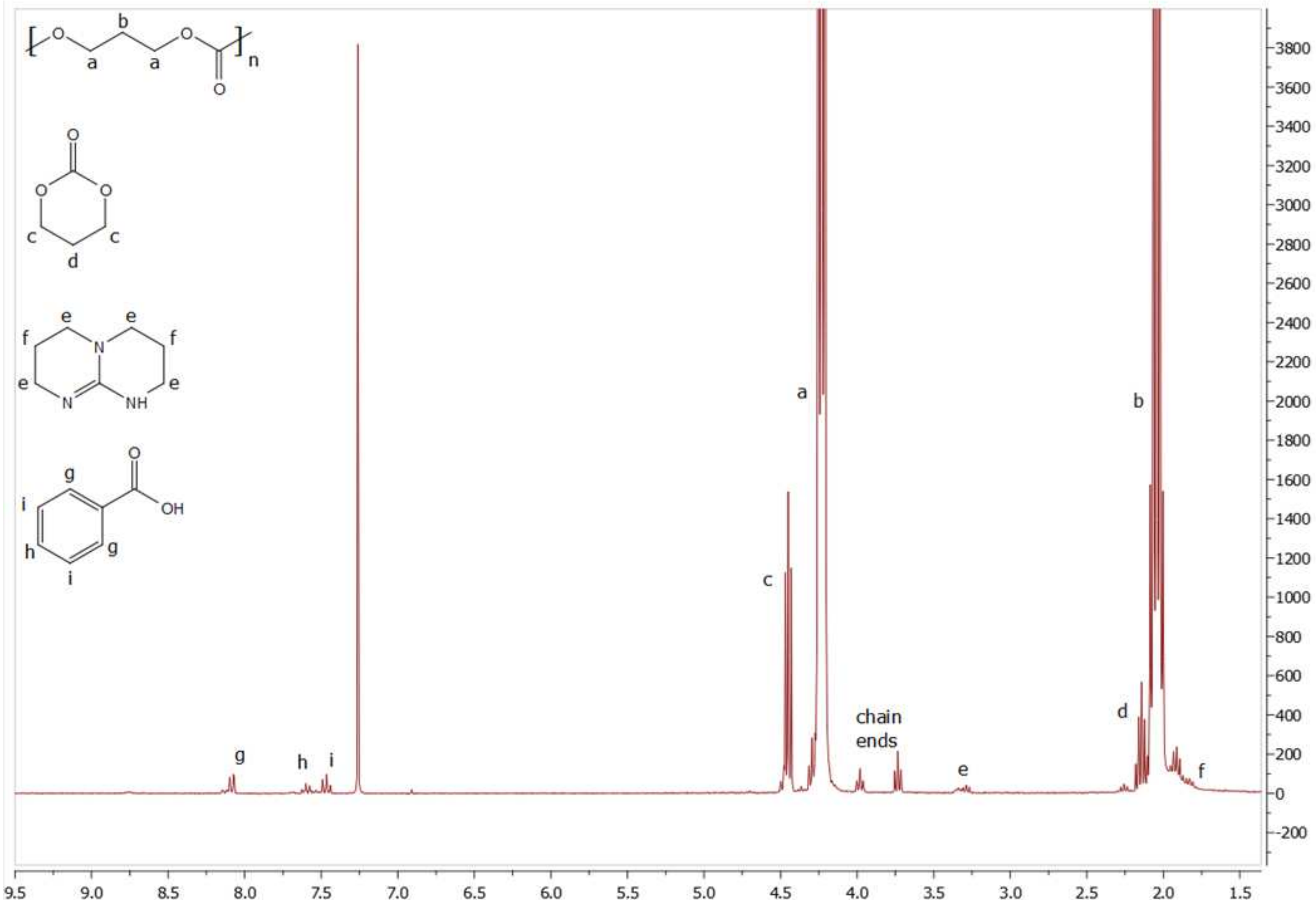
XPS





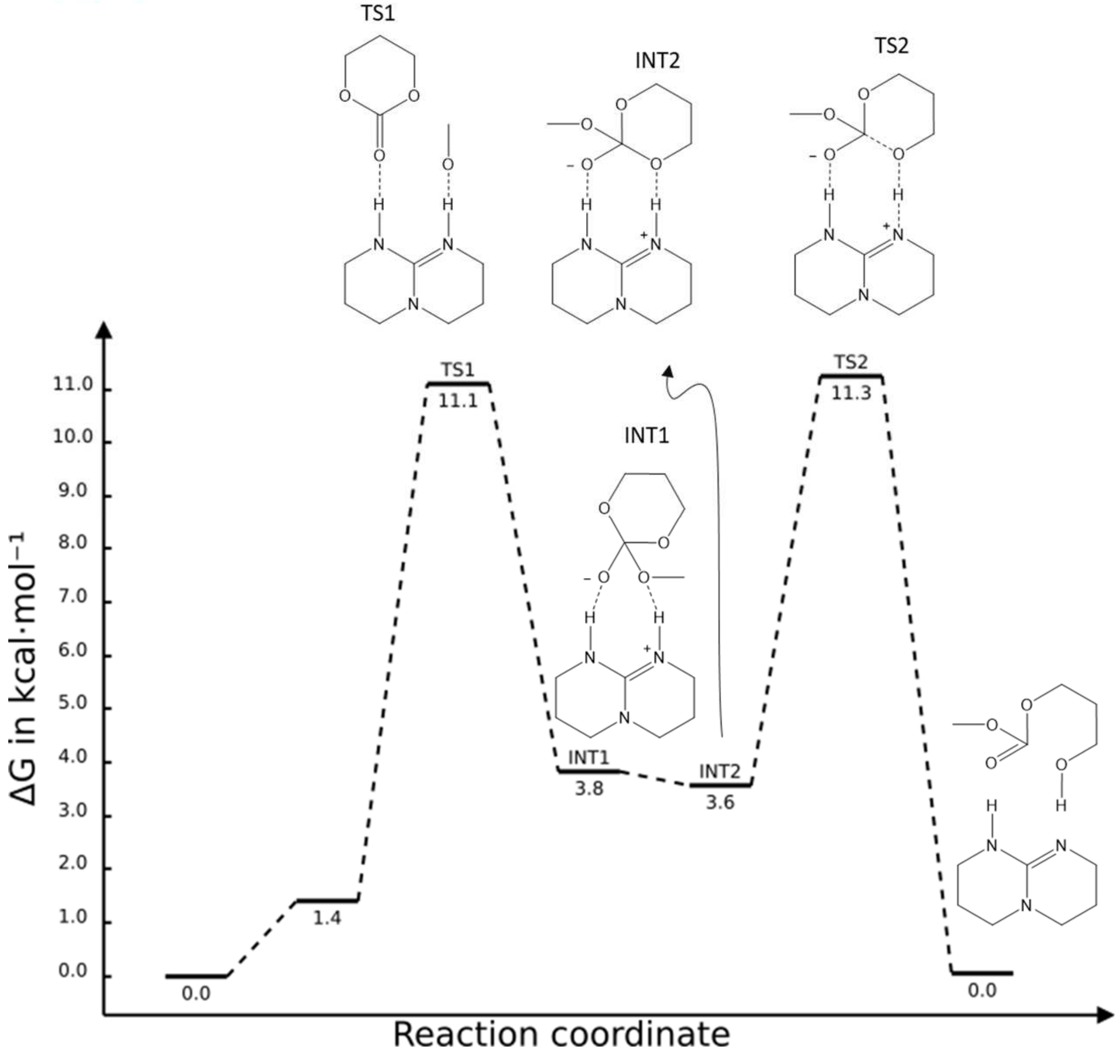
Additionnal information

NMR



Additionnal information

DFT



Additionnal information

DFT