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The effect of cellulose nanocrystals on latex and adhesive properties in emulsion- based polymer nanocomposites

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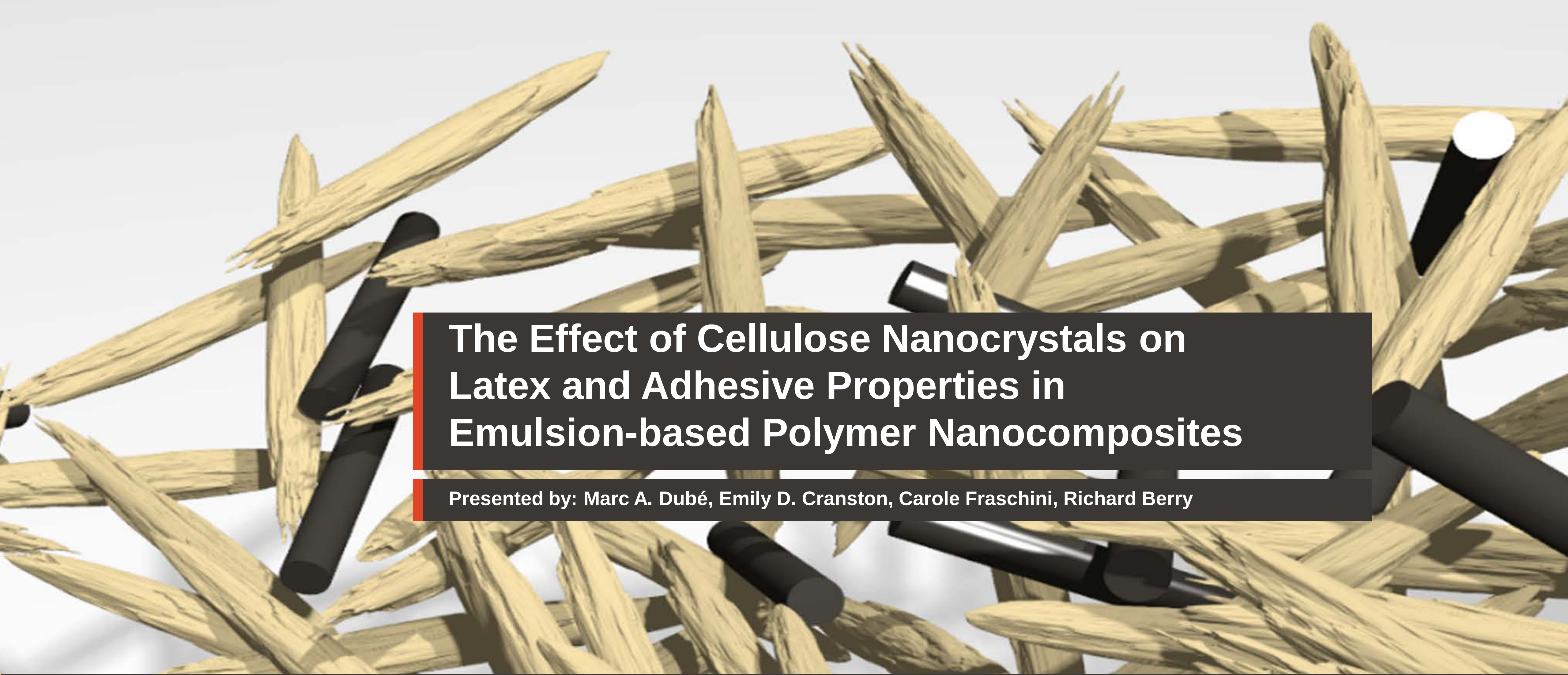

The Effect of Cellulose Nanocrystals on Latex and Adhesive Properties in Emulsion-based Polymer Nanocomposites

Presented by: Marc A. Dubé, Emily D. Cranston, Carole Fraschini, Richard Berry

NSERC CRSNG CRD Team:

McMaster University

- **Emily Cranston**
  - Expertise: Nanocellulose production, surface modification & characterization
- **Dr. Stephanie Kedzior (graduated)**
- **Dr. Elina Niinivaara, Postdoc**
- **Michael Kiriakou, BEng**

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- **Marc Dubé**
  - Expertise: Polymer reaction engineering, emulsion polymerization, PSAs
- **Dr. Zahra Dastjerdi (graduated)**
- **Alexandra Ouzas (graduated)**
- **Amir Pakdel, PhD**
- **Vida Gabriel, MASc**

Partners: Richard Berry, Carole Fraschini

CelluForce FPInnovations

Sustainable Polymer Reaction Engineering

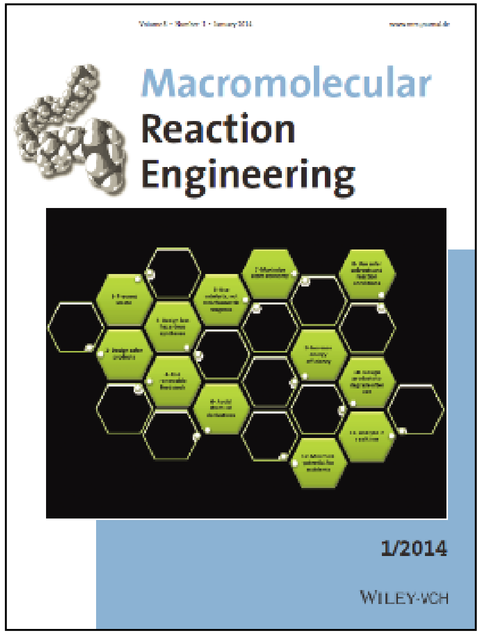
"Development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

World Commission on Environment and Development's report: Our Common Future (Oxford University Press, 1987).

More environmentally benign
More economically viable
Functions equivalent to or outperforms existing alternatives

Principles of green chemistry

1. Prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use renewable feedstock
5. Use catalysts
6. Avoid chemical derivatives
7. Maximize atom economy
8. Use safer solvents and reaction conditions
9. Increase energy efficiency
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents



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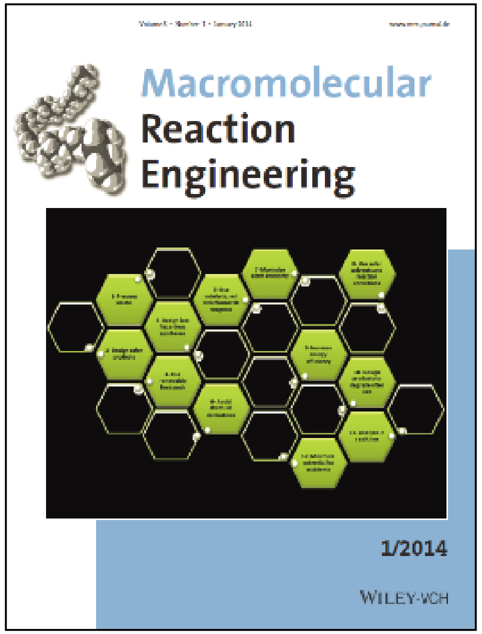

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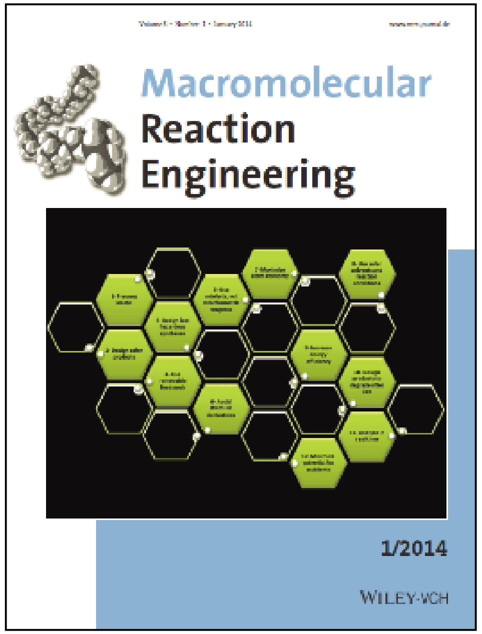

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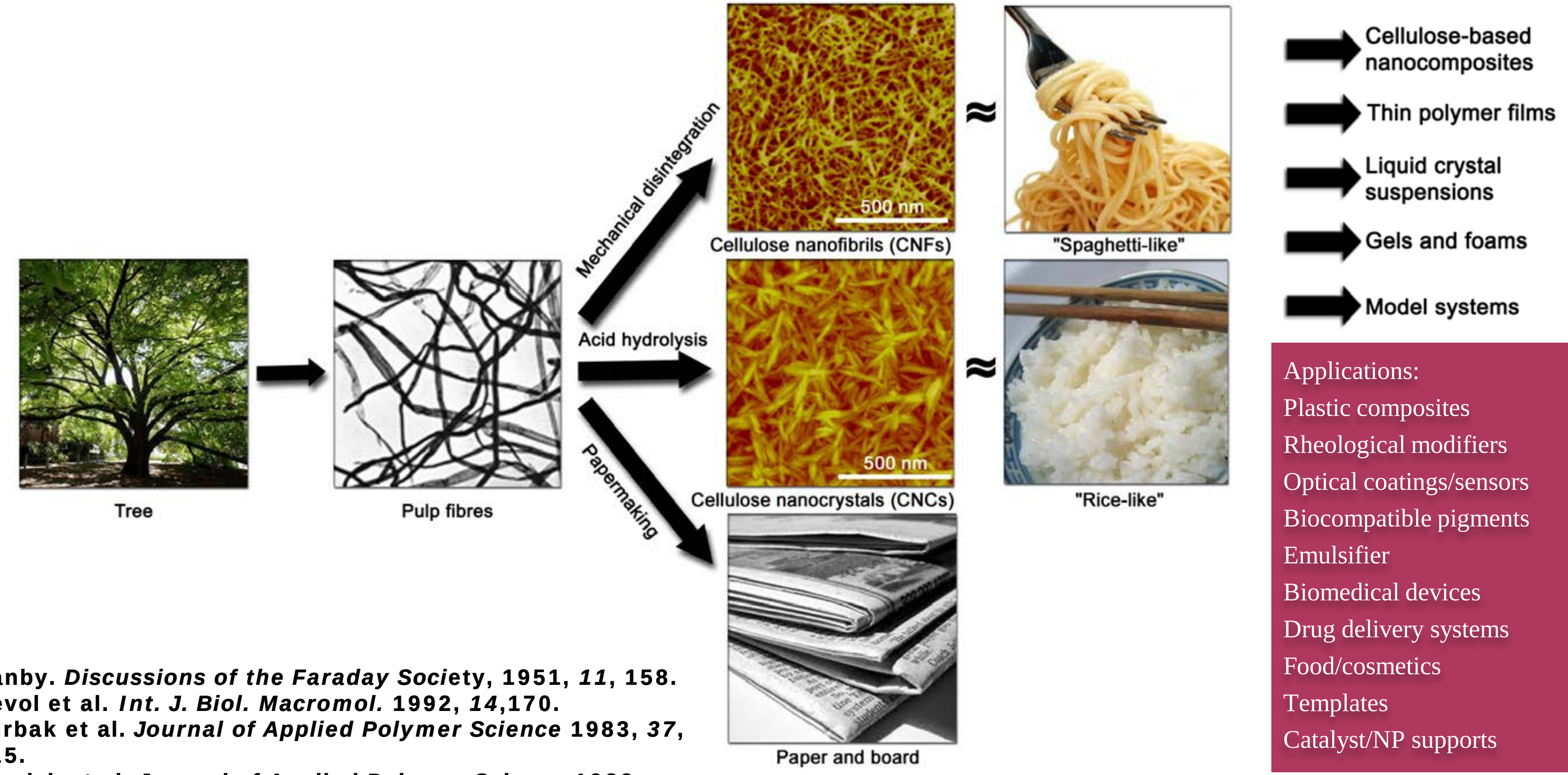
Nanocellulose

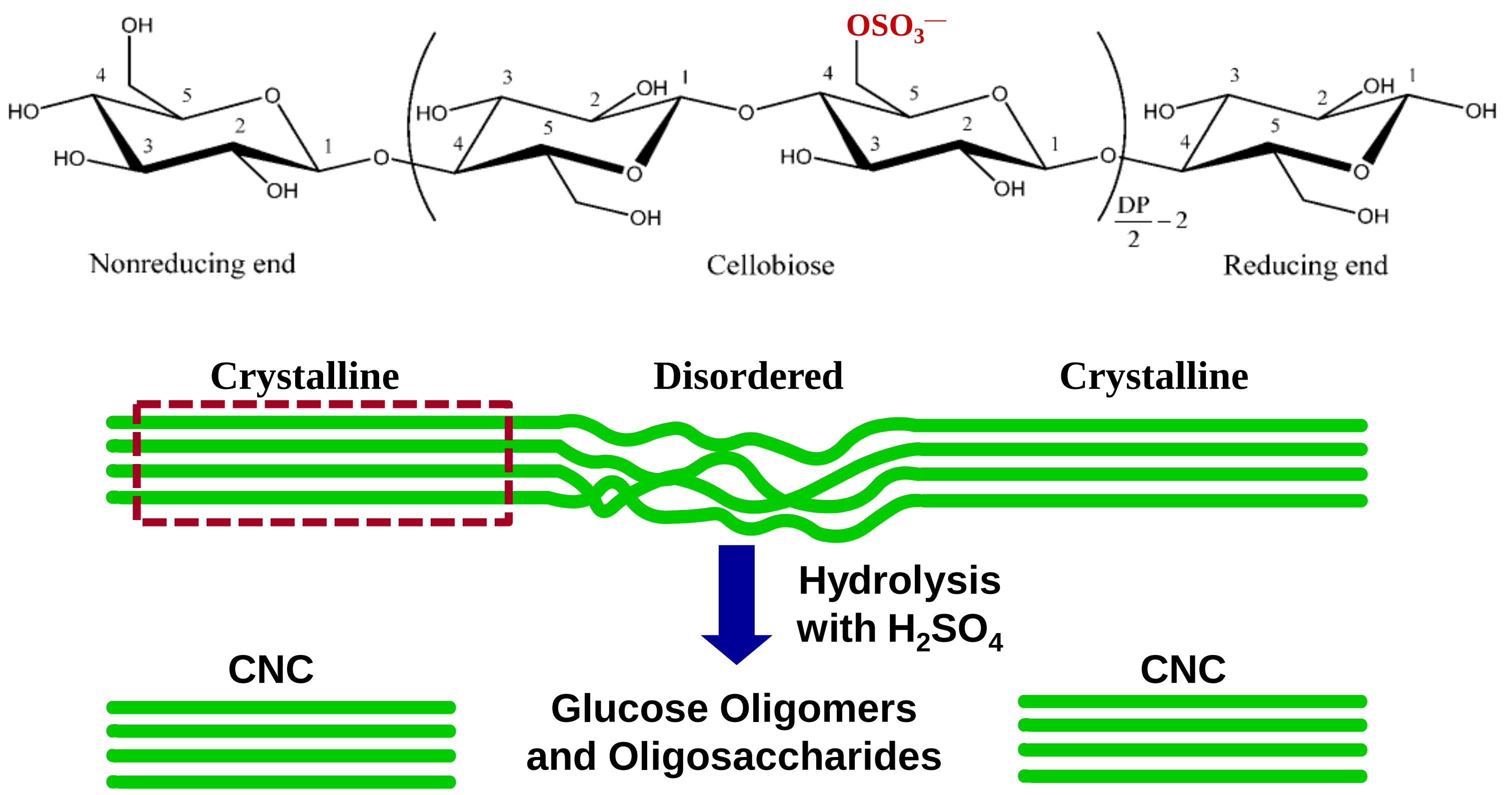
Sustainable bio-based nanomaterial derived from wood pulp and other natural cellulose sources



Applications:
Plastic composites
Rheological modifiers
Optical coatings/sensors
Biocompatible pigments
Emulsifier
Biomedical devices
Drug delivery systems
Food/cosmetics
Templates
Catalyst/NP supports

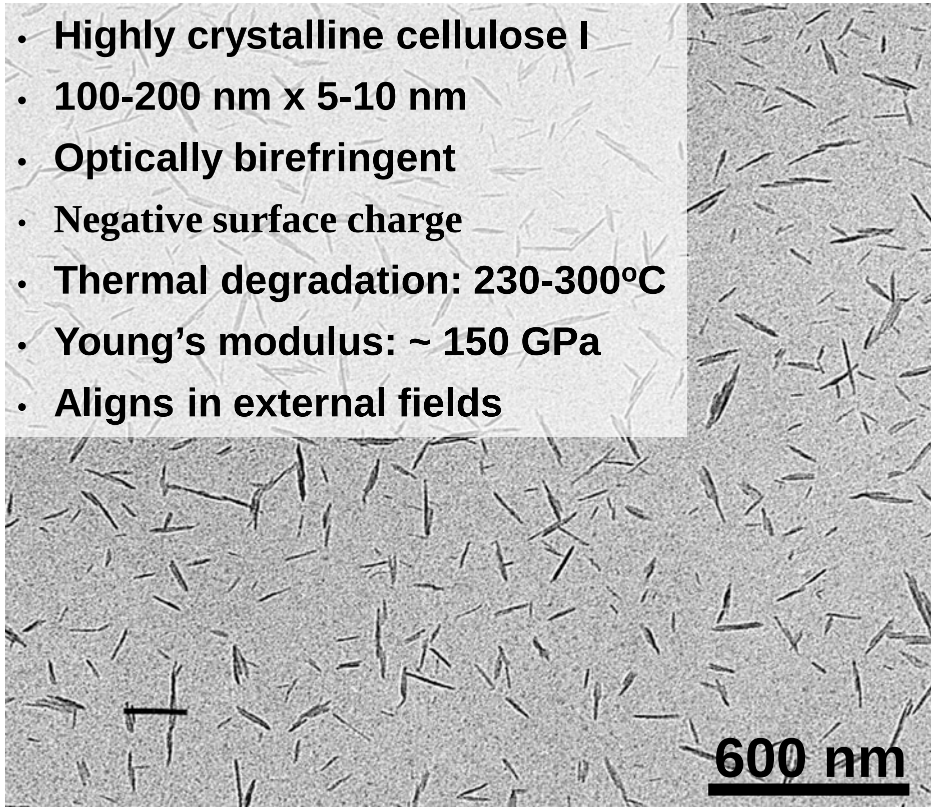
Rånby. *Discussions of the Faraday Society*, 1951, *11*, 158.
Revol et al. *Int. J. Biol. Macromol.* 1992, *14*,170.
Turbak et al. *Journal of Applied Polymer Science* 1983, *37*, 815.
Herrick et al. *Journal of Applied Polymer Science* 1983, *37*, 797.

Cellulose Nanocrystals

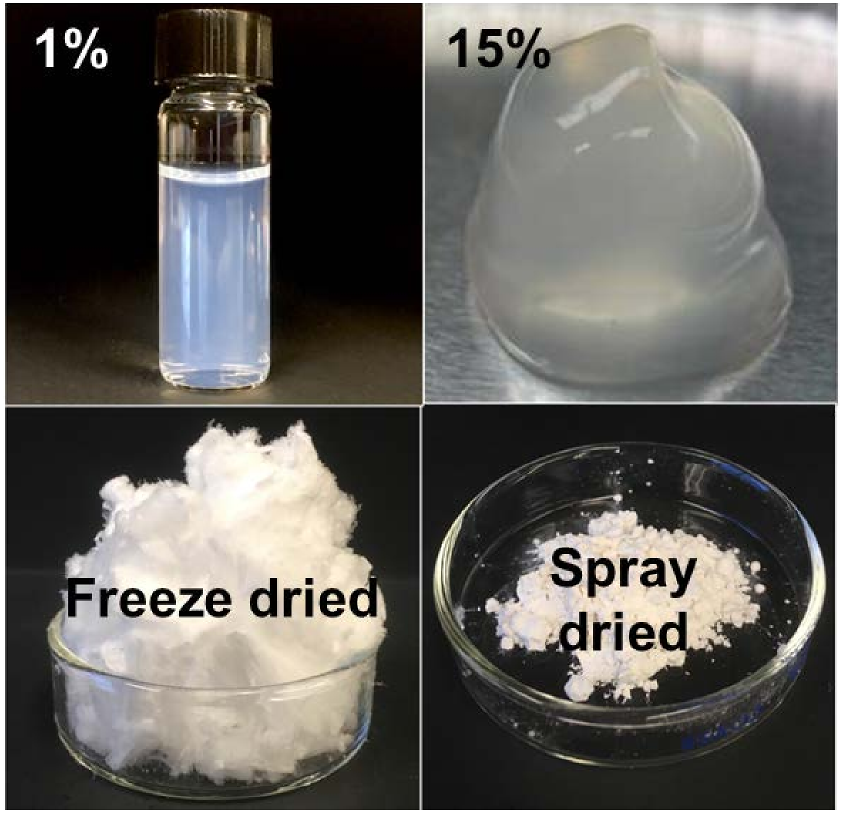


CNC Appearance & Properties

- Highly crystalline cellulose I
- 100-200 nm x 5-10 nm
- Optically birefringent
- Negative surface charge
- Thermal degradation: 230-300ºC
- Young's modulus: ~ 150 GPa
- Aligns in external fields

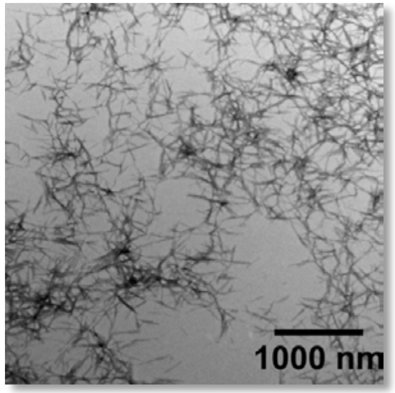


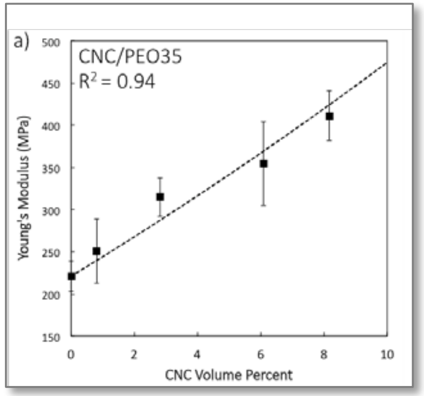
TEM from J.-F. Revol, Paprican circa 1990

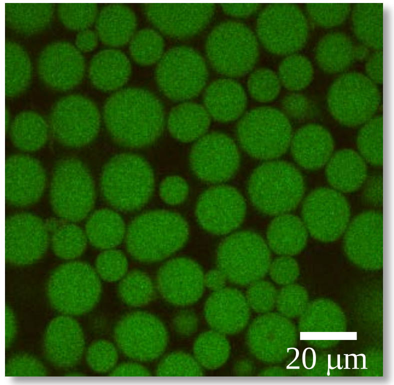


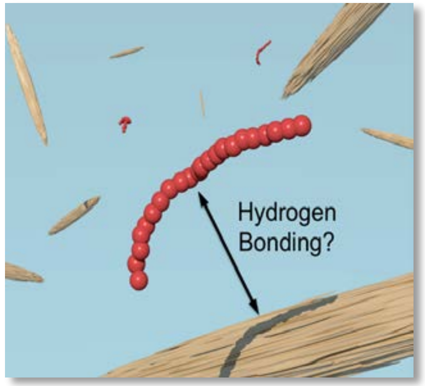
Nano-Advantage?

- Large aspect ratio and high surface-area-to-volume ratio (surface area 250 m^2/g)
  - ✓ A little goes a long way!
- Ideal reinforcing component in nanocomposites
  - ✓ Strong but flexible (specific modulus > steel & Kevlar)
- Ideal stabilizing agent in foams, gels, and emulsions (edible?)
  - ✓ Intermediate hydrophilicity





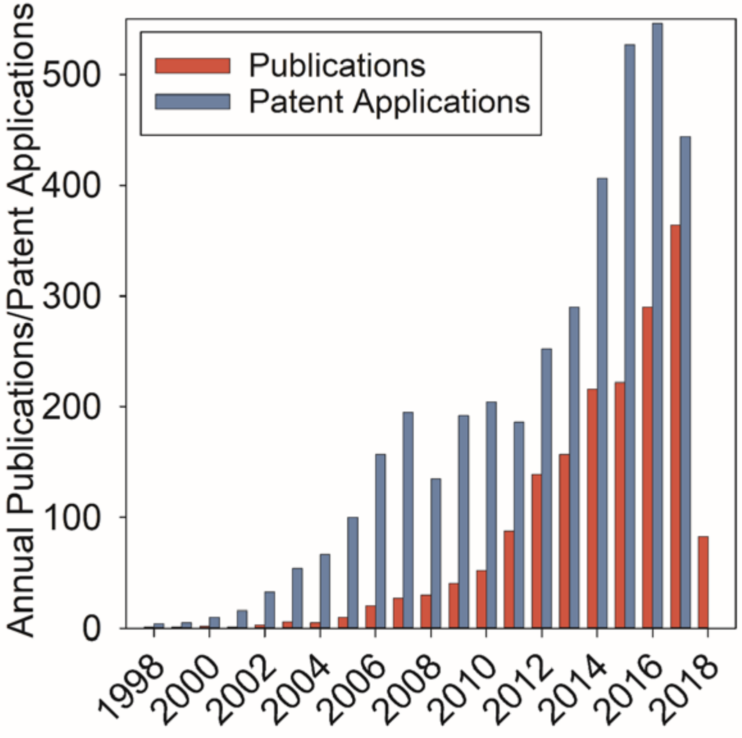


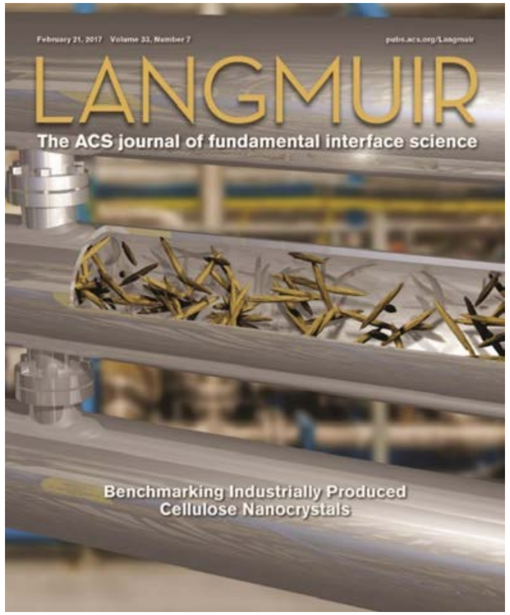


CNCs vs. Other Nanomaterials

- **Biocompatible, non-toxic & biodegradable**
  (Kovacs et al. *Nanotoxicology* 2010, 4, 1
  Roman. *Industrial Biotechnology* 2015, 11, 1125)
- **Chemical properties**
- **Morphology and aspect ratio**
- **Optical and barrier properties**
- **Mechanical properties**
- **Natural, renewable, sustainable**
- **Easily produced in industrial-scale quantities (green)**
  - Industrial production (kg to ton per day quantities)

An Emerging Nanomaterial





Reid, Cranston, *Langmuir* 2017, *33*, 1583

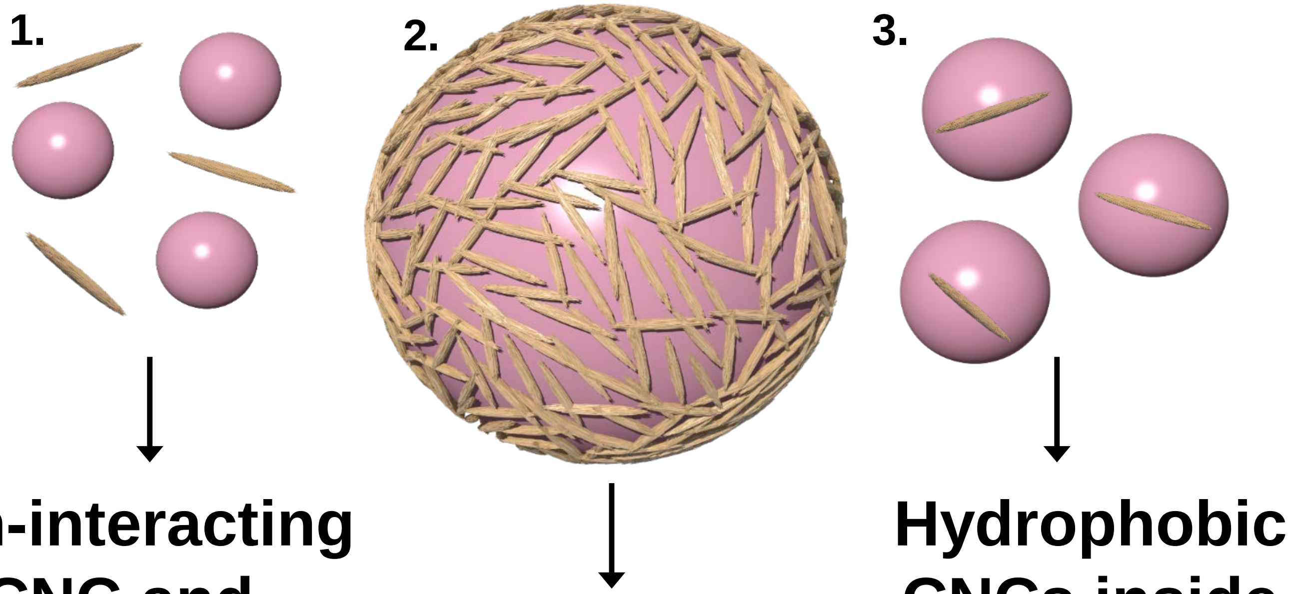
1. Are sulfuric acid hydrolyzed CNCs from various producers equivalent?
2. What are the key base properties?
3. Is further purification needed?
4. Situation not as clear for "other" nanocelluloses

Project Goals

- Develop a novel technology platform for incorporating CNCs into emulsion-based polymer systems
- Optimize interfacial compatibility of CNCs with latex polymers and emulsion polymerization components using a toolbox of available surface modification methods
- Use different compatibilization routes to control the location of CNCs in the latex
- Evaluate the effect of CNCs on polymer latex composites in terms of mechanical, thermal and adhesive properties

CNCs in Latex Systems

- <u>Hypothesis</u>: Controlling CNC role / location will tailor latex performance.



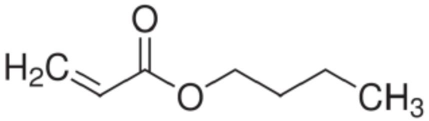
Non-interacting CNC and polymer particles

CNCs as particle stabilizers

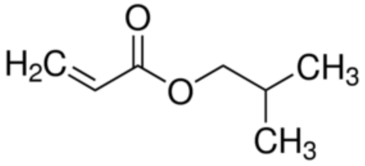
Hydrophobic CNCs inside polymer particles

Pressure Sensitive Adhesives (PSAs)

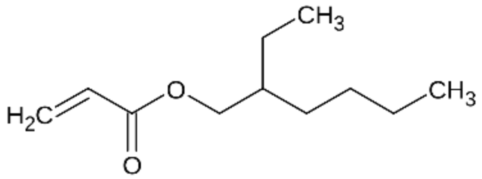
- PSAs: adhere to surfaces on contact with light pressure and no residue is left behind
- "Soft" monomer: low T_g, e.g., BA or IBA/BA or EHA/BA
- "Hard" monomer: high T_g, e.g., MMA
- Other additives: e.g., crosslinker, chain transfer agents, tackifier, nanoparticles



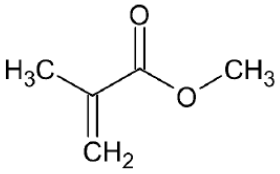
BA



IBA



EHA



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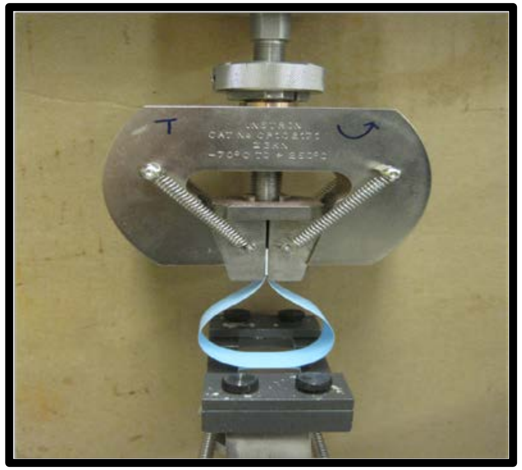
PSAs – Adhesive Performance

- **Tack**: How well bond will form with surface upon light contact
- **Peel strength**: Force required to remove adhesive from surface at 90º or 180º
- **Shear strength**: Cohesive strength of the adhesive



The PSA challenge

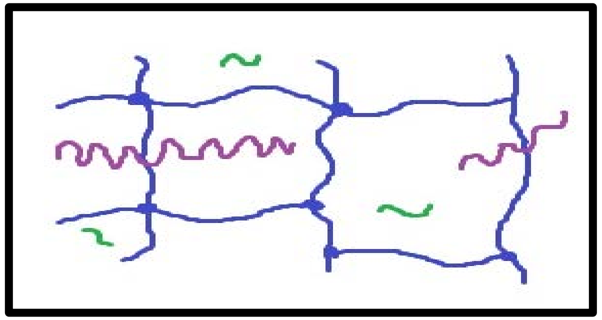
- Challenge: **simultaneously improving tack, peel strength and shear strength for latex-based PSAs**

Factors		Tack	Peel strength	Shear strength
Chemical	"Soft" monomers	↑	↓	↓
	"Hard" monomers	↓	Shows max.	↑
	Polar monomers	↓	Shows max.	↑
	Cross-linking agents	↓	Shows max.	↑
	Tackifiers	↑	Shows max.	↓
	Stabilizers, buffers	↓	Shows min./max.	↓
	Peel modifiers	-	↑	↓
Physical	Adhesive layer thickness	↑	↑	↓
	Carrier thickness/ flexibility (loop tack)	↑	Shows max.	-
	Dwelling time	↑	↑	-
	Temperature	↑	-	↓

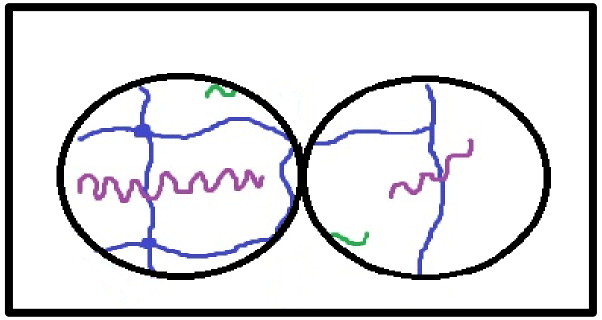
Jovanović and Dubé (2004). Emulsion-Based Pressure-Sensitive Adhesives: A Review. J. Macromol. Sci., Part C, 44: 1–51.

The PSA challenge

- Emulsion vs. solution:
  - Emulsion-based approach is more sustainable
  - Emulsion-based often leads to lower shear strength



Gel network formation in solution polymerization



Gel network formation in emulsion polymerization

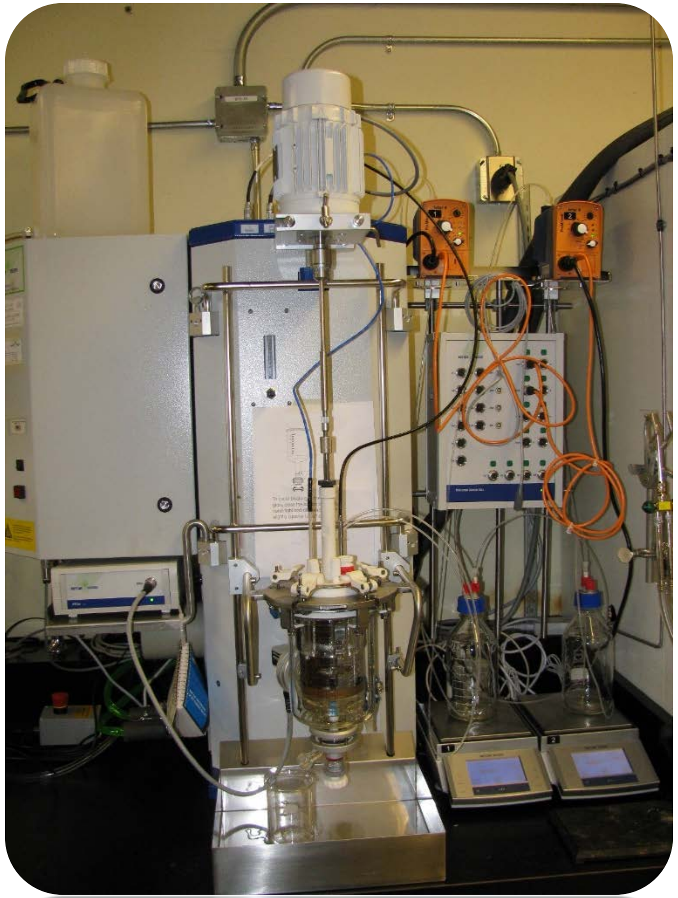
Qie and Dubé (2011). Manipulating Latex Polymer Microstructure using Chain Transfer Agent and Cross-linker to Modify PSA Performance and Viscoelasticity, Macromol. React. Eng., 5:117-128.

Outline – Key Results

- **Emulsion polymerization with unmodified CNCs (reactor scale)**
- **CNC Toolbox: Established surface modification routes**
- **Emulsion polymerization with modified CNCs (model system, small scale)**

Batch and Seeded Semi-batch Emulsion Polymerization

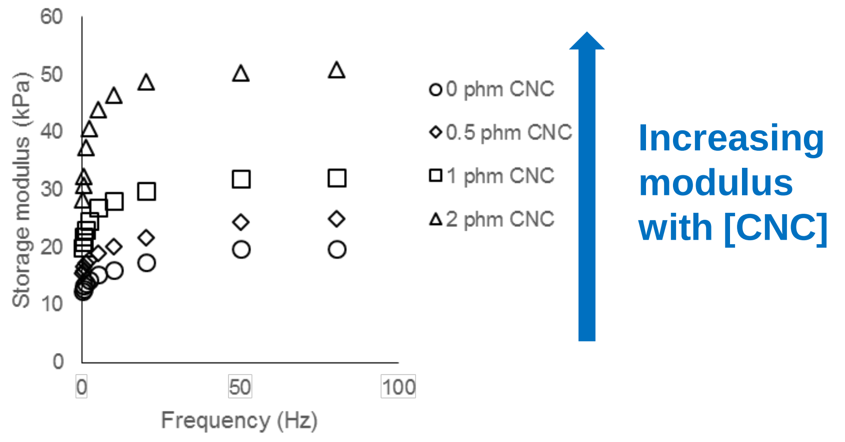
- 1.25 L reactor
- Reactor temperature: 60 ºC
- Feed lines: initiator and pre-emulsion
- Anchor stirrer: 250 rpm
- Nitrogen purge



1. Batch stage (seed, CNC addition) (1 h)
2. Continuous feed stage (4 h)
3. Cook stage (30 min)

Emulsion Batch Polymerization – BA / MMA

- Batch formulation that avoids coagulation with 0.1-2 wt.% CNC
  - SDS, no buffer, decreased [KPS]
  - Gradually charge CNC using feed pump
- Latex properties
  - No change: reaction rate, particle size and T_g
  - Changed: gel content, latex viscosity and storage / loss moduli



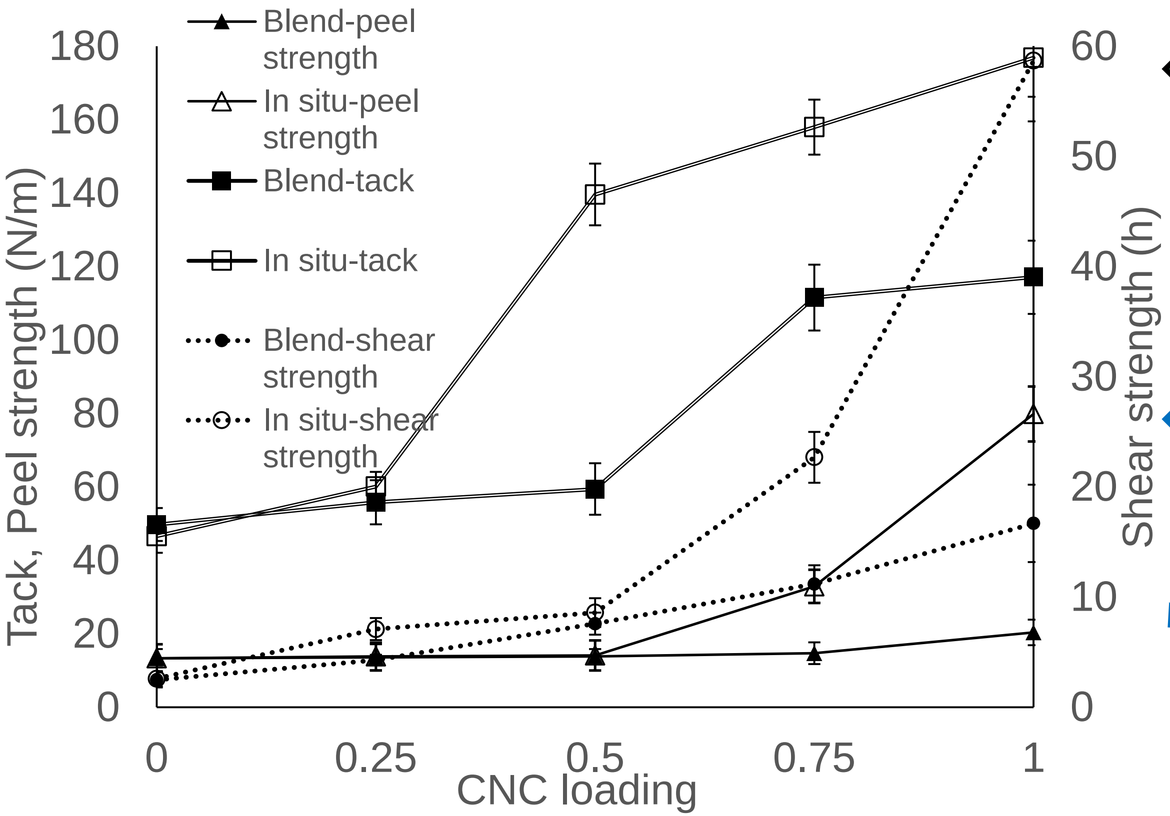
CNC loading (phm)	Gel content (wt.%)
0	28.4
0.5	53.3
1	62.1
2	68.5

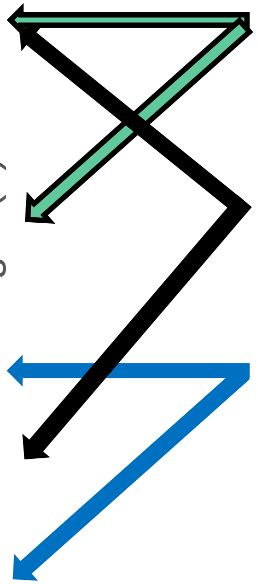
Dastjerdi, Cranston and Dubé (2017) Synthesis of Poly(n-butyl acrylate / methyl methacrylate) / CNC Latex Nanocomposites via in situ Emulsion Polymerization, Macromol. React. Eng., 11:1700013

Seeded Semi-batch Emulsion Polymerization: Formulation

Component	Seed stage (g)	Feed stage (g)
CNC	2.2	-
Monomer	22	198
KPS	0.06	0.54
SDS	0.7	2.6
Water	165/40	122

Emulsion Seeded Polymerization – BA/MMA



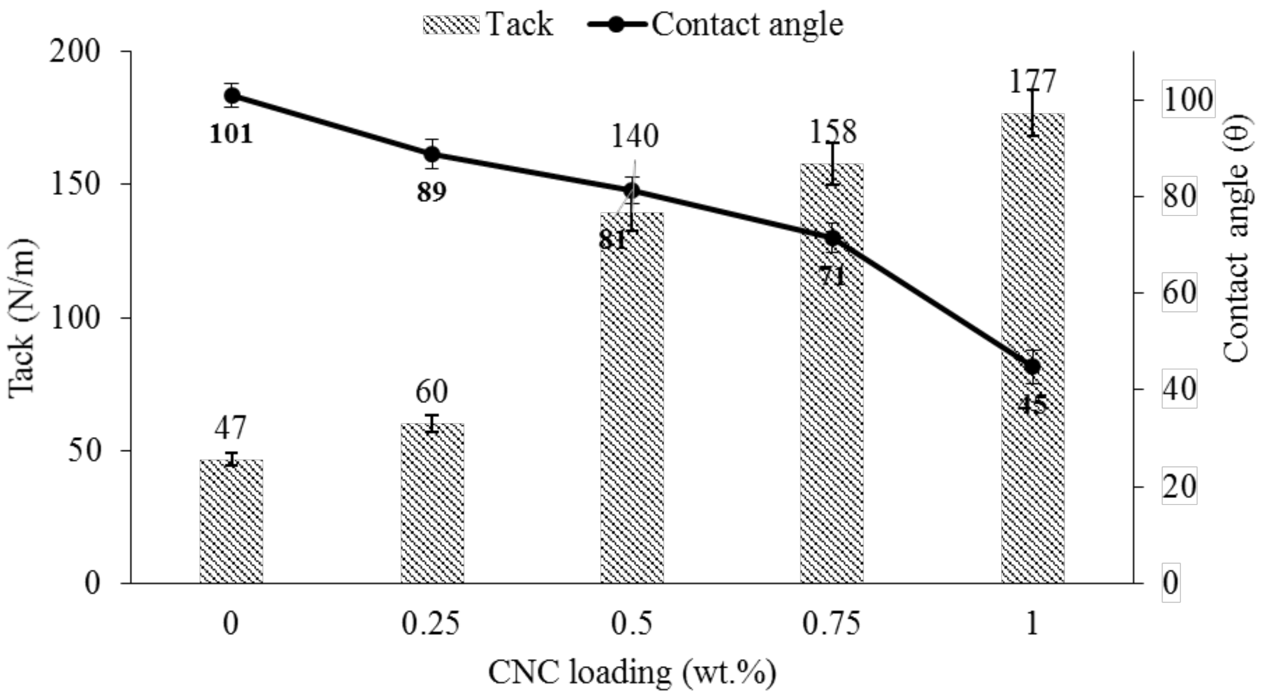


Tack	4x
Shear	20x
Peel	6x

In situ CNC-latex outperforms blends – PSA performance meets/exceeds commercial specifications.

Dastjerdi, Cranston and Dubé (2018) Pressure Sensitive Adhesive Property Modification Using Cellulose Nanocrystals, Int. J. Adh. Adh., 81:36-42

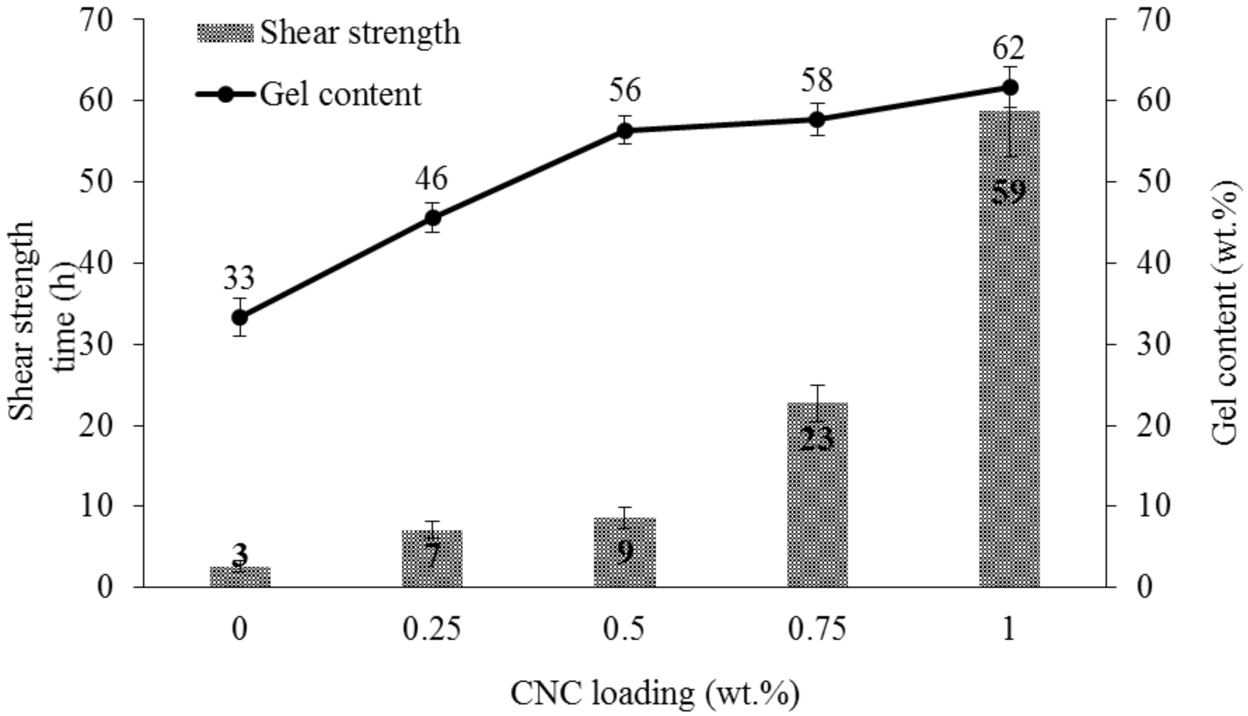
Emulsion Seeded Semi-Batch Polymerization – BA / MMA



- Improved contact of PSA films with substrate (SS) due to hydroxyl groups – hydrophilicity ↑
- Improved wettability → better contact between PSA & substrate
- Polar hydroxyl groups present on CNCs improve work of adhesion
- Same for peel strength

Dastjerdi, Cranston and Dubé (2018) Pressure Sensitive Adhesive Property Modification Using Cellulose Nanocrystals, Int. J. Adh. Adh., 81:36-42

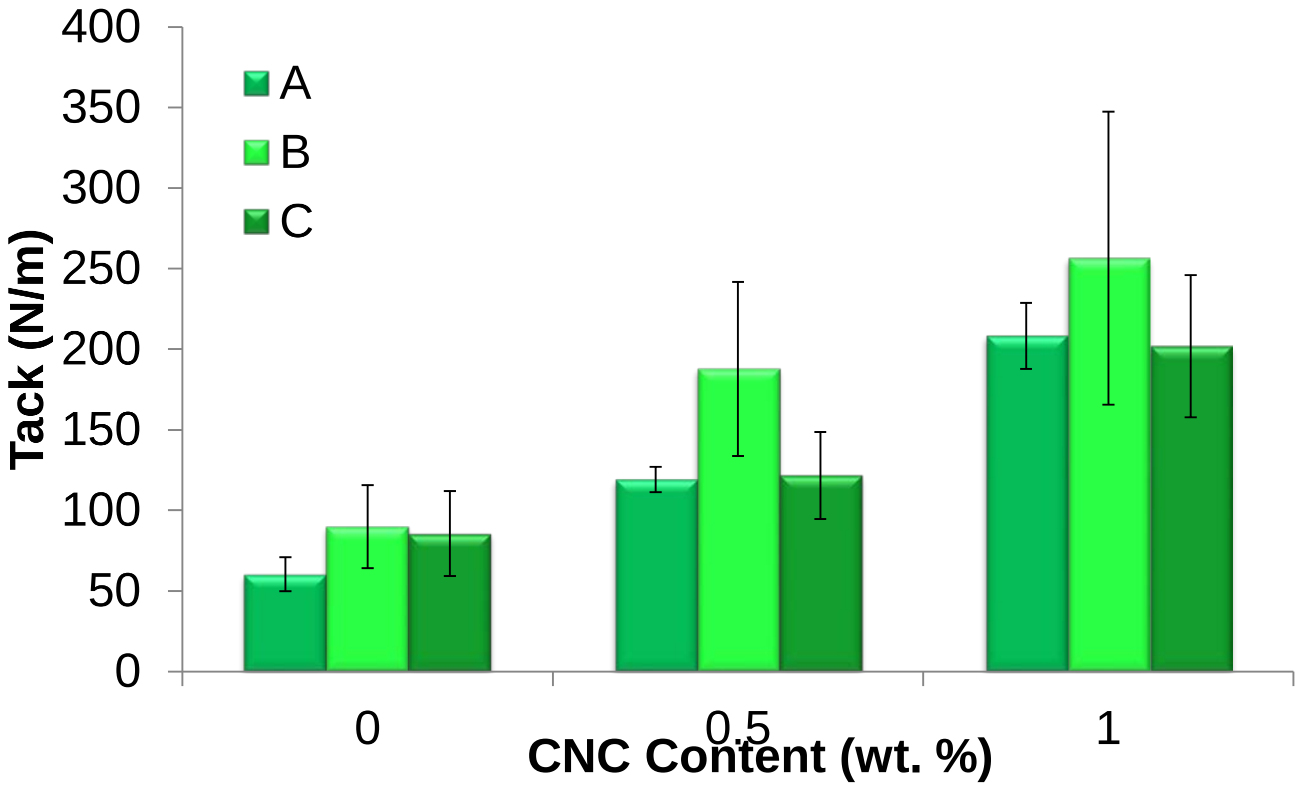
Emulsion Seeded Semi-batch Polymerization – BA / MMA



- Shear strength ↑ with gel content (typical)
- Shear strength ↑ with CNC
- Effect of CNC increase >> than gel content
- Suggests CNC contribution not due to cross-linking but rather association with polymer (grafting or hydrogen bonding)

Dastjerdi, Cranston and Dubé (2018) Pressure Sensitive Adhesive Property Modification Using Cellulose Nanocrystals, Int. J. Adh. Adh., 81:36-42

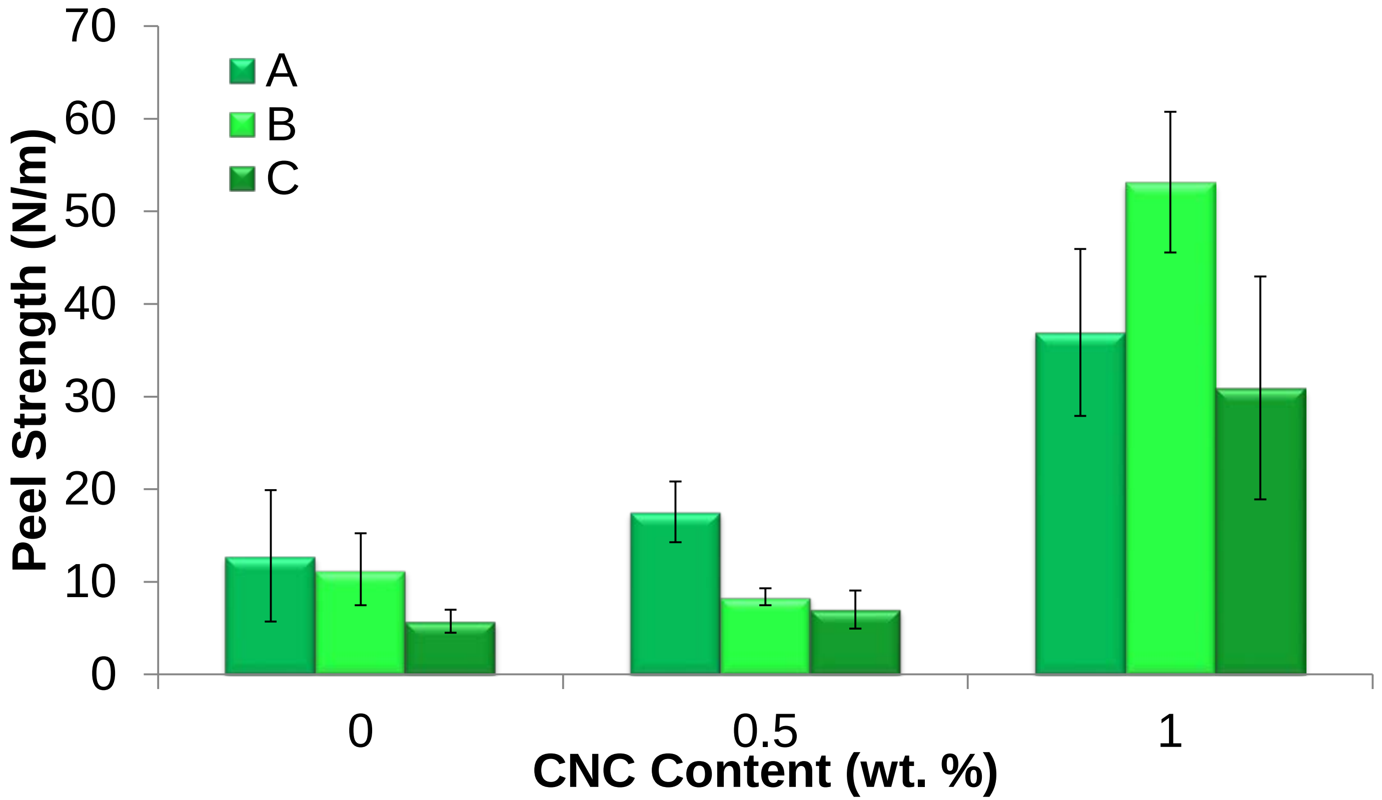
Extension to IBA/BA/MMA: Loop Tack



Composition	IBA/BA/MMA (wt. %)	Target T_g (°C)
A	69/21/10	-21
B	39/51/10	-31
C	9/81/10	-40

Ouzas, Niinivaara, Cranston and Dubé (2018) Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., *in press*

Extension to IBA/BA/MMA: Peel Strength



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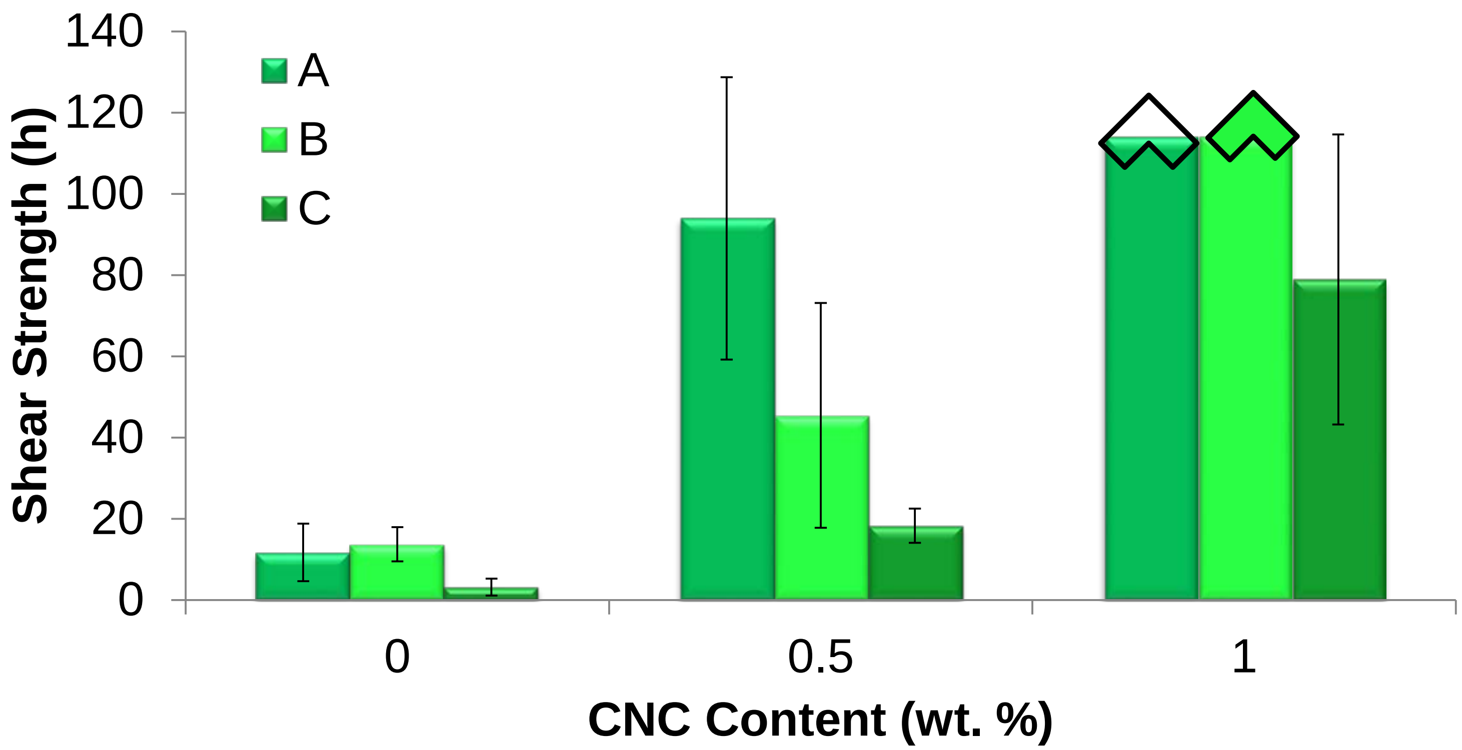
Extension to IBA/BA/MMA: Shear Strength



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Blending vs. in situ approach

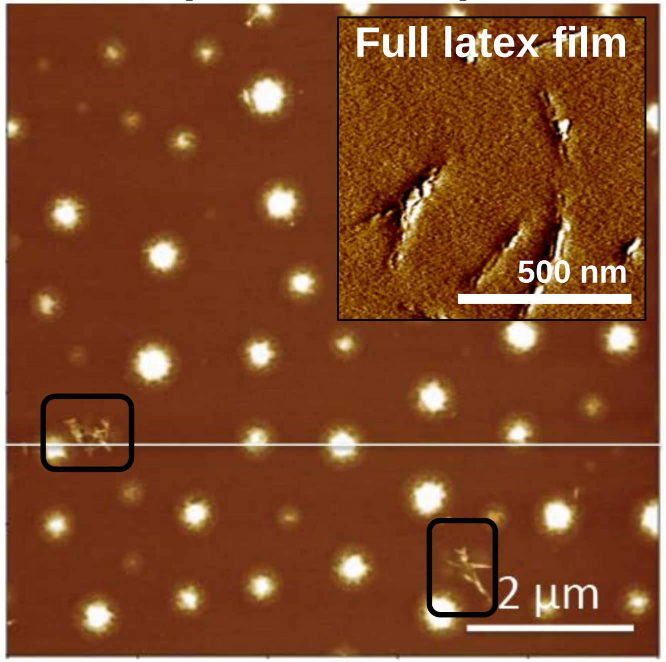
Run	CNC Loading (wt%)	Tack (N/m)	Peel Strength (N/m)	Shear (h)	Viscosity (Pa·s)
Base Case	0	90±25	11±4	13±4	0.18
In Situ	1	256±90	53±7	*114+	0.23
Non-Heated Blend	1	201±56	37±12	63±17	0.78
Heated Blend	1	215±37	40±15	86±20	0.15
Extended Base Case	0	242±2	108±46	24±6	0.14

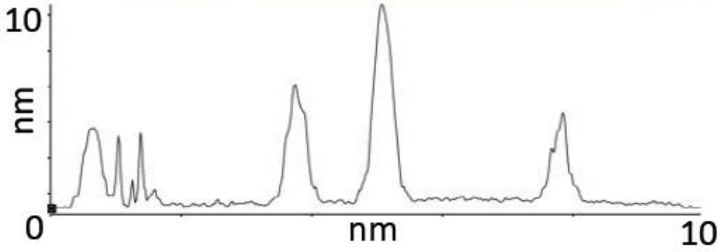
- **Heated blend = 2 h, 60 ^{o}C + mixing**

Ouzas, Niinivaara, Cranston and Dubé (2018) Synthesis of Poly(Isobutyl Acrylate/n-Butyl Acrylate/Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., *in press*

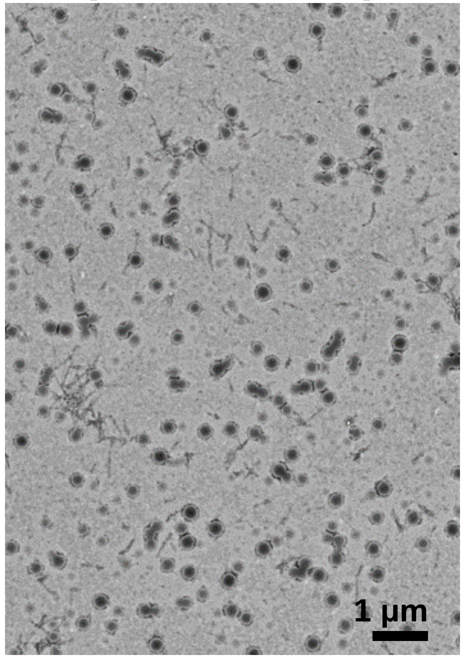
Locating CNCs in IBA / BA / MMA Latex

AFM: Diluted spin-coated latex (1 wt.% CNC)

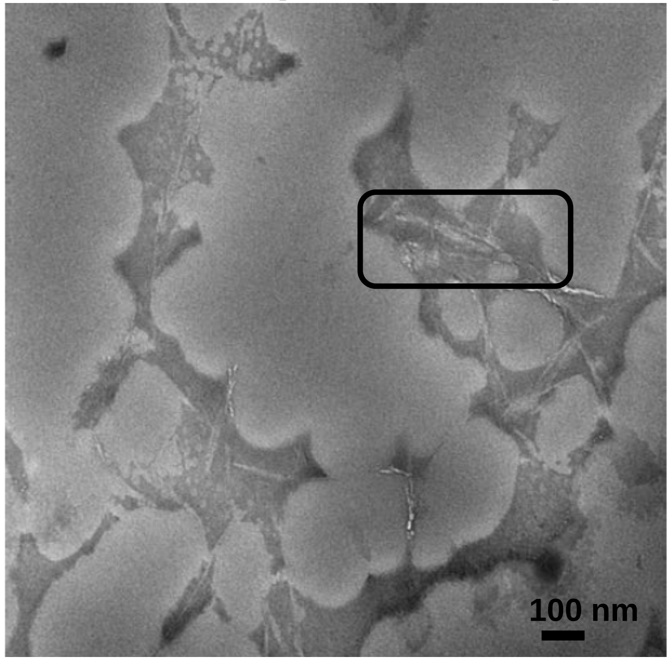




TEM: Extra diluted (1 wt.% CNC)



TEM: More concentrated latex film (1 wt.% CNC)

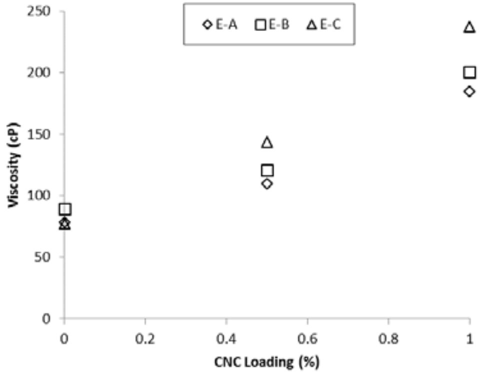


CNCs distributed evenly but outside latex particles

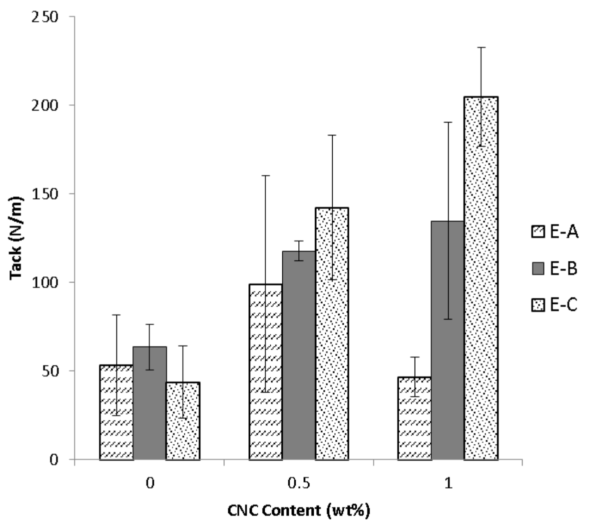
Ouzas, Niinivaara, Cranston and Dubé (2018) Synthesis of Poly(Isobutyl Acrylate / n-Butyl Acrylate / Methyl Methacrylate) CNC Nanocomposites for Adhesive Applications via In Situ Semi-Batch Emulsion Polymerization, Polym. Comp., *in press*

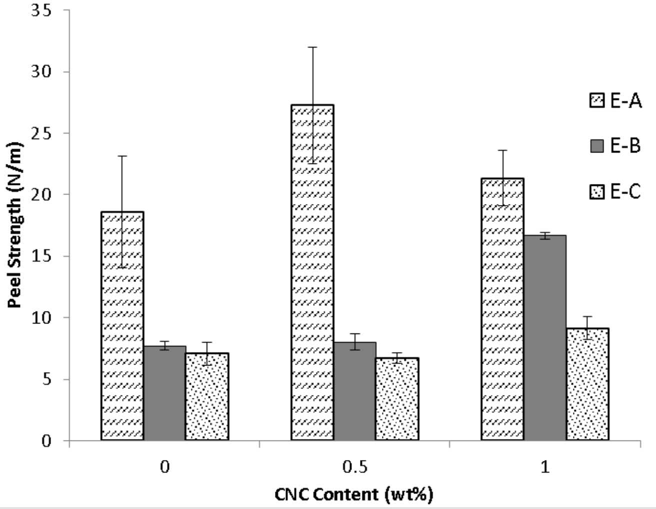
Extension to EHA / BA / MMA

Run*	EHA/BA/MMA (wt%)	EHA/BA/MMA (mol%)	T_g (ºC)
E-A	29/41/30	20/41/39	-18
E-B	39/41/20	29/28/43	-30
E-C	49/41/10	39/46/15	-40



EHA Formulation	Shear Strength [h]
E-0A	293±210
E-0.5A	385+
E-1A	850+
E-0B	10±4
E-0.5B	32±9
E-1B	39±29
E-0C	1.3±0.4
E-0.5C	1.7±0.4
E-1C	4.2±1.0





Ouzas, Niinivaara, Cranston and Dubé (2018) In Situ Semi Batch Emulsion Polymerization of 2-Ethyl Hexyl Acrylate / n-Butyl Acrylate / Methyl Methacrylate / Cellulose Nanocrystal Nanocomposites for Adhesive Applications, Macromol. React. Eng., *in press*

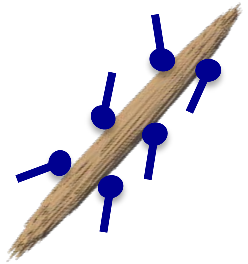
uOttawa

CNC Toolbox:

Established Surface Modification Routes

CNC Toolbox: Non-Covalent Modification

Mix CNCs with adsorbing species in water



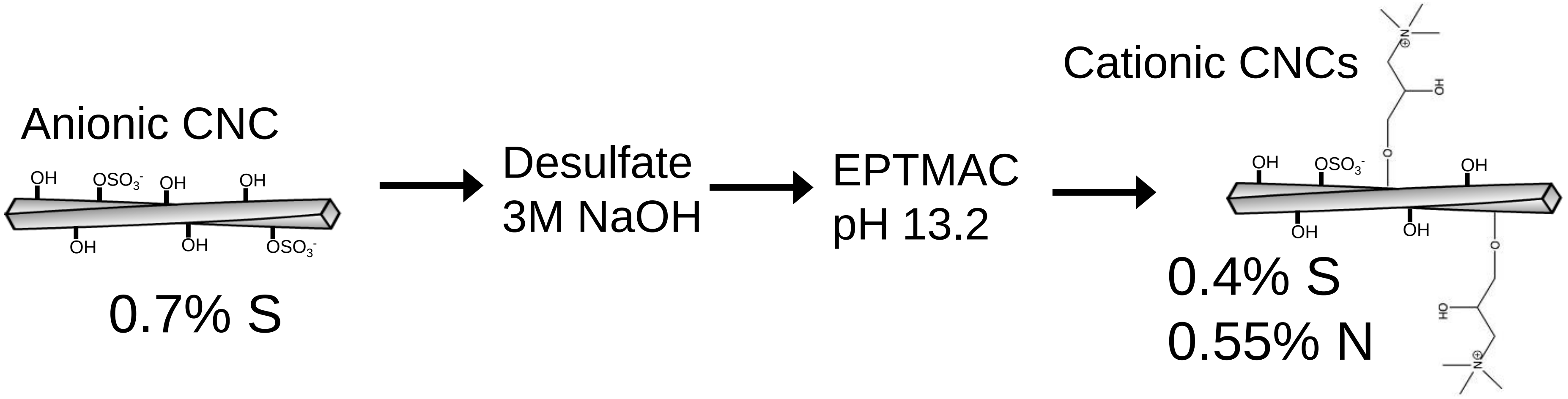
- Cationic surfactants
  - (Anionic surfactants do not bind, change CNC size/zeta)
  - CTAB (single tailed) vs. DMAB (double tailed)
- Adsorbing polysaccharides
  - Non-ionic & water soluble
  - MC, HEC, LBG, HPG

- Result: CNCs that are more surface active, less hydrophilic, just mix in water & no purification needed

Kedzior, Marway and Cranston (2017) Macromolecules, 50:2645
Hu, Patten, Pelton and Cranston (2015) ACS Sust. Chem. & Eng., 3:1023
Hu, Ballinger, Pelton and Cranston (2015) J. Coll. Int. Sci., 439:139

CNC Toolbox: Cationic CNCs

Water-based epoxy small molecule modification of cellulose's hydroxyl groups

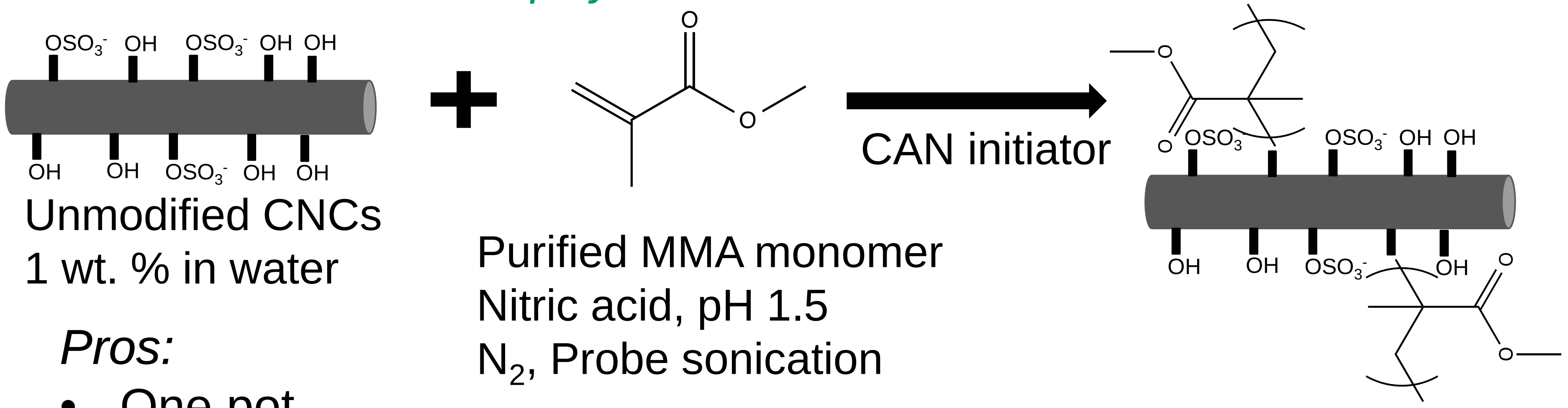


	Anionic CNC	Cationic CNC
Zeta Potential (mV)	-26.8	30.4
Size (DLS)	88 nm	134 nm

Protocol from: Hasani, Cranston, Westman and Gray (2008) Cationic Surface Functionalization of Cellulose Nanocrystals. Soft Matter, 11:2238.

CNC Toolbox: PMMA-g-CNC

Water-based free radical polymerization from CNCs with ceric ion initiation



Unmodified CNCs
1 wt. % in water

Purified MMA monomer
Nitric acid, pH 1.5
N_2, Probe sonication

PMMA-*g*-CNCs
+ PMMA homopolymer

Pros:

- One pot
- Water-based

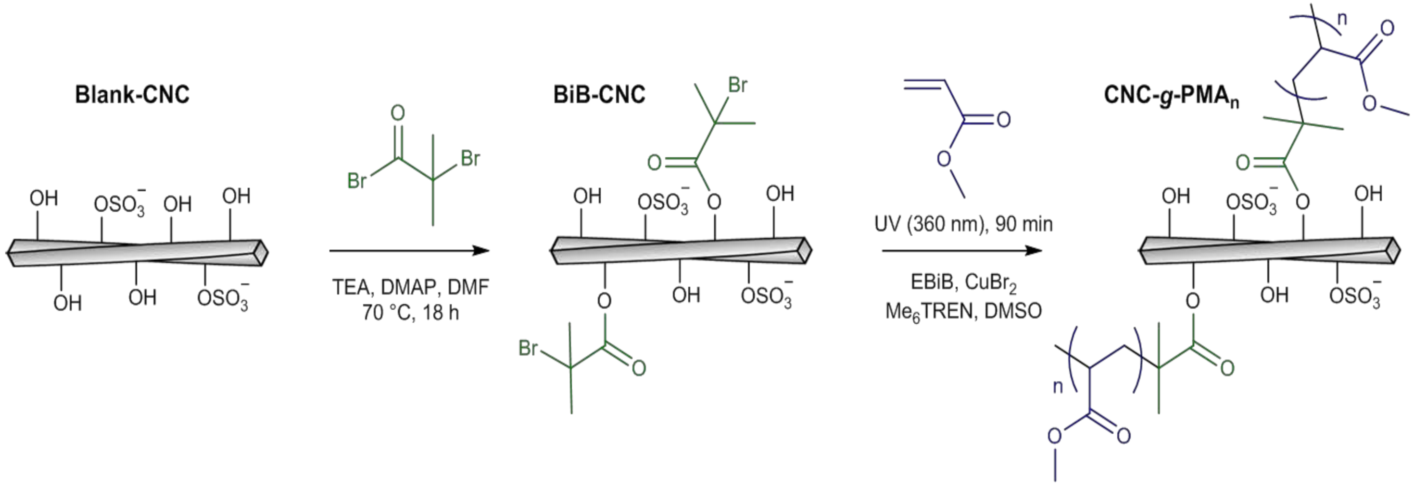
Cons:

- Lacks control of polymer chain length
- Lacks control of polymer chain density
- Long clean up process to remove PMMA homopolymer

Kedzior, Graham, Moorlag, Dooley and Cranston (2016)
Can. J. Chem. Eng., 94:811

CNC Toolbox: PMA-g-CNC

Solvent-based controlled grafting from CNCs with surface-initiated photo-induced Cu-mediated reversible-deactivation radical polymerization (SI-RDRP)



Pros:

- Initiator grafting step allows for control of polymer grafting density
- Controlled nature of RDRP allows for control of polymer graft length
- Photo-induced RDRP provides short reaction times (90 min)

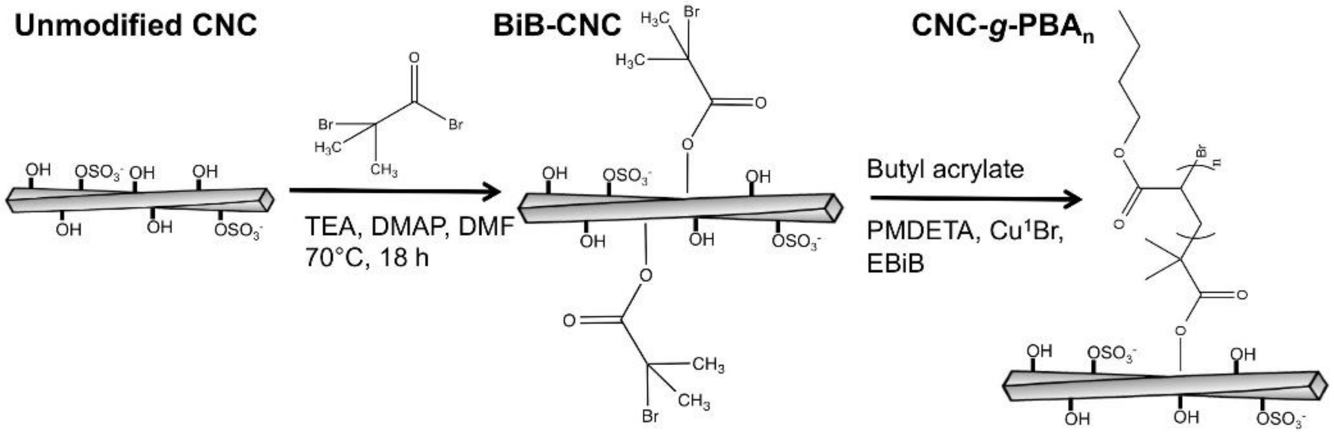
Cons:

- Multi step process (initiator grafting is separate reaction in DMF)
- Solvent-based (reaction in DMSO)
- Still requires purification (though simpler than other grafting rxns)

Hatton, Kedzior, Cranston and Carlmark (2017) Carbohydrate Polymers, 157:1033

CNC Toolbox: PBA-g-CNC

Solvent-based controlled grafting from CNCs using surface initiated atom transfer radical polymerization (SI-ATRP)



Pros:

- Initiator grafting step allows for control of polymer grafting density
- Controlled nature of RDRP allows for control of polymer graft length

Cons:

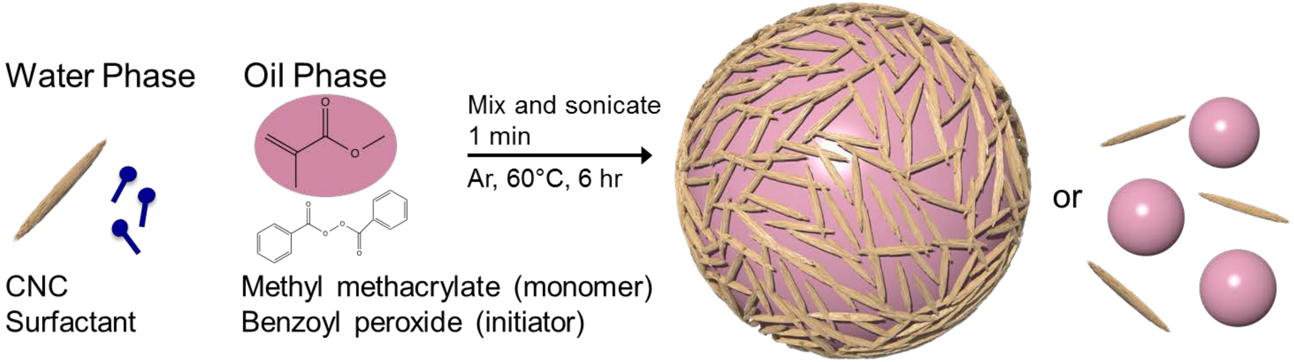
- Multi step process (initiator grafting is separate reaction in DMF)
- Solvent-based (reaction in toluene)
- Still requires purification

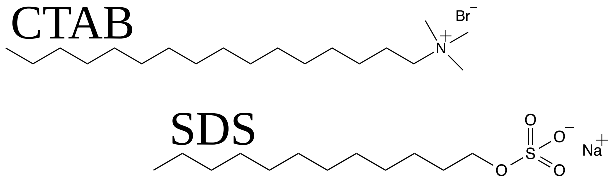
Emulsion Polymerization with Modified CNCs (Model System, Small Scale):

Key Results

Miniemulsion Polymerization

- Combine CNCs + surfactants to stabilize mini emulsion polymerization of **methyl methacrylate** (model system)
- Polymer particle size (latex) depends on the interactions between CNC and surfactant

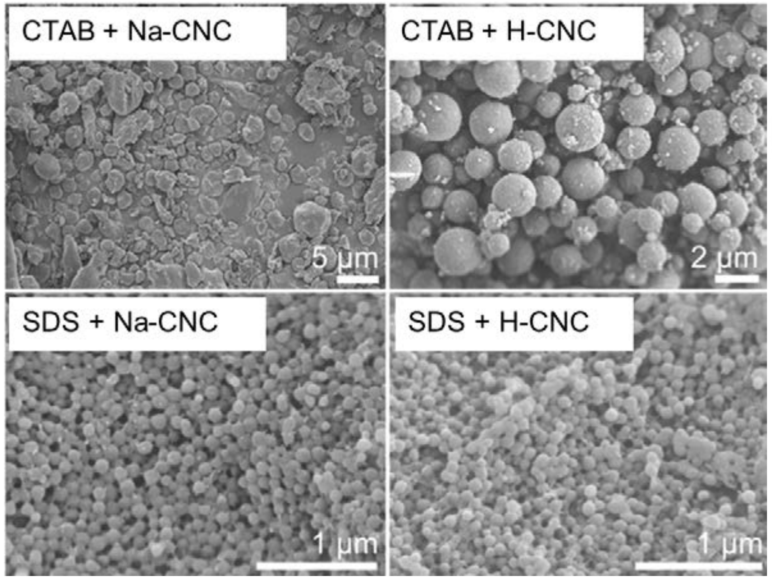




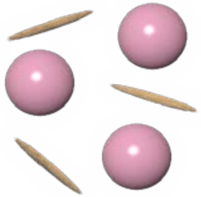
Kedzior, Marway and Cranston (2017) Macromolecules, 50:2645

Miniemulsion Polymerization

- Most stable monomer-in-water emulsions give the most uniform latexes



Micron-sized latexes when CNCs and surfactant are *oppositely* charged



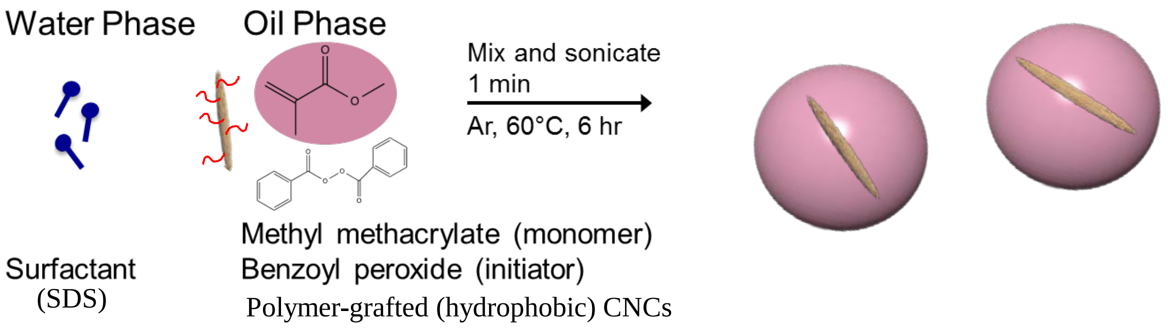
Nano-sized latexes when CNCs and surfactant are *similarly* charged

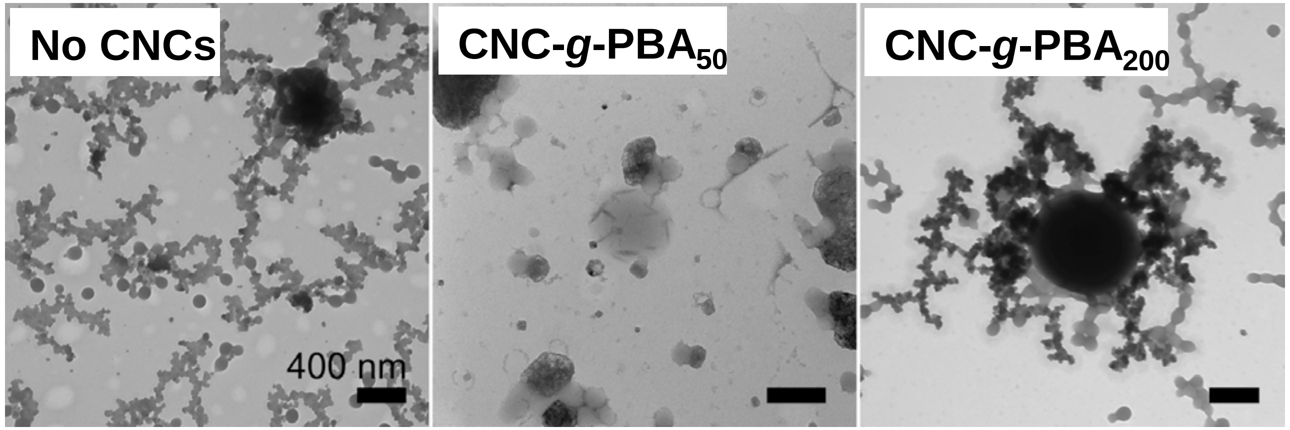
CNCs + surfactant co-stabilizers allow us to tailor latex size, shape, surface roughness, charge, Mwt, PDI and properties.

Kedzior, Marway and Cranston (2017) Macromolecules, 50:2645

Polymer Grafted CNCs in Latexes

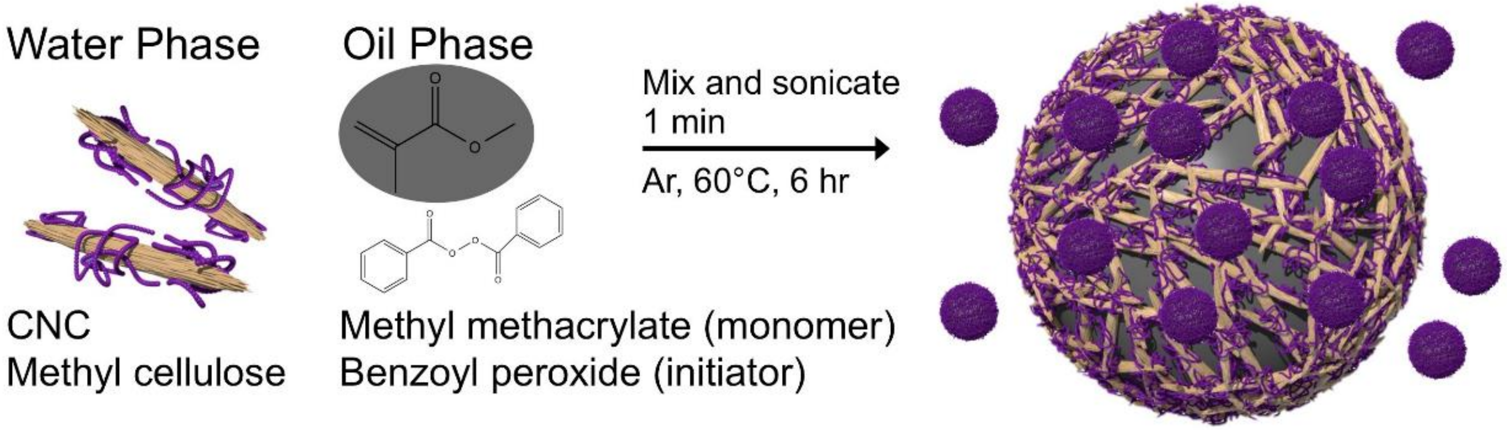
- Mini emulsion polymerization with ATRP polymer grafted CNCs

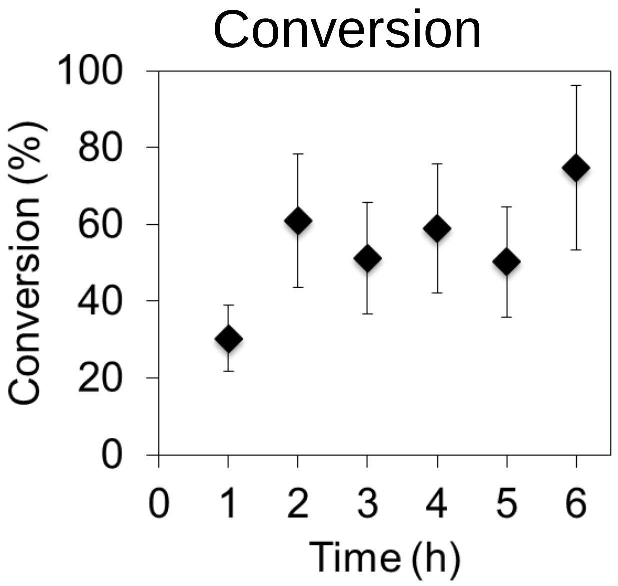


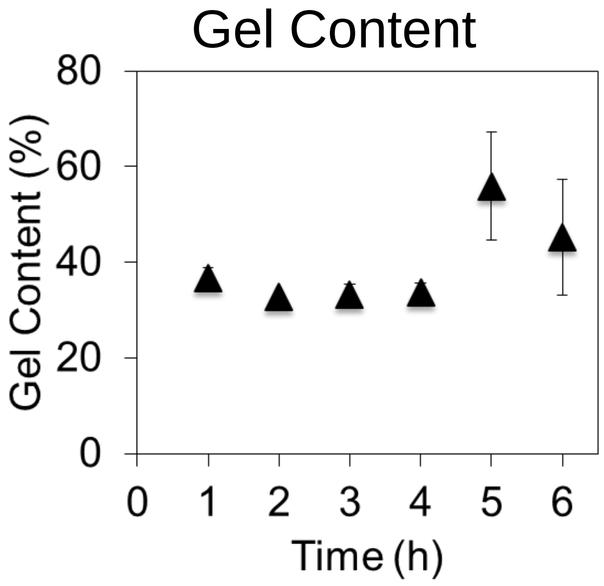


PMMA latex particles remain nano-sized with incorporated hydrophobic CNCs.

Microsuspension Polymerization - PMMA

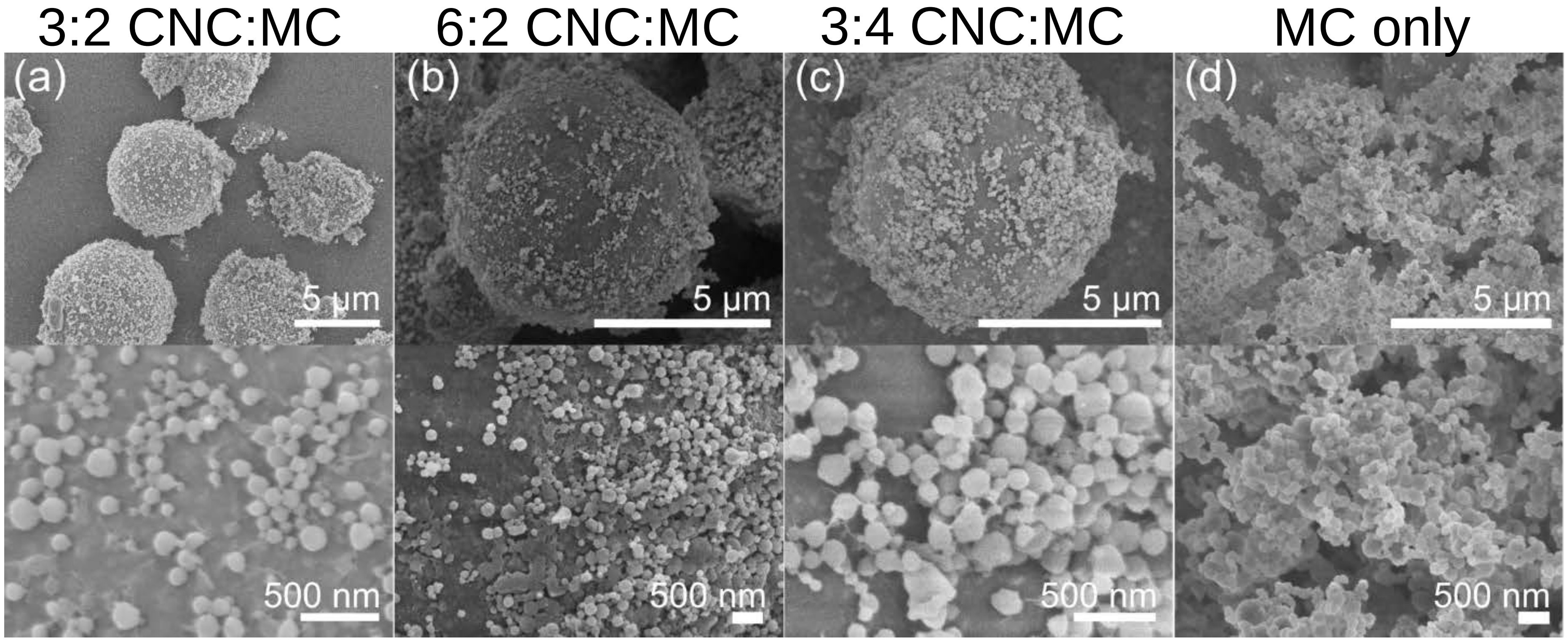






Kedzior, Dubé and Cranston (2018) **<u>Polym. Chem.</u>**, ***submitted*****.**

Microsuspension Polymerization - PMMA



Polymer particles have tunable double morphology based on the ratio of CNC:MC used.

Kedzior, Dubé and Cranston (2018) Polym. Chem., *submitted*.

Conclusions

- CNCs produced industrially are **reproducible and uniform**
- Synergy between CNCs with adsorbing polymers or surfactants provides a **new range of latex and other materials**
- **Toolbox of CNC surface modification** routes exist along with methods to **control CNC location** and function in polymer latexes
- PSAs with CNCs **show improved and surprising performance**

CNC are ideal for stabilizing interfaces and providing structural support - complex yet tailorable materials can be designed.

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