New polymers for wet-strength – an academic perspective

Robert Pelton

Interfacial Technologies Group
Department of Chemical Engineering
McMaster University
1280 Main St. W., Hamilton, Ontario, Canada L8S 4L7
E-mail: peltonrh@mcmaster.ca

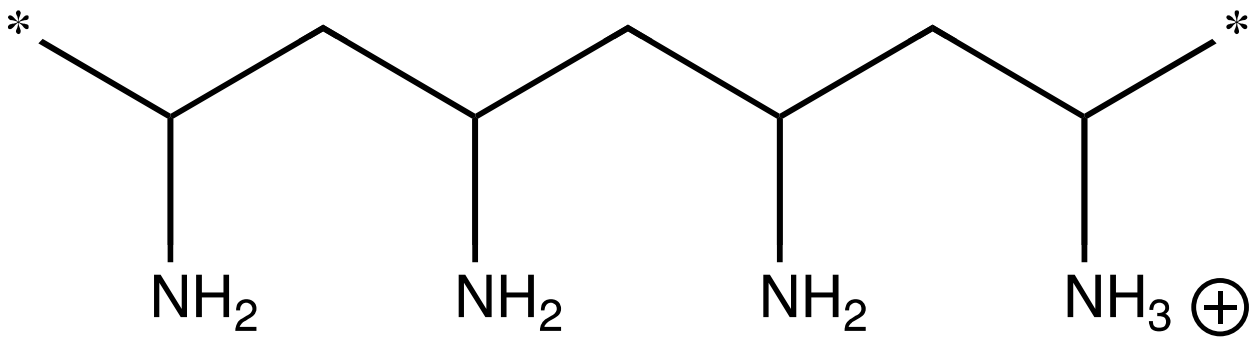
Acknowledgements

NSERC
CRSNG

BASF
The Chemical Company

Pengchao Ren

Polyvinylamine

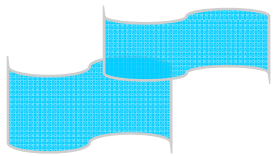


- 2000 we initiated a major project to understand the influence of PVAm on the mechanical properties of wet paper
- A problem in wet adhesion.

Our First Effort in Wet Strength

- **Pelton, R.; Hong, J., Some properties of newsprint impregnated with polyvinylamine. *Tappi J. 2002, 1 (10), 21***
  - ***PVAm increased newsprint wet strength***
  - ***More amine groups (degree of hydrolysis), the better***
- **We needed a better wet adhesion test.**

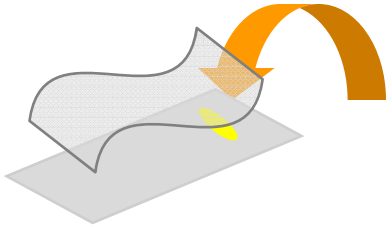
Film Delamination – A Model for Fiber-Fiber Wet Adhesion



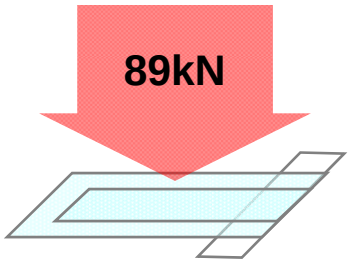
Regenerated Cellulose (Dialysis Membrane)

Chemical Modification

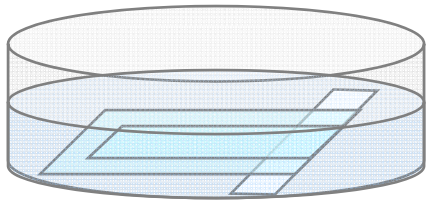
Polymer addition



Apply Polymer



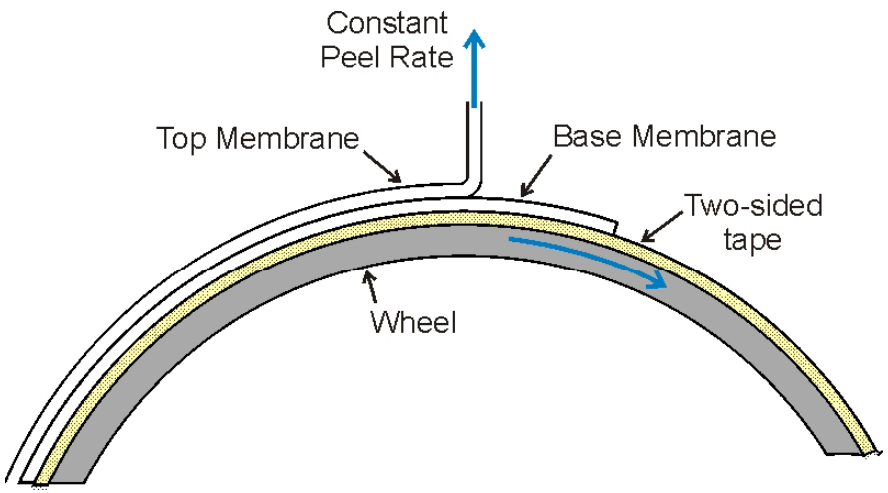
Press at 89kN and dry at 23° C and 50%RH

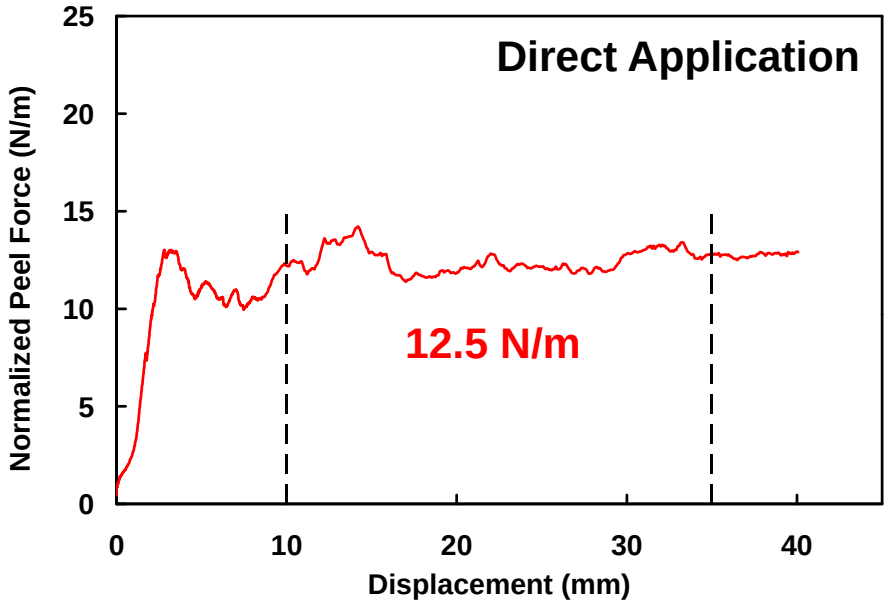


Soaking

Adhere to wheel & 90° peel

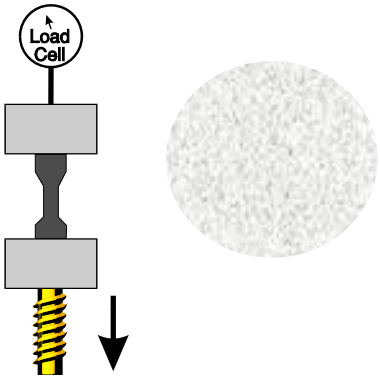
Wet Adhesion Test – 90° Peel

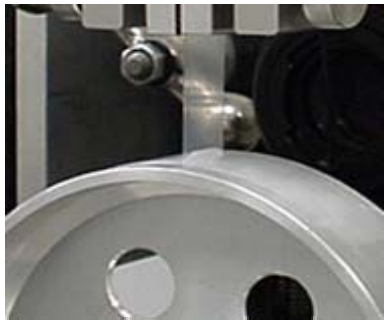


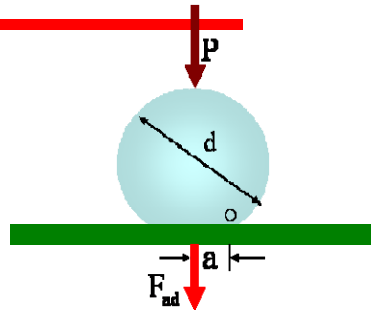


- **Figure: typical force vs. displacement trace**
- **Summarized by average normalized force**
  - ***Force/width of top laminate N/m***

How our Method Fits In







Paper Testing

Peel Delamination

Surface Force Apparatus
Atomic Force Microscopy, JKR

Technical (fast) ⟷ **(tedious) Fundamental**

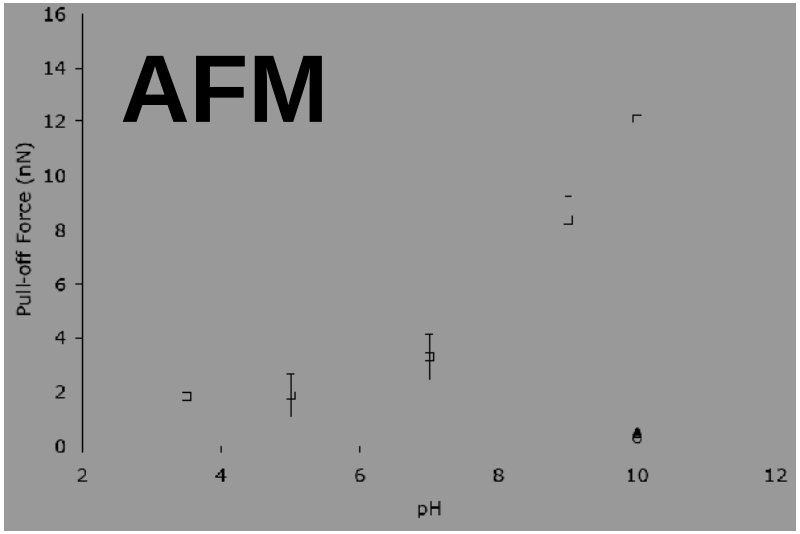
Wet Paper Testing
- standard methods
- fast, large database
- relevant substrates
- too complex for fundamental interpretation

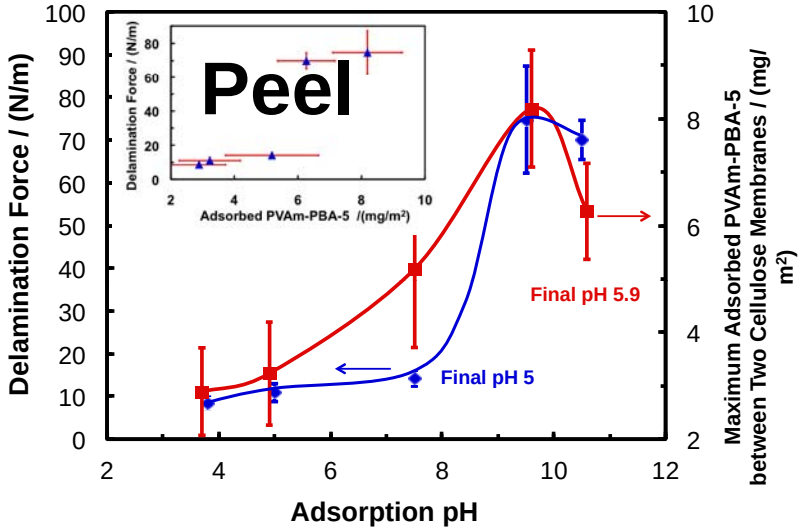
Wet Cellulose Delamination
- fast, standard equipment
- widely available substrate
- reproducible results
- a crude model for fibers
- somewhat well characterized

McLaren (1948)
Kurosu & Pelton (2004)

SFA, AFM, JKR
- gives a lot of information
- requires very smooth surfaces
- well defined physics
- tedious

AFM and Peel Delamination Give Similar Results



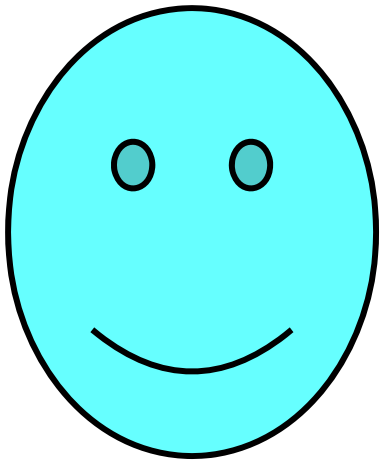


Notley, S.; Chen, W.; Pelton, R., The extraordinary adhesion of phenylboronic acid derivatives of polyvinylamine to wet cellulose a colloidal probe microscopy investigation. *Langmuir 2009, 25 (12), 689*

Chen, W.; Leung, V.; Kroener, H.; Pelton, R., Polyvinylamine-phenylboronic acid adhesion to cellulose hydrogel. *Langmuir 2009, 25 (12), 6863*

Summary – Wet Adhesion Test

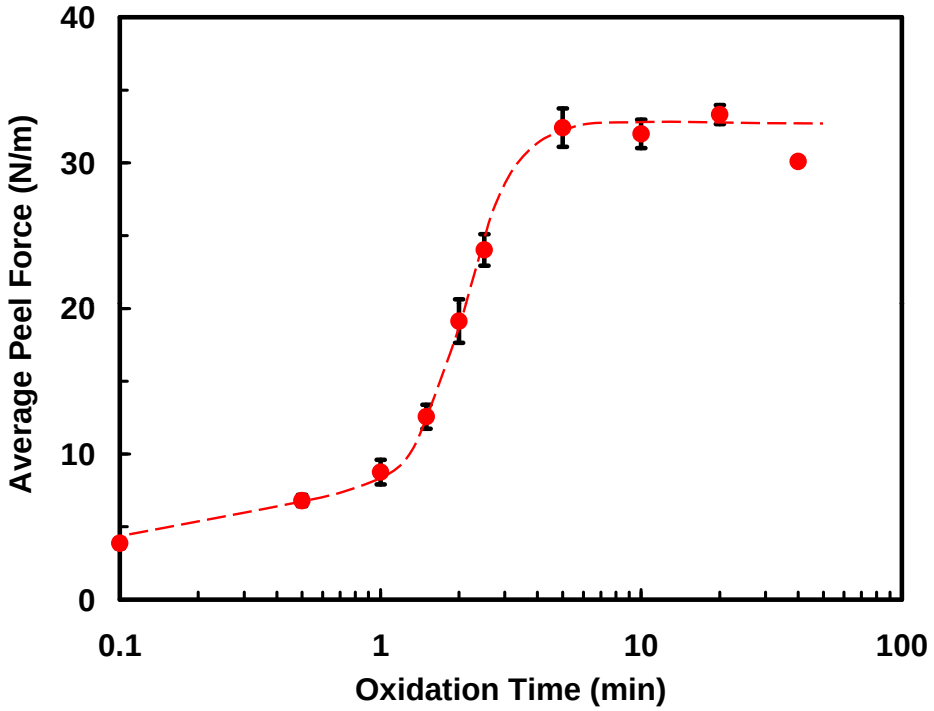
- A model for fiber-fiber bonds (joints if you are Swedish).
- Reproducible
- Can control the amount of polymer in the adhesive joint



The Bad News

- **We we tried to measure PVAm wet adhesion with our new method – the forces were very small.**

The Solution - Oxidation

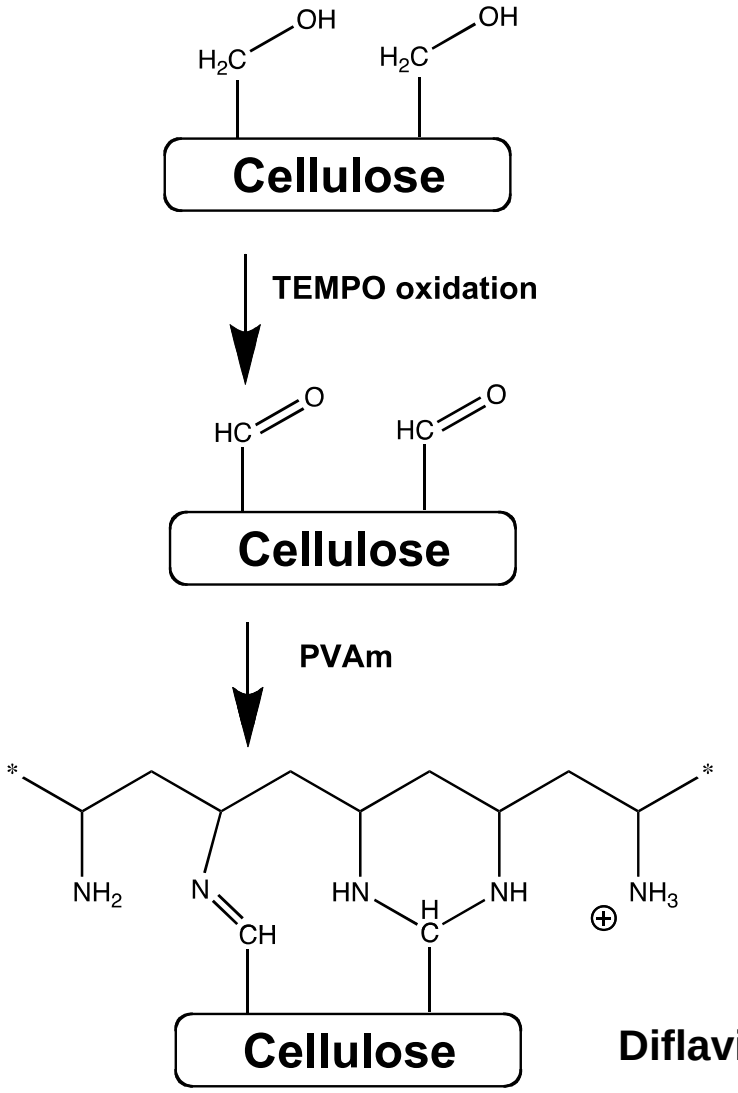


- pH 7, 10mM NaCl, ~7.5 mg/m^2

- DiFlavio applied Isogai's oxidation recipe to cellulose film
- Adhesion increases with cellulose oxidation

DiFlavio, J*FRC: Cambridge, UK, 2005; pp 1293-1316.*

Proposed Mechanism

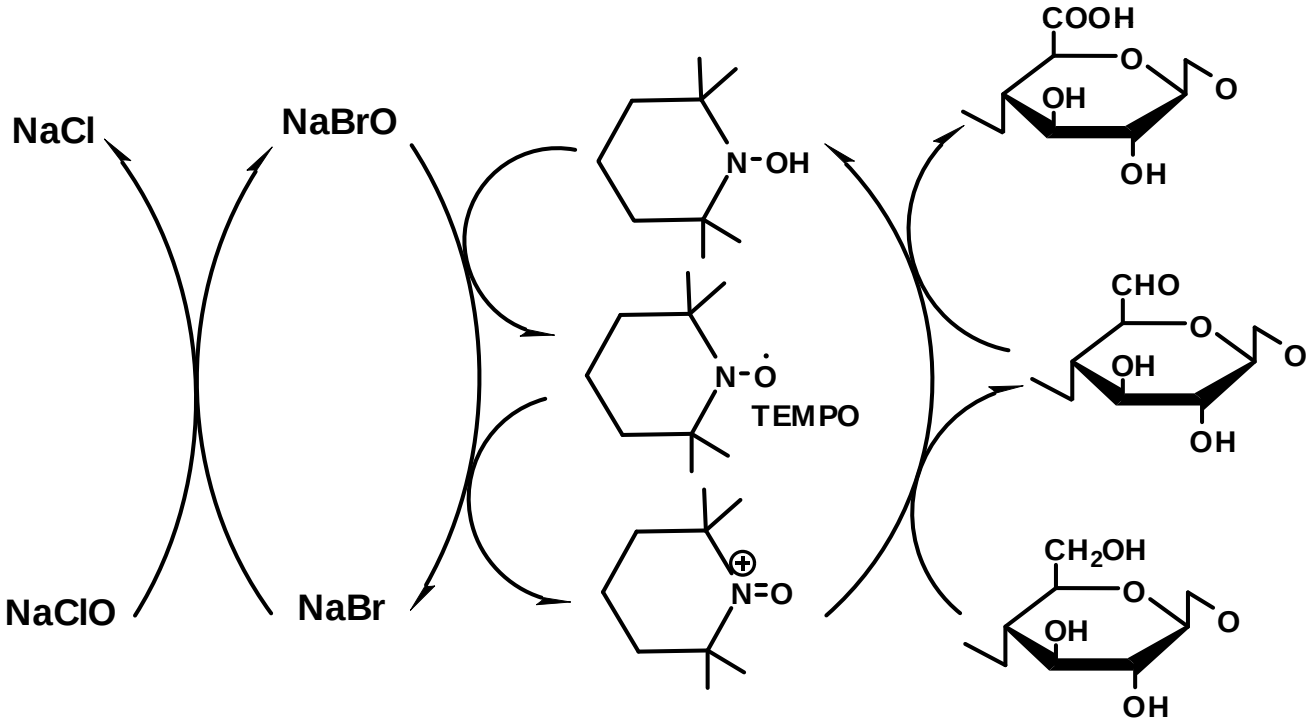


- TEMPO oxidation produces aldehyde/hemiacetals
- PVAm reacts to form imine and aminal covalent bonds with cellulose

Diflavio et al. *Cellulose 2007, 14 (3), 257*

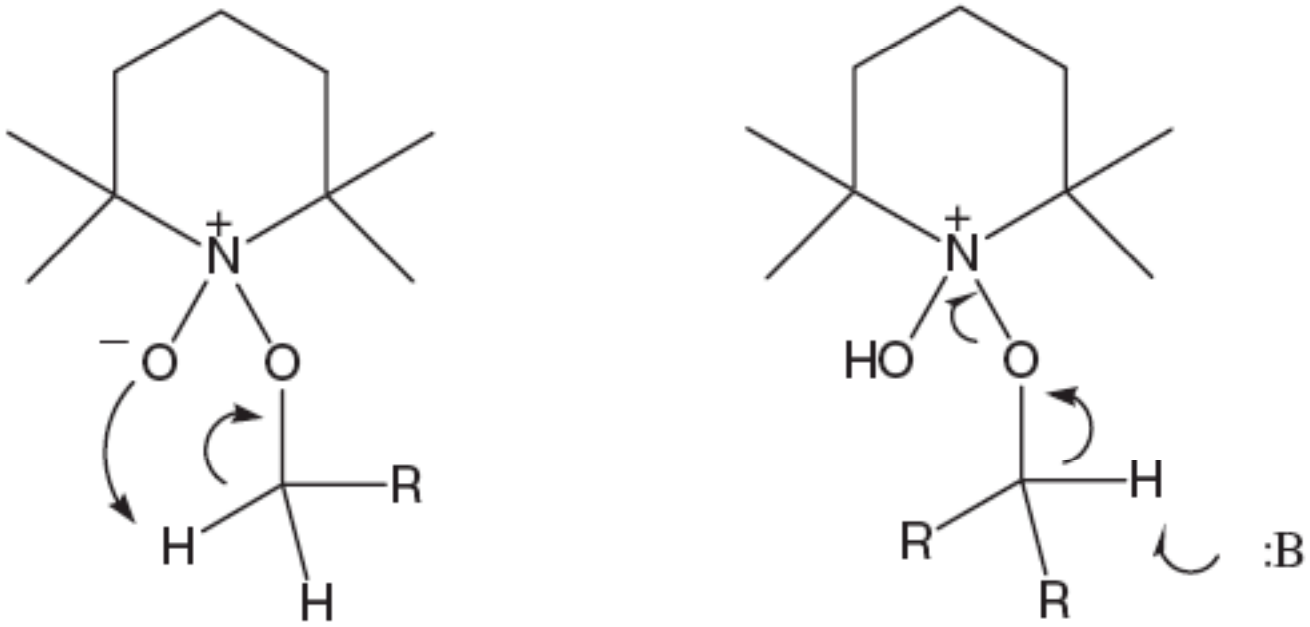
TEMPO oxidation on cellulose

- Primary oxidant: NaClO/NaBr
- Catalyst: TEMPO
- Selectively oxidizes primary OH – C6OH on cellulose



1 T.Saito, A.Isogai. Colloids and surfaces A: Physicochem.Eng.Aspects. 289(2006), P219

Transition State Requires Molecular Contact



VI VII

Scheme 10. Proposed mechanistic adducts in alkaline (VI) and acidic conditions (VII).

Bragd, P. L. et al. *Topics in Catalysis 2004, 27, (1-4), 49*

Practical Issues with TEMPO Applications in Papermaking

- 90 g water
- 10 g od fiber
- 0.025 g TEMPO (0.25% on o.d. pulp)
- 0.25 g NaBr (2.5% on o.d. pulp)
- 0.45 g NaClO (4.5% on o.d. pulp)

- Adding base to maintain pH at 10

- High chemical concentrations
- High pH
- Chemicals in white water

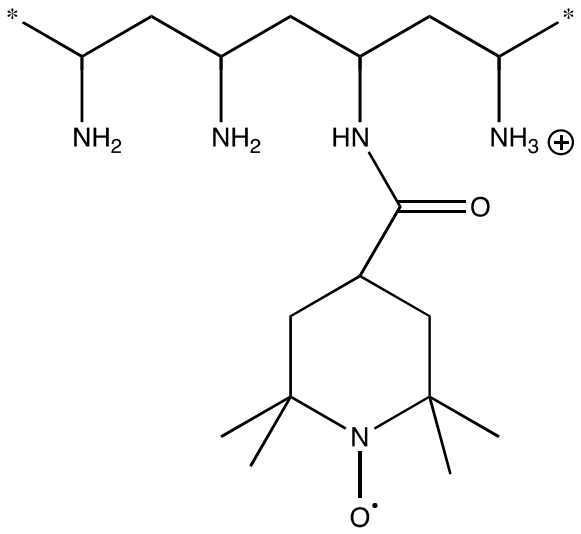
Cellulose Oxidation for Increased Wet Strength -Relevant Literature

- Luner et al. *Tappi 1967, 50 (1), 3*
  - *Aldehydes, not carboxyls give wet strength*
  - *Paper must be dried for strength to develop*
- Kitaoka, T.; Isogai, A.; Onabe *Nordic Pulp & Paper Res. J. 1999, 14 (4), 279*
  - *Higher wet strength with PAE*
- Jaschinski, et al. Pat. US 6,987,181 B2, 2006
  - *SCA patent –TEMPO oxidation to improve wet strength*
- Saito, T.; Isogai, A., *Ind. Eng. Chem. Res. 2007, 46 (3), 773*
  - *Good series of TEMPO papers*
  - *Aldehydes on pulp enhance many polymers*
- *Many other papers and patents involving water-soluble polymers bearing aldehyde groups.*

Summary - 2008

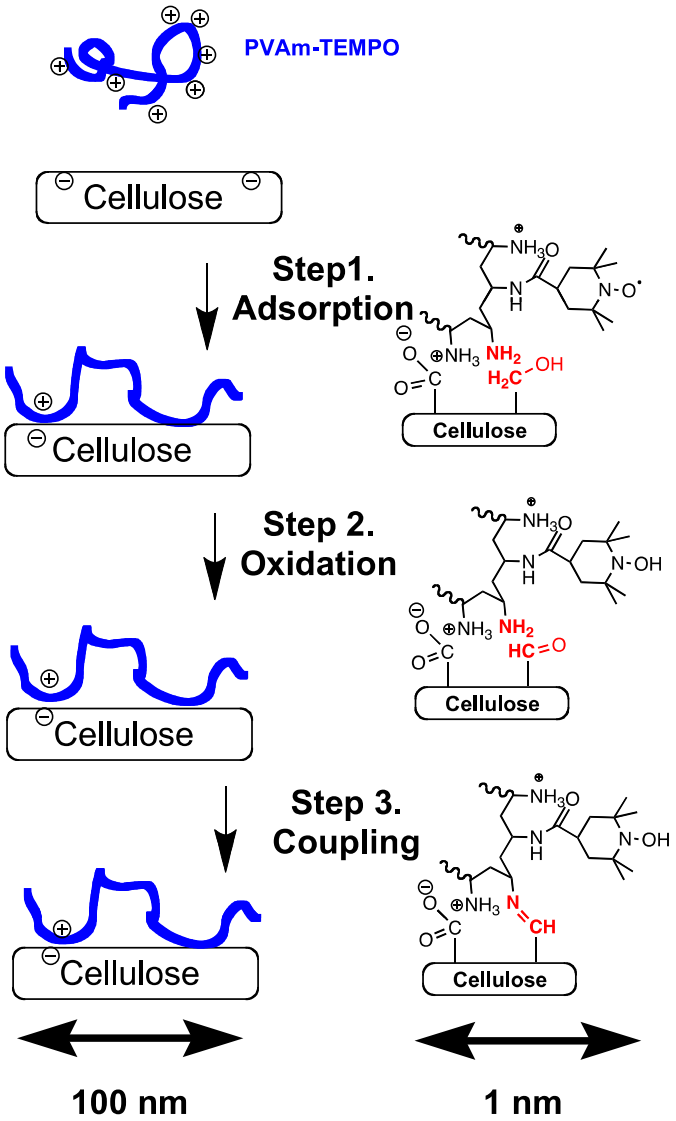
- **We learned a lot about PVAm adhesion to wet cellulose**
  - ***Molecular weight, pH***
  - ***Hydrophobic substitution***
  - ***Phenylboronic acid substitution (wet web strength)***
  - ***Microgels vs linear polymer***
- **Scientifically interesting but some problems with technological application**
  - ***TEMPO – expensive, toxic (Haseloff et al 1997)***
  - ***Easy to produce carboxyls instead of aldehydes***

Hypothesis



- TEMPO must be in physical contact with cellulose
- For covalent attachment of PVAm to cellulose we need only a few oxidized sites.
- PVAm with grafted TEMPO will oxidize the cellulose and then form covalent bonds between the amines and the cellulose aldehydes.

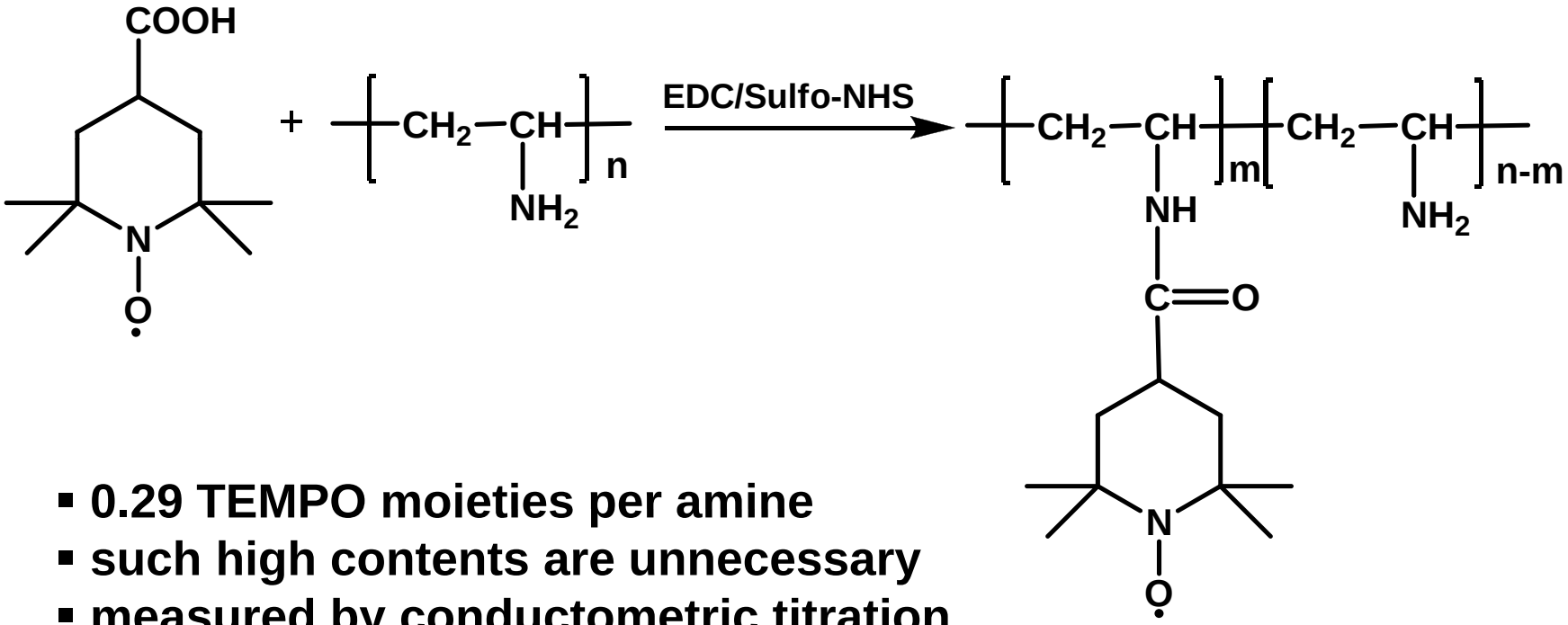
Hypothesis -Continued



- **Potential advantages**
  - ***Much less TEMPO***
  - ***Amines react with aldehydes before further oxidation***
  - ***Only exterior fibers or other porous substrates are oxidized***
  - ***Immobilized TEMPO should be less toxic and not present in water.***

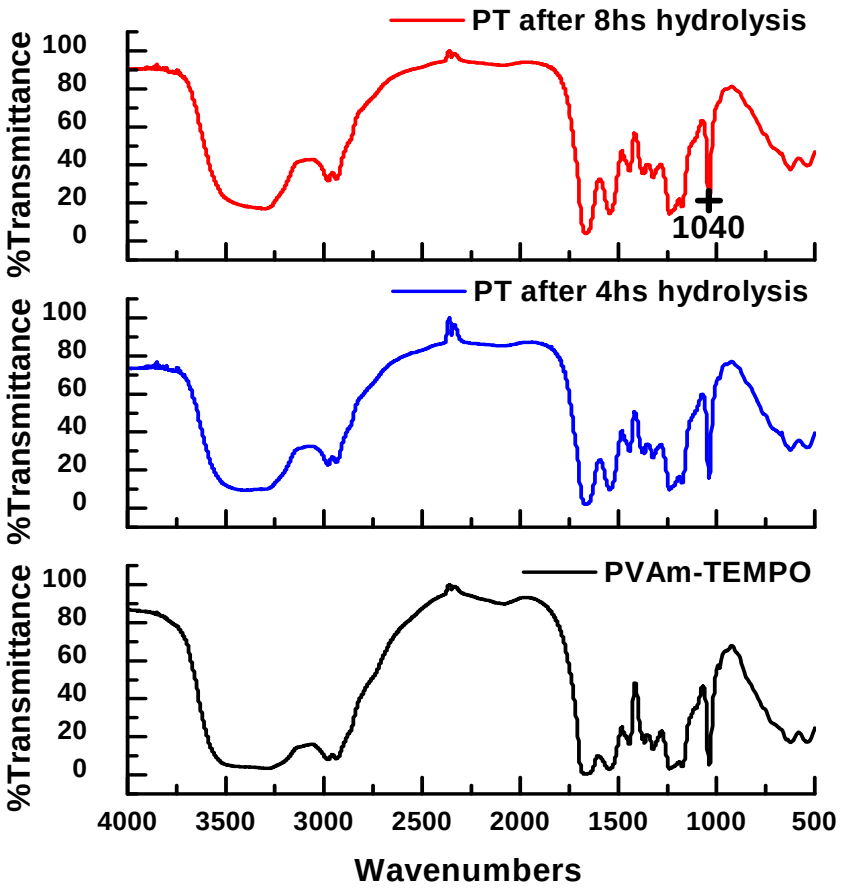
Preparation of PVAm-TEMPO

Amidation reaction catalyzed by EDC/Sulfo-NHS



- 0.29 TEMPO moieties per amine
- such high contents are unnecessary
- measured by conductometric titration
- activity confirmed by soluble molecule oxidation

Stability of PVAm-TEMPO under oxidation conditions



Peak ratio to quantify TEMPO content:

1240 cm^{-1}: C-N stretching vibration, from PVAm

1040 cm^{-1}: N-O vibration, from TEMPO-COOH

Samples	Peak Ratio (1040 /1240 cm^{-1})
Original PT	0.874
PT, after 4hs' hydrolysis	0.809
PT, after 8hs' hydrolysis	0.809

PVAm-TEMPO is stable under oxidation conditions!

Direct coating method

Experimental procedure

PVAm-TEMPO oxidation in aqueous solution, pH 10.3 2h

↓

Oxidized films were rinsed with water and laminated with additional PVAm, then pressed

↓

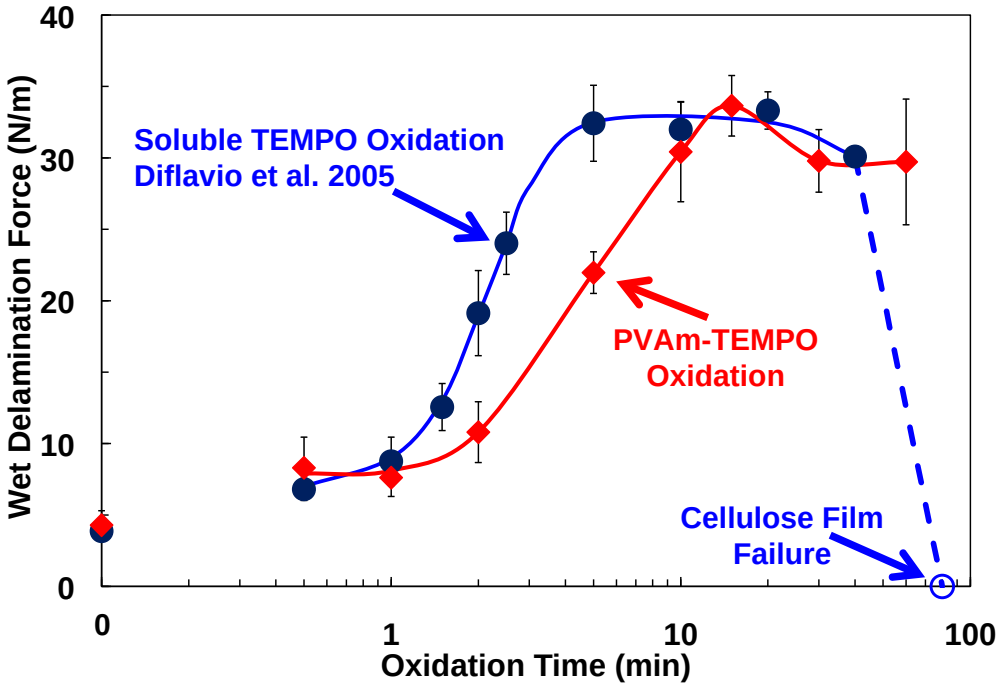
Laminated films were conditioned and peel force was tested

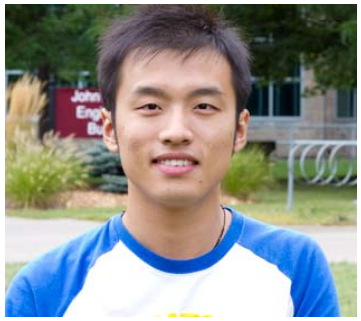
Wet adhesion of treated cellulose films

Trials	NaBr (mg/L)	PVAm-TEMPO (mg/L)	NaClO (mmol/g cellulose)	Coated PVAm (mg/m^2)	Average peel force (N/m)
1	0	0	0	6.25	1.9
2	82.5	0	1.8	6.25	2.9
3	82.5	66.7	1.8	6.25	25.2

PVAm-TEMPO works well as a catalyst!

Influence of Oxidation Time





Jieyi (Jerry) Liu

- Soluble TEMPO diffuses into film interior and weakens whole film
- Grafted TEMPO gives similar kinetics without oxidizing film interior pores

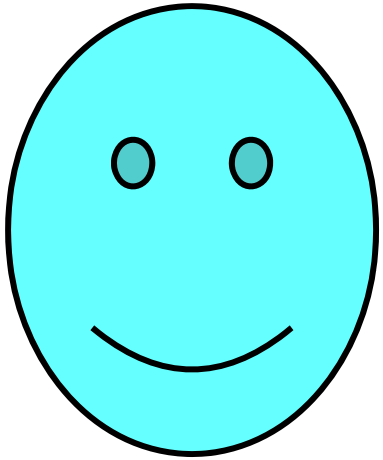
Comparing Soluble to Tethered TEMPO

- **Assume:**
  - ***Adsorbed density PVAm-g-TEMPO 1mg/m2***
  - ***Adsorbed layer thickness 5 nm***
  - ***TEMPO conc. On cellulose surface 5 M/L***
- **Tethered TEMPO concentration 1000> Saito and Isogai solution concentration.**
- **Much scope to lower TEMPO grafting and optimization.**

Conclusions

- **PVAm-TEMPO does oxidize cellulose**
- **Many potential advantages**
  - ***Less TEMPO***
  - ***No soluble TEMPO effluent***
  - ***No fiber strength loss (exterior oxidation only)***
- **Scope for optimization**
- **Ultimate goal self-catalyzing adhesive with no other chemical additions.**

See Pelton, R.; Ren, P. R.; Liu, J.; Mijolovic, D., Polyvinylamine-graft-tempo adsorbs onto, oxidizes and covalently bonds to wet cellulose. *Biomacromolecules 2011, on-line. http://dx.doi.org/10.1021/bm200101b*



That's All

Bioactivepaper.com

Papersci.mcmaster.ca