Improved Cellulose Composites for Packaging Applications

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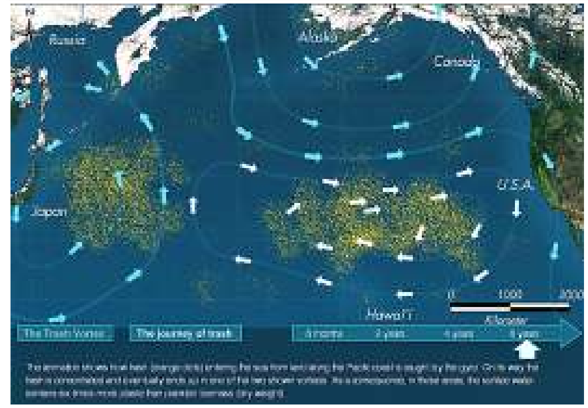
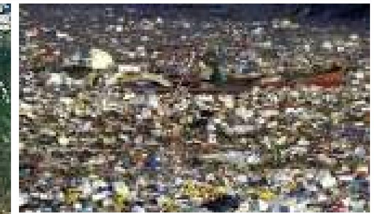
Sociotechnological challenge: disposable packaging





- Non-biodegradable plastics are not only filling up our land fills – but the ocean as well.

http://www.dailygalaxy.com/my_weblog/2008/05/is-there-a-natu/comments/page/2/

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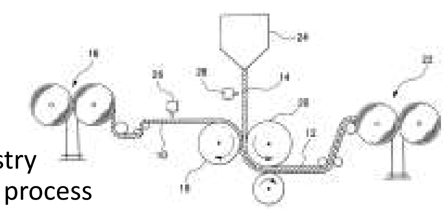
Objectives

To develop a compostable liquid barrier paper composite or coating for disposable/short term (days) exposure applications with the following constraints:

- Cost competitive with LDPE laminates
- Use compostable materials
- If possible, use food-grade materials to allow immediate commercialization into the food packaging/handling industry
- Ecologically compatible manufacturing process
- Consume minimal production energy
- Manufactured with existing capital infrastructure
- Functions over pH 3-9
- Stable in water and oil
- Stable to 80C+
- Clear
- Recyclable



Examples of LDPE (polyethylene) paper laminate packaging products

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Potential solution: Polysaccharide and/or protein blends

- Engineered colloidal particulate systems are finding increasing application within the food industry:
  - Encapsulation, protection and delivery systems:
    - Bioactive lipids, minerals, enzymes, peptides, dietary fibers, nutraceuticals
  - Engineer the physicochemical and sensory properties of foods:
    - Optical properties (appearance)
    - Rheological properties (texture)
    - Release characteristics (flavor or bioactivity)
      - Time/location (mouth, stomach, small intestine, colon)
    - Encapsulation properties (for stable delivery)
    - Physicochemical stability (ex: slow melting ice cream)

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Potential solution: Polysaccharide and/or protein blends

Food Grade proteins and polysaccharides

Table 2–Summary of important molecular characteristics among common food-grade proteins for assembling biopolymer particles. Derived from Damodaran (1997) and Fox and McSweeney (2003).

Name	Source	Main structural type	pI	~T_m (°C)
β-Lactoglobulin	Whey protein	Globular	4.8–5.1	75
Caseins	Milk	Rheomorphic	~4.6	125–140
Bovine serum albumin	Bovine blood/milk	Globular	4.7	70–90
Ovalbumin	Egg white	Globular	4.5–4.7	74; 82[S]
Soy glycinin	Soybean	Globular	~5	67[7]; 87[11]
Gelatin	Animal collagen	Linear	7–9.4[A]; 4.8–5.5[B]	40

A: Type A gelatin; B: Type B gelatin; S: S-type ovalbumin; 7: 7S soy glycinin fraction; 11: 11S soy glycinin fraction.

Table 3–Summary of important molecular characteristics[A] among common food-grade polysaccharides for assembling biopolymer particles. Derived from Stephen and others (2006).

Name	Source	Main structure type	Major monomer	Gelation
Carrageenan	Algal	Linear/helical	Sulfated galactan	Cooled set
Xanthan gum	*Xanthomonas campestris* exudate	Linear/helical (high MW)	β-D-Glucose (backbone)	None; thickens with concentration
Methyl cellulose	Wood pulp	Linear	Methylated glucose	Heat-set (rev.)
Pectin	Plant cell walls	Highly branched coil	Glucuronate (backbone)	Sugar/heat (HM); calcium (LM)
Beet pectin	Sugar beet pulp	Branched coil with protein	Glucuronate (backbone)	Sugar/heat (HM); calcium (LM)
Gum arabic	Acacia sap	Branched coil domains on protein scaffold	Galactose	Conc.-dependent
Inulin	Plants or bacteria	Linear with occasional branches	β-D-Fructose	Conc.-dependent
Chitosan	Crustaceans, invertebrates	Linear	2-Amino-2-deoxy-β-D-glucose	No common application
Alginate	Algal	Linear	β-D-Mannuronic acid	Calcium cross-linking

[A]Polysaccharide ingredients available commercially generally possess appreciably different molecular and functional properties; the listed information describes general characteristics for industrial usage.

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Jones, O.G., and D.J. McClements. 2010. Functional Biopolymer Particles: Design, Fabrication, and Applications. *Comprehensive Reviews in Food Science and Food Safety* 9: 374-397.

Interactions between biopolymers

Table 4–General features of some physicochemical interactions among food biopolymers and relevant factors.

Interaction type	Sign	Magnitude, factors	Range, factors	Effect of environment
Electrostatic interactions	Attractive: opposing charge; Repulsive: similar charge	Strong; Factors: charge density, surface charge density, solvent dielectric constant	Long range; Factors: solvent dielectric properties, ionic screening (ions or dipoles)	Magnitude: pH, dielectric constant, biopolymer conformation[a]; Range: pH, ionic strength, dielectric constant
Hydrogen bonding	Attractive	Relatively weak; Factors: density of interactive species	Short range	Magnitude: temperature, solvent dielectric constant
Hydrophobic interactions	Attractive	Strong; Factors: interfacial tension with solvent, exposed surface area	Medium range	Magnitude and Range: biopolymer conformation[a], dielectric constant, temperature
Excluded volume effects *Ex: Phase separation; steric exclusion*	Attractive	Variable; Factors: concentration and biopolymer gyration radius	Proportional to gyration radius	Magnitude and Range: biopolymer conformation[a]

[a]Biopolymer conformation refers to any environmental factor that significantly alters the conformation of the biopolymer, changing possible physicochemical interactions.

Van der Waals (ex: stacking) interactions and entanglement could also play a role.

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Jones, O.G., and D.J. McClements. 2010. Functional Biopolymer Particles: Design, Fabrication, and Applications. *Comprehensive Reviews in Food Science and Food Safety* 9: 374-397.

Polysaccharides examined

Chitosan (CS)

- Amino group
- Soluble in weak acid sol

$R\text{-}NH_2 + H^+ \Leftrightarrow R-NH_3^+$

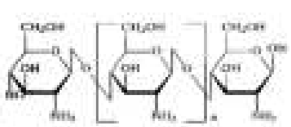
- Cationic
- pI ~ 6.5
- Binds to cellulose by hydrogen and electrostatic bonding

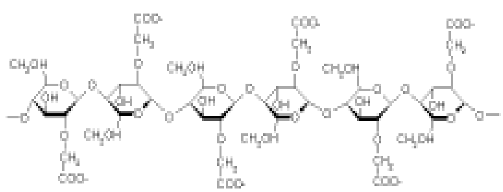
Carboxymethyl cellulose (CMC)

- Carboxylic group
- Soluble in water

$RCOOH \Leftrightarrow RCOO^- + H^+$

- Anionic
- pI ~ 3.7
- Binds to cellulose by hydrogen bonding as both are anionic





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Other variations of interest:

- Use starches (anionic or cationic).
- Use casein (hydrophobic, pI ~ 4.6) and other proteins.
- Incorporate clays and minerals for improved performance.
- Adding cellulose nanocrystals (CNCs) for improved performance.

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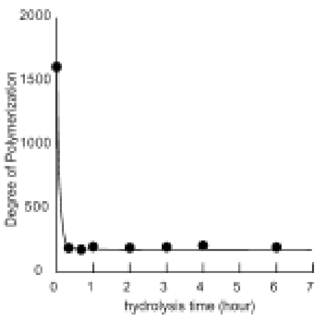
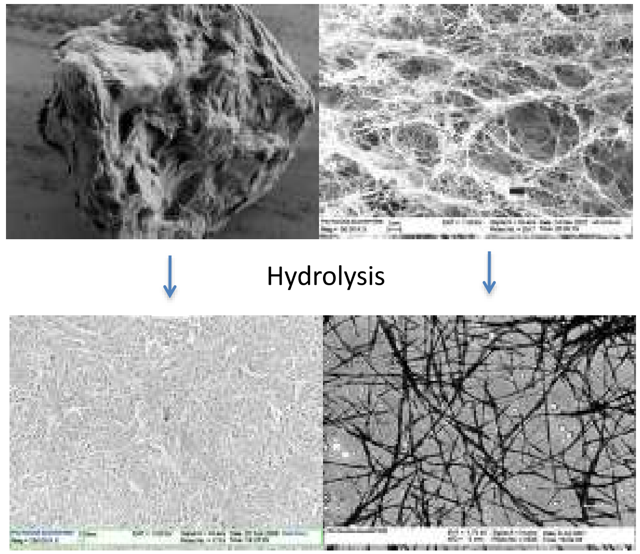
CNCs from cotton and bacteria



Nishiyama, et. al.,Periodic Disorder along Ramie Cellulose Microfibrils, Biomacromolecules 2003, 4, *1013-1017*



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Production process for coating

- Production process for basic blend could not be simpler:
  - Dissolve CS (3-6% w/w) in an acid (pH 3 formic acid works best).
  - Dissolve CMC (3-6% w/w, molar ratio of functional groups in range of 0.8:1 to 1:0.8, ~1:1 typical) also in an acid (pH 3 formic acid).
  - Combine and vigorously blend (~>25,000 RPM) for 3-20 minutes, typically 3 minutes.
  - Spray onto surface to obtain a density of ~10^{-5} g/mm^2, typically 3 seconds for 3% solids solution.
    - Substrate density optimally higher than ~10^{-4}g/mm^3.
  - Dry at room or elevated temperature.
  - Add plasticizer (glycerol, 10-25%, before blending) if flexibility in coating desired.

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Why focus on polysaccharide blends?

- Polysaccharide blends offer the following advantages:
  - Blending of cationic and anionic polysaccharides dramatically reduces viscosity allowing 3%-6% solids solutions to be formed.
  - Blending creates dispersed, stable, uniform and well suspended (depending upon particle size) solutions.
  - Electrostatic interactions are insoluble allowing insoluble particles and films to be formed.
  - Polysaccharides inherently oil-resistant (ex: starch and dextran paper adhesives).

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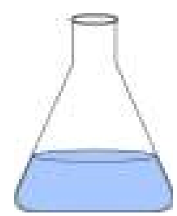
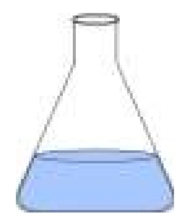
Blends examined

10:10:0 CS:CMC:CNC



- **192.5g DI Water**
- **3g CS blended**
- **3g CMC**
- **1.5g Formic Acid**
- **pH ~3**
- **3% solids**

10:10:4 CS:CMC:CNC



- **191.3g DI Water**
- **3g CS blended**
- **3g CMC**
- **1.2g CNC**
- **1.5g Formic Acid**
- **3.6% solids**

10:10:20 CS:CMC:CNC

- **186.5g DI Water**
- **6g CNC**
- **3g CS blended**
- **3g CMC**
- **1.5g Formic Acid**
- **6% solids**

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Tensile testing performed on TA Q-800

Wet testing
- Sample is completely submerged in a pool of DI Water at a constant temperature (25-80C).
- Holds bottom of the sample stationary.
- Applies a constant strain on the sample by pulling the top of the sample until failure.

Dry testing
- Sample is subjected to air at a constant temperature (25-80C).
- Holds bottom of the sample stationary.
- Applies a constant strain on the sample by pulling the top of the sample until failure.

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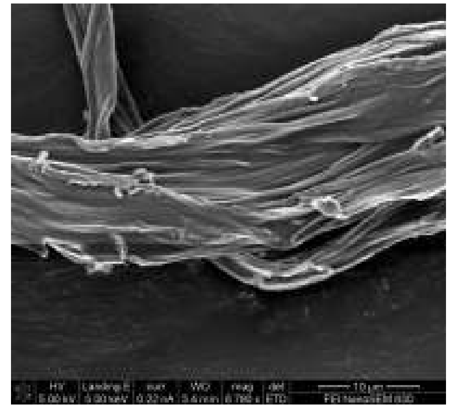
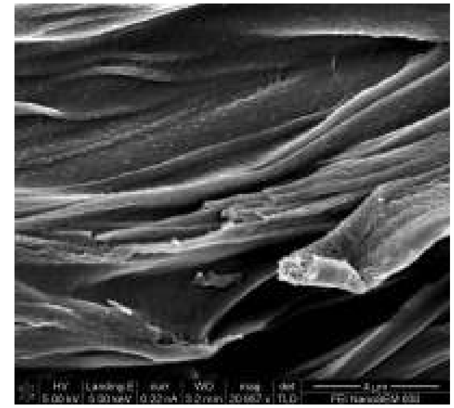
Morphology of blends

10:10:0 (CS:CMC:CNC) blend (3% solids blended for 3min at 25,000 RPM) contain fiber like particles measuring ~150-250 microns long (average).





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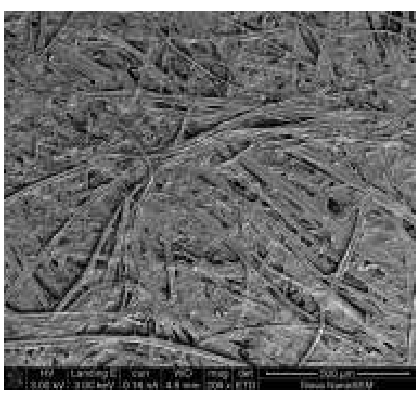
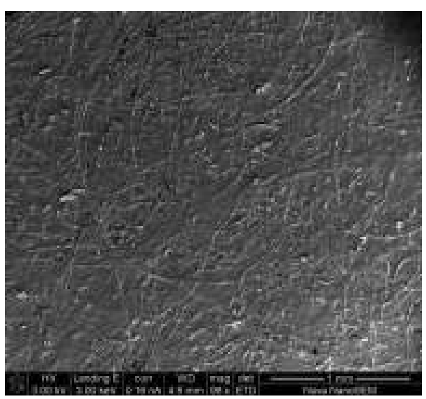
Morphology of surface

SEM images of copy paper (a) uncoated and (b) coated with 10:10:4 (CS:CMC:CNC) blend (density ~5.8×10^{-6} g/mm^2).



(a)



(b)

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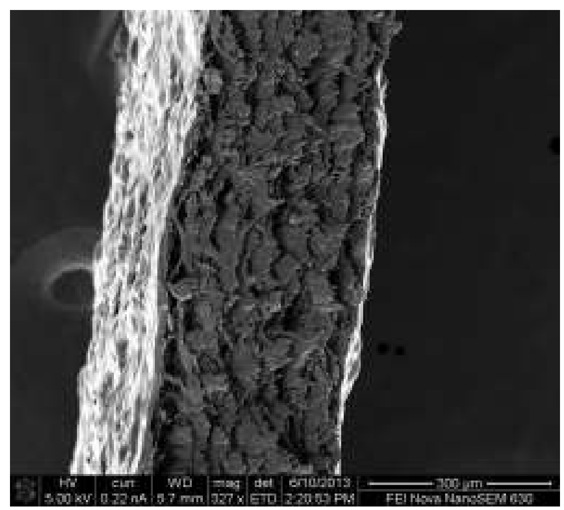
Production process for coating solution



Scanning electron microscope image of a cross section of a cellulose sheet coated with the 10:10:0 (CS:CMC:CNC) blend. The polymer blend coating is clearly seen on the surfaces and measures approximately 12-15 microns in thickness. The coating is continuous across the surface of the sheet.

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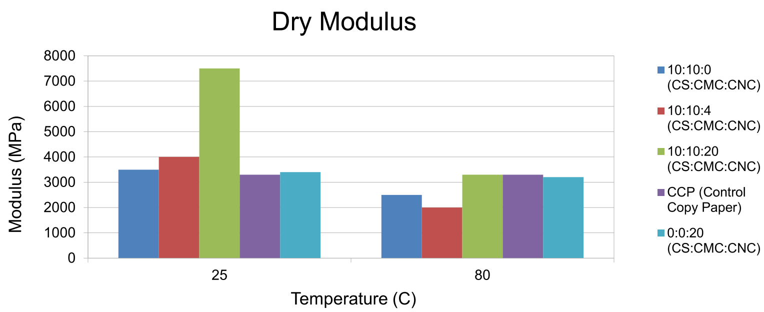
Dry and wet modulus



A key finding: Blend+CNCs performs significantly better than either independently. Could this be a new paper sizing agent? Can be made at 3-6% solids content.

Blend	Density
10:10:0 (CS:CMC:CNC)	1.6E-5 g/mm2
10:10:4 (CS:CMC:CNC)	5.8E-6 g/mm2
10:10:20 (CS:CMC:CNC)	6.3E-6 g/mm2
0:0:20 (CS:CMC:CNC)	6.6E-5 g/mm2

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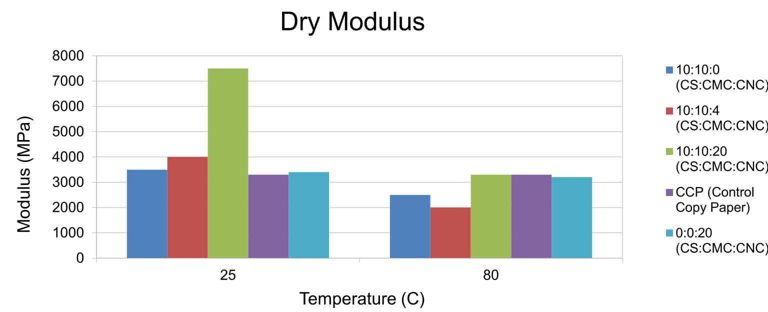
Dry and wet modulus



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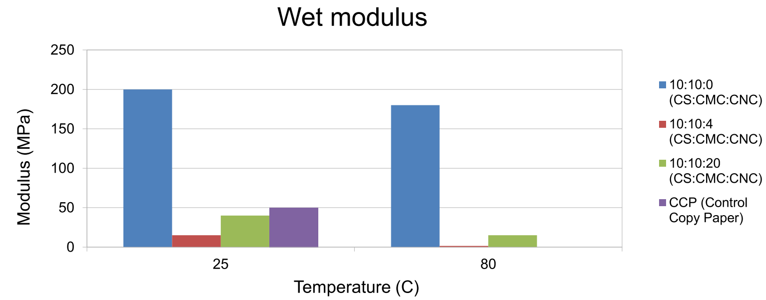
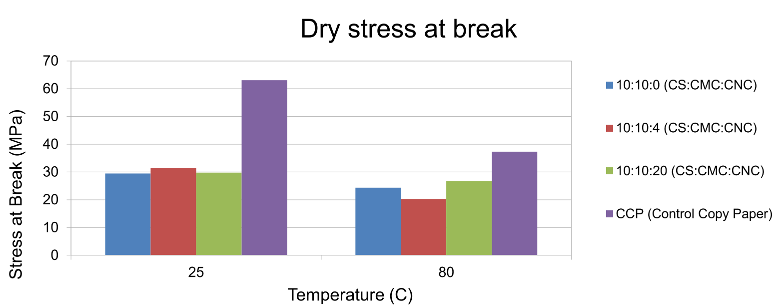
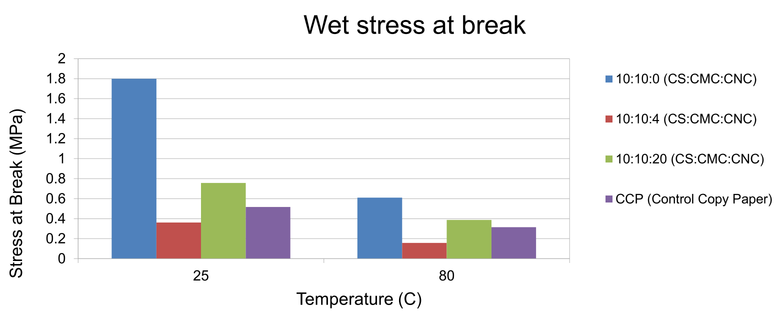


The addition of CNCs may either introduce porosity or shift the optimal blend stoichiometry point resulting in lower wet modulus.

Stress at break



Rehydration of the copy paper and the addition of the blend may reduce the dry strength of the paper substrate.



Water vapor permeability

WVP test fixture

- Substrates are held above a 100mL column of DI water (No Contact)
- Tests were conducted at 38C with a constant flow of air to comply with ASTM Standard E96-95
- The weight of each sample was recorded every 24 hours.

Substrate	WVTR (g/m2/d)
LDPE (1mil)	16
10:10:0 (CS:CMC:CNC)	493
10:10:4 (CS:CMC:CNC)	2467
10:10:20 (CS:CMC:CNC)	2467
0:0:20 (CS:CMC:CNC)	2467

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LDPE WVTR value taken from the *Handbook of Plastic Films*, 2003.

Liquid penetration time

Liquid penetration time studies conducted using a sealed humid chamber (containing ~300ml of DI water). Samples are examined every ~2h during the day to determine when the liquid had penetrated the coating.

After ~1 minute

After ~ 76 hours

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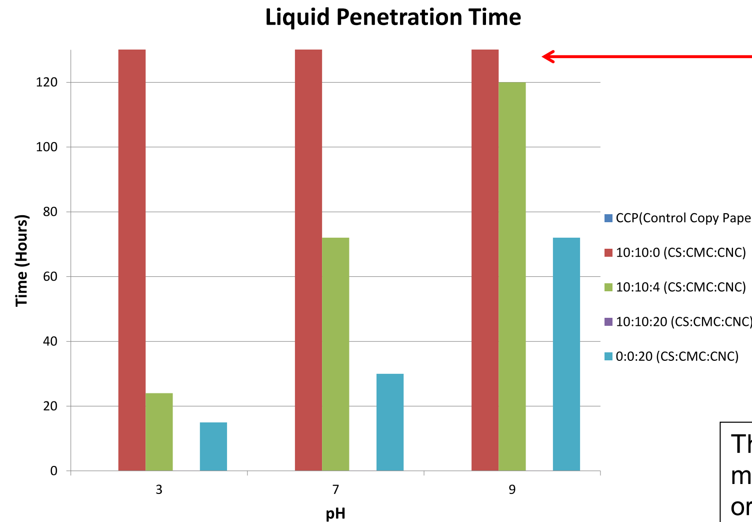
Liquid penetration time



0% CNC at any pH has a penetration time grater than 120 hours.

The addition of CNCs may introduce porosity or shift the optimal blend stoichiometry causing the coating to be soluble.

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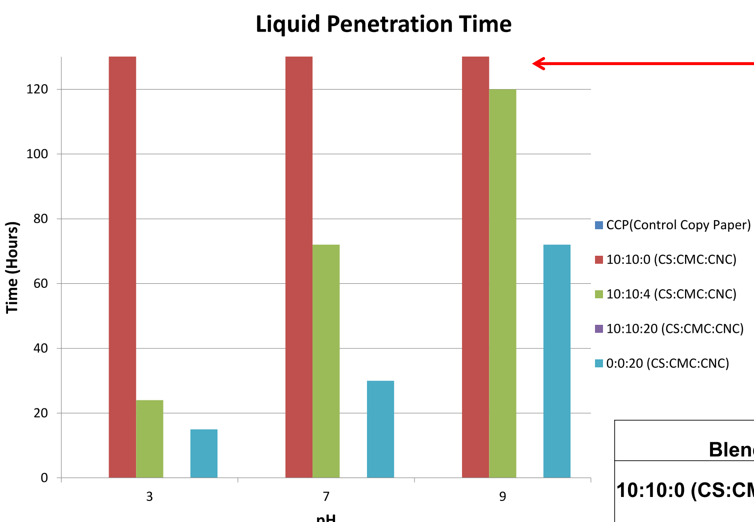
Liquid penetration time



0% CNC at any pH has a penetration time grater than 120 hours.

Blend	Density
10:10:0 (CS:CMC:CNC)	1.6E-5 g/mm2
10:10:4 (CS:CMC:CNC)	5.8E-6 g/mm2
10:10:20 (CS:CMC:CNC)	6.3E-6 g/mm2
0:0:20 (CS:CMC:CNC)	6.6E-5 g/mm2

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Summary

- CS:CMC blend coating dramatically improves wet strength and barrier properties.
- Coatings (density ~10^{-5} g/mm^2) on copy paper serve as an effective liquid barrier for > 5 days over pH 3-9.
- Blend composition and solids content (3-6%) potentially make this an ideal paper sizing product.
- Other applications:
  - Blends for engineered foods.
  - Food coatings.
  - Coatings for other products: drywall, ceiling tiles, cardboard pallets, etc.
  - Improved adhesives (to replace dextran and starch adhesives).
  - Additives/adhesives for wood fiber composites:
    - Flooring, wall board, particle/flake board, gypsum, etc.

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THANK YOU!

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