Cellulose Nanomaterials – A Path Towards Commercialization
May 20-21, 2014

Large Volume User Panel

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Aalto University

NC STATE UNIVERSITY

High Volume

Replacement -Plastic Packaging

Automotive (body & Interior)

Cement

Oil and gas

Packaging Coatings

Textiles & clothing

Hygiene and Absorbent

Paper and packaging filler

Plastic Film Replacement

Paper Coatings

Low volume

Wallboard Facing
Insulation
Aerospace Structure
Aerospace Interiors
Aerogels for Oil & Gas
Paint-Architectural
Paint-Special Purpose
Paint Applications

NOVEL + Emerging Applications

Sensors (medical, env., ind.)
Reinforcement fiber
Water & air filtration

Viscosity modifiers
Purification
Cosmetics
Excipients
Organic LED

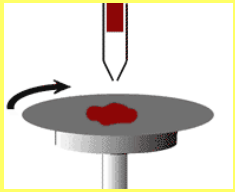
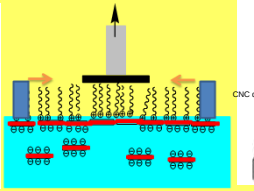
Photovoltaics
Recyclable
Electronics
3D printing
PhotonicFilms

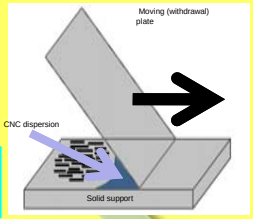
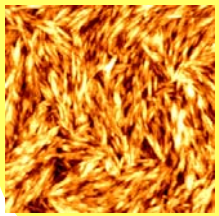
Market Projections For Nanocellulose-enabled Products, J. A. Shatkin (October, 2013)

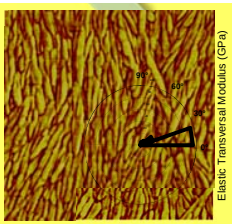
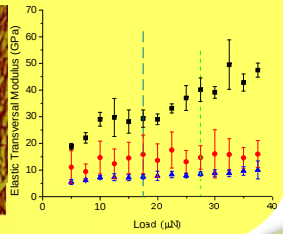
Cellulose Nanocrystals CNC

Coatings and anti-scratch surfaces

Film casting | Spin coating | Langmuir-Schaeffer | Shear/Convection

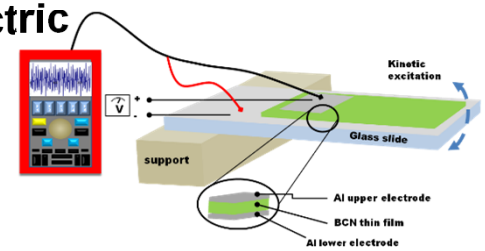



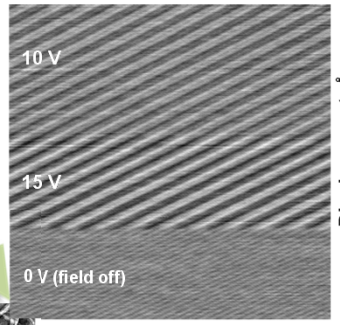




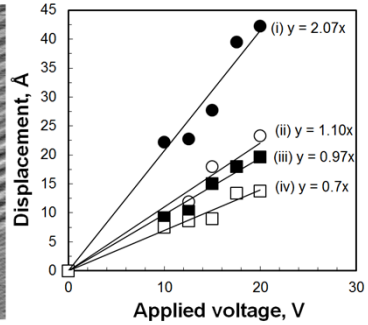
Soft Matter 7 , 1957 (2011)
Biomacromolecules, 11, 2683 (2010)
Biomacromolecules , 11, 674 (2010)

Appl. Mater. Interfaces , 1, 1996 (2009)
Langmuir, 26, 990 (2010)
Thin Solid Films, 517(15), 4348 (2009)

Piezoelectric materials

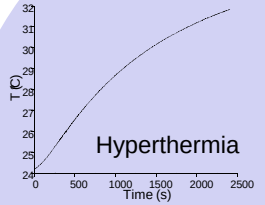


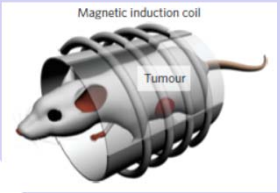




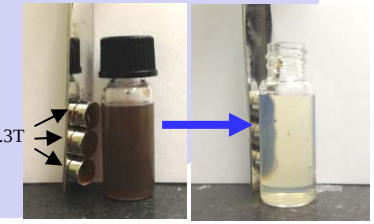
ACS Macro Letters, 1, 867 (2012)
JCIS, 363, 206 (2011)
Soft Matter, 7, 1957 (2011)

Organic-inorganic hybrids



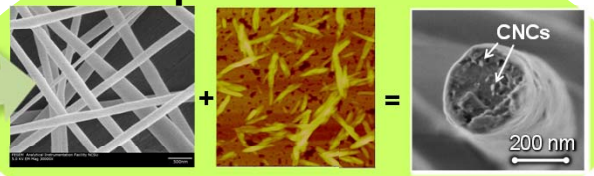


Magnetic separation



Bioresource Technol, 101, 596 (2010)
Chem Rev, 3479 (2010)

Composite nanofibers



Biomacromolecules,13: 918 (2012)
J. Polym. Env, 20, 1075 (2012).
Biomacromolecules, 11, 2471 (2010)
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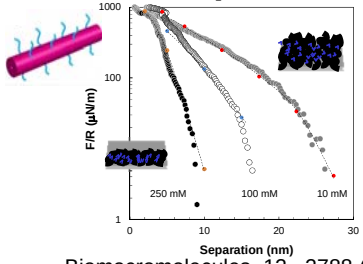
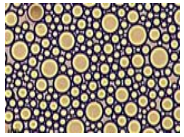
Appl. Mater. Interfaces, 1, 1996 (2009)
J. Appl. Polym. Sci. 113, 927 (2009)

Stimuli responsive CNCs

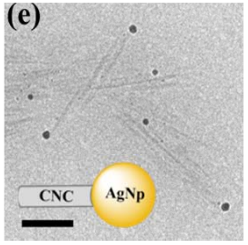


poly(NiPAAm)-g-CNCs



Biomacromolecules, 12, 2788 (2011)
J Colloid & Interface Sci, 369, 202 (2012)

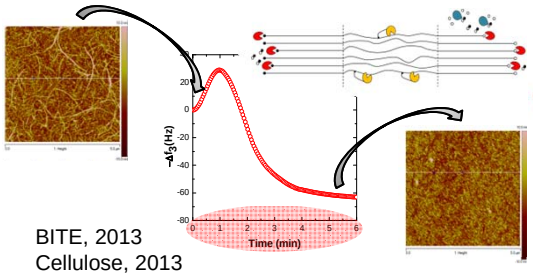
Asymmetric CNC



Reductive amination at the reducing ends of a CNC and Ag silver NP labeling of thiol functionalized CNCs

Biomacromoleules, 2013

Bioconversion



BITE, 2013
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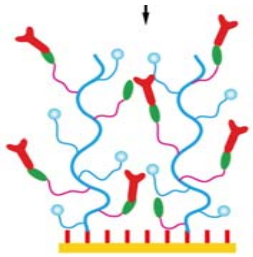
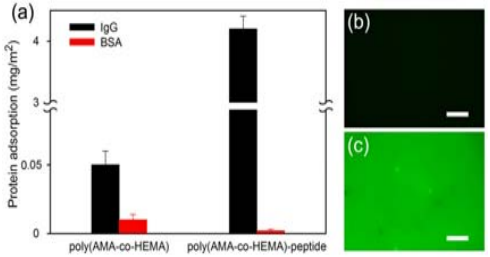
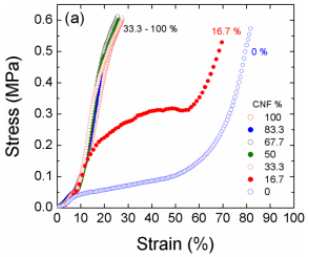




Bioactive materials

Anal. Chem, 2013
Biointerphases, 7, 61 (2012)
Biomacromolecules, 12, 4311 (2011)
Biomacromolecules, 13, 2802 (2012)
Carbohydrate Polymers, doi:10.1016/j.carbpol.2012.11.063

Super-strong Hydrogels & Aerogels



Cellulose 20, 2417 (2013)

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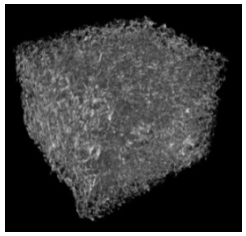

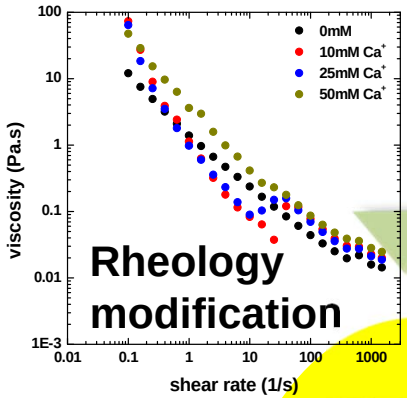

Rheology modification

Cellulose Nanofibrils NFC and BC

J. Renewable Resources, 2013, 1, 195
Carbohydrate Polymers, 89,1033-1037 (2012)

Nanopaper

Appl. Mat. Interfaces, 2013

BITE125, 249 (2012)
Cellulose, 19, 2179 (2012)
Bioresources, 6, 4370 (2011)
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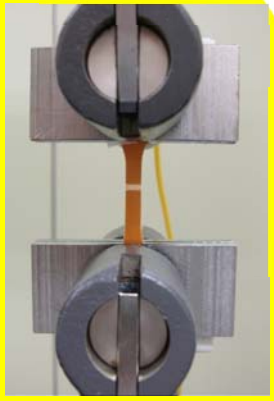
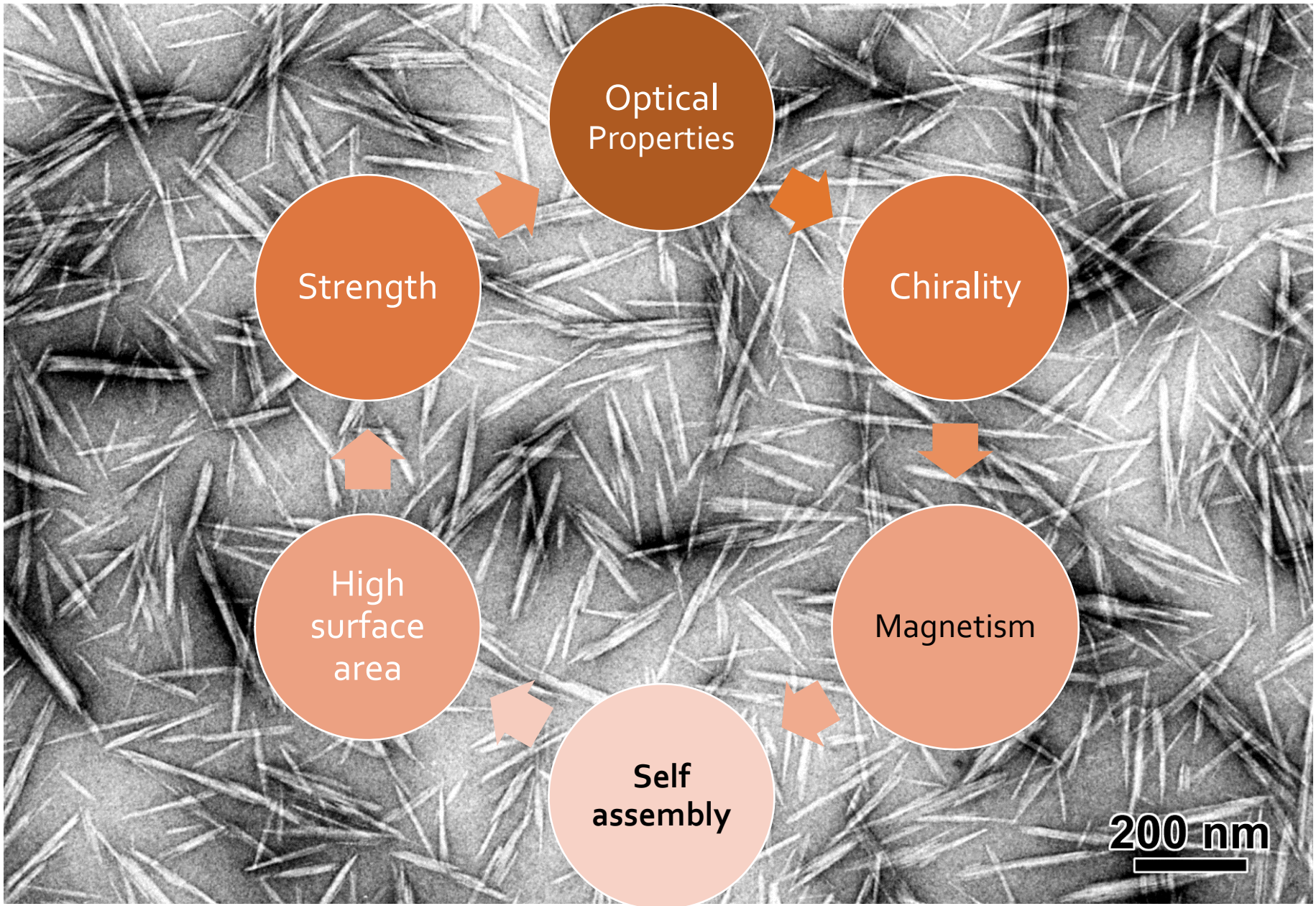
Cellulose, 17, 835 (2010)
BITE 101, 5961 (2010)



Composites (reinforced materials)

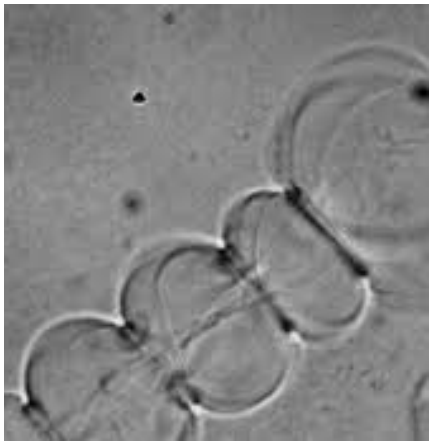
Conductive nanopaper (+ Pyrrole, click chemistry): 37.4 10^{-3} S/cm

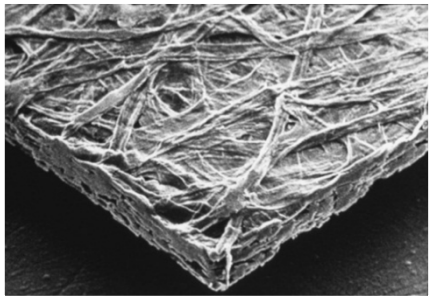


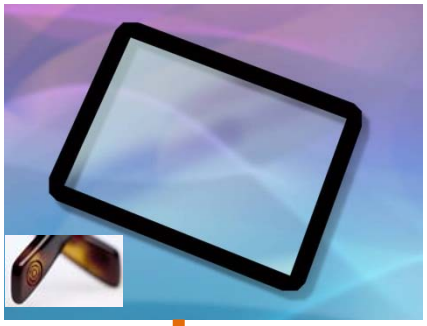
See review: Chem. Rev. 110, 3479 (2010)

Shapes Anisotropy across 10^{10} scale



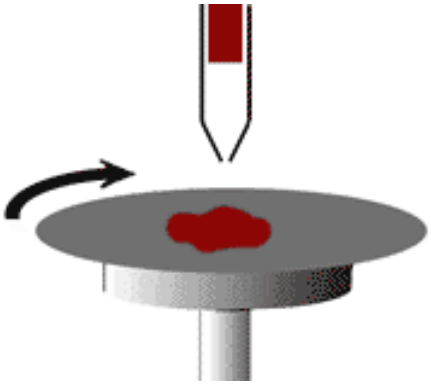





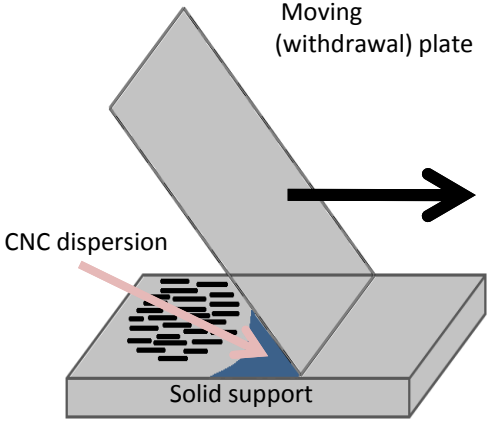


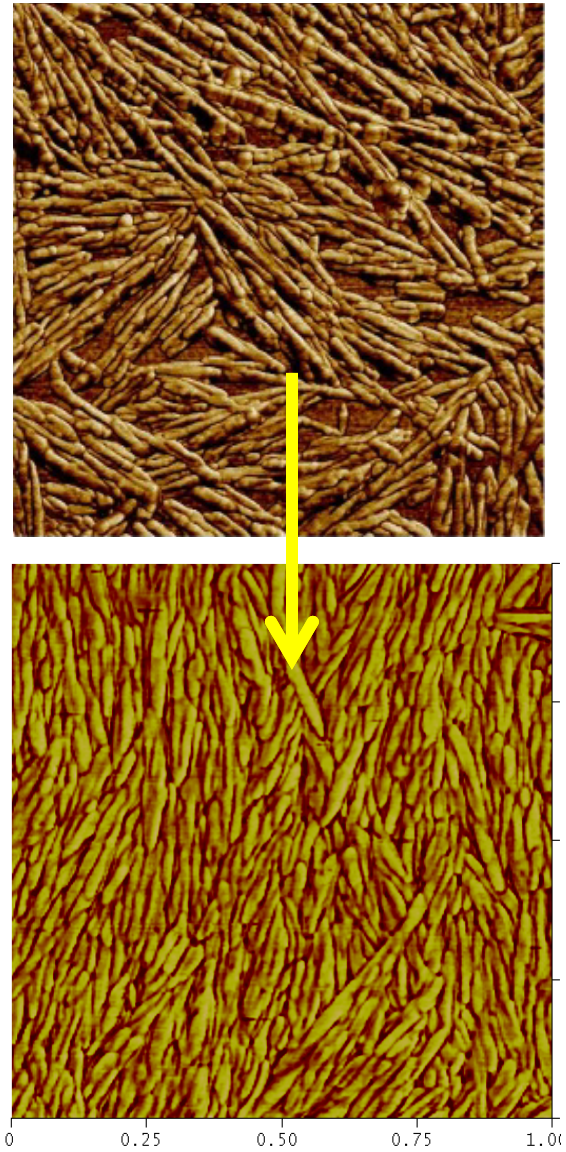
Bottom-up construction

Spin coating



Shear/Convection





Song, et al., *Thin Solid Films*, 517, 4348 (2009)
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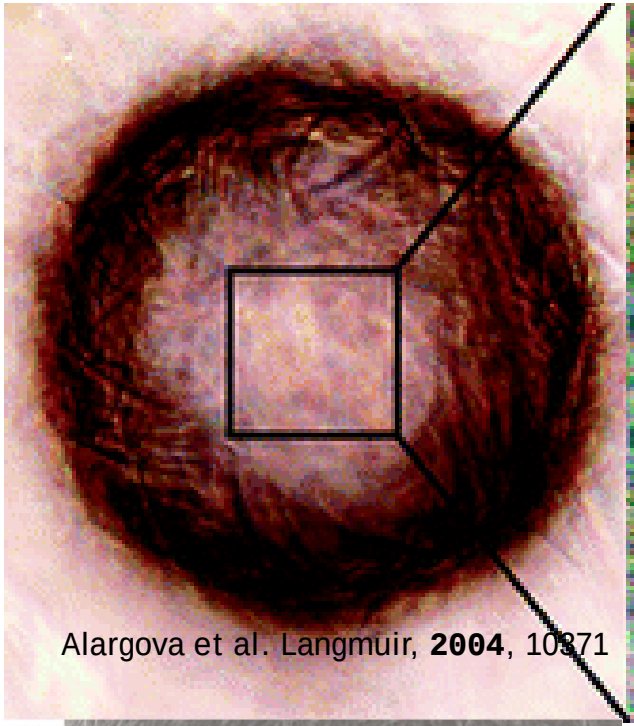
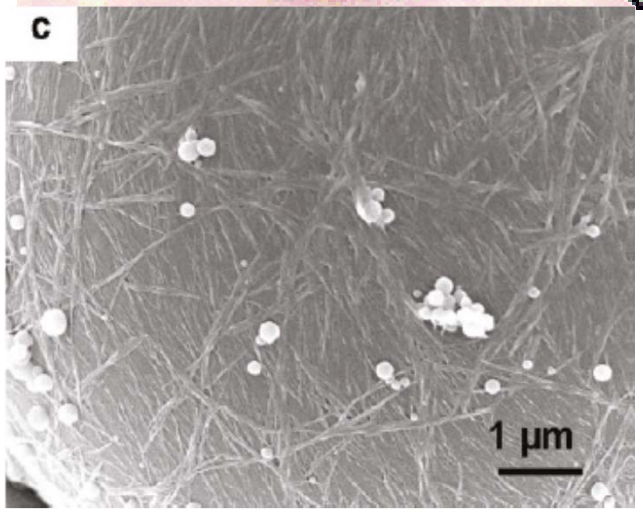
Hoeger, et al., *Soft Matter*, 7, 1957 (2011)
Csoka, et al., *J. Colloid & Interface Sci*. 363:206(2011)





Kalashnikova et al.:

Langmuir 2011, 7471
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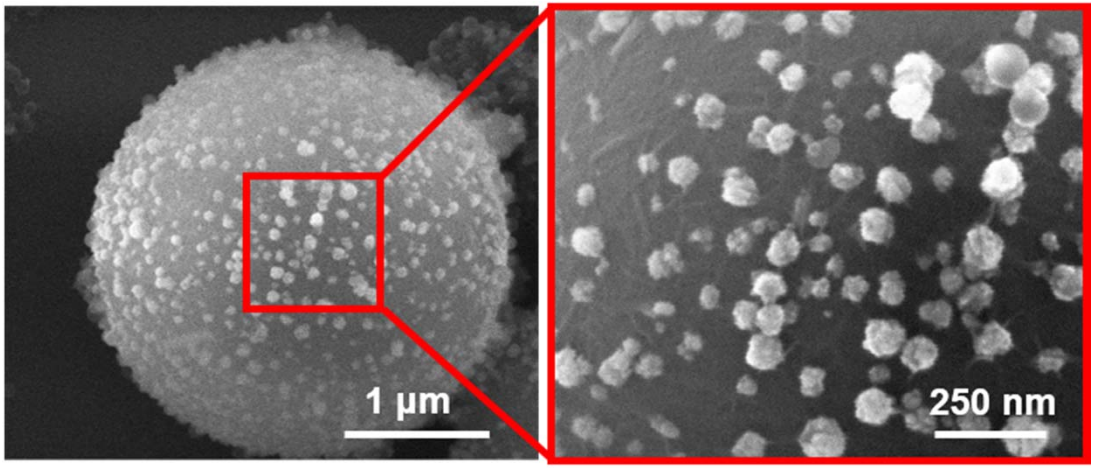
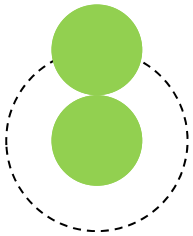
Soft Matter 2013, 9,952
Zoppe, et al. JCIS. 2012, 202



Shape Anisotropy & Structuring

Structuring with spheres

$$w \sim 1/\cancel{D^3} \times \rho\cancel{D^3}$$

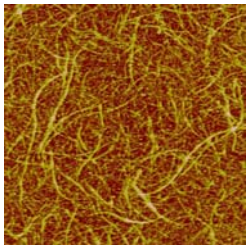


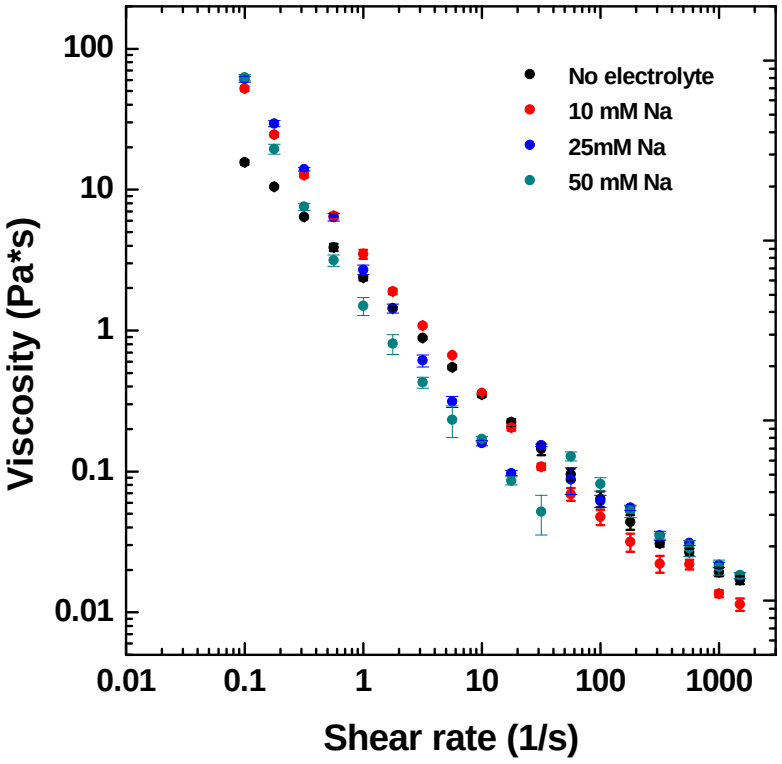
Structuring with rods

Structuring efficiency of rod increases with increasing aspect ratio

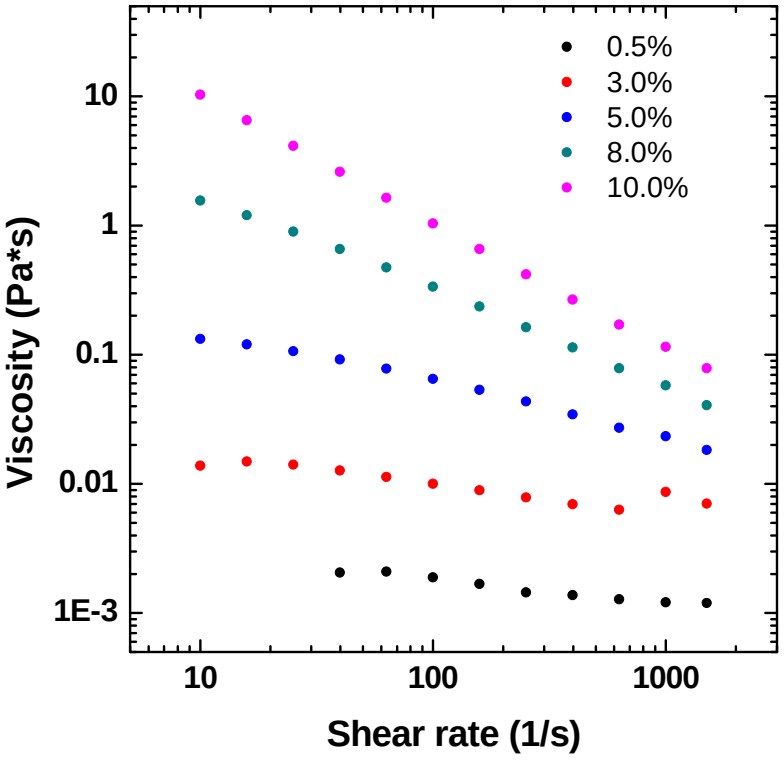
Shape-anisotropic colloids are more efficient space fillers than spheres
(better structuring with less material)

CNF




Viscosity (Pa*s)
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
Shear rate (1/s)
No electrolyte
10 mM Na
25mM Na
50 mM Na

CNC


Viscosity (Pa*s)
10
1
0.1
0.01
1E-3
10
100
1000
Shear rate (1/s)
0.5%
3.0%
5.0%
8.0%
10.0%

Oil industry

Drilling fluids are fluids used in the natural gas and oil industries.

The drilling fluids are used to lubricate, provide hydrostatic pressure, and to keep the drill cool, and the hole as clean as possible of drill cuttings.

"A CNC-based drilling fluid with low addition levels of CNC was developed. The fluid has synergistic effects giving superior fluid loss and filtration characteristics. The field trials with this novel water-based CNC drilling mud will be carried out …"

…Assess ability to affect rheological properties and filter cake formation characteristics so that fluid losses and formation damage can be minimized…

http://www.arboranano.ca/Investigating-Nanocrystalline-Cellulose-NCC-as-Loss-Circulation-Material-in-Drilling-Fluids---Boluk.aspx

Global Drilling Fluids Market Analysis by Product (OBF, SBF, WBF) by Application (Offshore, Onshore) Expected to Reach USD 14.9 Billion by 2020

Market Size - $8.61 bn in 2013; Market Growth - CAGR of 8.2% over the period 2013-2018.

One of the key factors contributing to this market growth is the increasing exploration of unconventional gas.

The key vendors dominating this space are Baker Hughes Inc., Halliburton Co., Newpark Resources Inc., and Schlumberger Ltd.

http://www.researchandmarkets.com/research/mx4dlt/global_drilling

Market trends use of nanotechnology in development of drilling fluids.

(Grand View Research, Inc / http://www.prweb.com/releases/Drilling-Fluids-Market/GrandViewResearch/prweb11805565.htm)

United States Patent [19]

Meyer

[11] **3,852,200**

[45] **Dec. 3, 1974**

[54] **DRILLING LIQUID CONTAINING MICROCRYSTALLINE CELLULOSE**

[75] Inventor: **W. Keith Meyer,** Indiana Township, Pa.

[73] Assignee: **Gulf Research & Development Company,** Pittsburgh, Pa.

[22] Filed: **Feb. 8, 1973**

[21] Appl. No.: **330,567**

[52] **U.S. Cl.**..... **252/8.5** A, 51/303, 175/65, 252/8.5 B, 252/8.5 C

[51] **Int. Cl.**..... **C09k 3/14**

[58] **Field of Search** ..... 252/8.5 A, 8.5 B, 8.5 C; 51/308, 295, 303; 175/65, 67

[56] **References Cited**

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3,583,911	6/1971	Lang	252/8.5 A

Primary Examiner—Donald J. Arnold

[57] **ABSTRACT**

A drilling liquid for use in abrasive jet drilling is formed by first dispensing microcrystalline cellulose in an aqueous liquid. The dispersion can be accomplished by severe shearing of the microcrystalline cellulose in the aqueous liquid. Thereafter, ferrous abrasive particles are suspended in the dispersion of microcrystalline cellulose in water to form the drilling liquid. The microcrystalline cellulose is ordinarily in a concentration in the range of 4 to 7 percent by weight of the abrasives-free liquid, but a portion of the cellulose can be replaced with clay to form a liquid capable of suspending ferrous abrasive particles and thereby form a drilling liquid suitable for use in the abrasive jet drilling process.

5 Claims, 1 Drawing Figure

US005362713A

United States Patent [19]

Westland et al.

[11] **Patent Number: 5,362,713**

[45] **Date of Patent: Nov. 8, 1994**

[54] **DRILLING MUD COMPOSITIONS**

[75] Inventors: **John A. Westland,** Bothell, Wash.; **Glenn S. Penny,** Duncan, Okla.; **Deborah A. Lenk,** Federal Way, Wash.

[73] Assignee: **Weyerhaeuser Company,** Tacoma, Wash.

[21] Appl. No.: **860,291**

[22] Filed: **Mar. 26, 1992**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 714,913, Jun. 13, 1991, abandoned, which is a continuation-in-part of Ser. No. 450,360, Dec. 13, 1989, Pat. No. 5,009,797.

[51] **Int. Cl.**[5] **C09K 7/02**

[52] **U.S. Cl.** **507/110;** 507/113; 507/114; 507/115; 507/120

[58] **Field of Search** 252/8.551, 8.554; 166/273; 435/101; 507/110

[56] **References Cited**

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Brown, Jr. et al, *J. Applied Polymer Science,* vol. 37, pp. 33–78 (1983).

Primary Examiner—Gary Geist

Attorney, Agent, or Firm—Stoel Rives Boley Jones & Grey

[57] **ABSTRACT**

The addition of relatively small quantities of reticulated bacterial cellulose to well bore drilling muds improves their rheological properties. A preferred reticulated bacterial cellulose is one produced under agitated culture conditions using strains of a bacterium from the genus Acetobacter. Reticulated bacterial cellulose may be used in place of a conventional gellant or in combination with conventional gellants to provide improved drilling muds.

11 Claims, No Drawings

US006348436B1

(12) **United States Patent**
Langlois et al.

(10) **Patent No.: US 6,348,436 B1**
(45) **Date of Patent: Feb. 19, 2002**

(54) **FLUID COMPRISING CELLULOSE NANOFIBRILS AND ITS USE FOR OIL MINING**

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(52) **U.S. Cl.** **507/112**; 507/104
(58) **Field of Search** 507/112, 104

(56) **References Cited**

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Primary Examiner—Philip Tucker
(74) *Attorney, Agent, or Firm*—Jean-Louis Seugnet

(57) **ABSTRACT**

The present invention relates to a drilling fluid comprising cellulose nanofibrils comprising at least 80% of cells with primary walls and charged with carboxylic acids and with acidic polysaccharides, alone or as a mixture. This additive, alone, gives the drilling fluid shear-thinning properties and is stable up to temperatures of about 180° C.

18 Claims, No Drawings

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(19) **United States**

(12) **Patent Application Publication**

Rincon-Torres et al.

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(54) **CELLULOSE NANOWHISKERS IN WELL SERVICES**

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(73) Assignee: **HALLIBURTON ENERGY SERVICES, INC.**, Houston, TX (US)

(21) Appl. No.: **13/561,158**

(22) Filed: **Jul. 30, 2012**

Related U.S. Application Data

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Publication Classification

(51) **Int. Cl.**

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C09K 8/00	(2006.01)
C09K 8/68	(2006.01)
C09K 8/10	(2006.01)

(52) **U.S. Cl.**

USPC **507/112**; 507/214

(57) **ABSTRACT**

A method is provided for use in various well services, the method including the steps of: (a) forming or providing a well fluid comprising cellulose nanowhiskers; and (b) introducing the well fluid into a well. The method can be used, for example, for increasing the strength of a cement, for increasing the viscosity of a water-based well fluid, such as for a kill pill, a fracturing fluid, a gravel packing fluid.

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(19) **United States**

(12) **Patent Application Publication**

Lafitte et al.

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(43) **Pub. Date: Oct. 17, 2013**

(54) **FLUIDS AND METHODS INCLUDING NANOCELLULOSE**

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(73) Assignee: **SCHLUMBERGER TECHNOLOGY CORPORATION**, Sugar Land, TX (US)

(21) Appl. No.: **13/834,841**

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Related U.S. Application Data

(60) Provisional application No. 61/624,038, filed on Apr. 13, 2012.

Publication Classification

(51) **Int. Cl.**

C09K 8/90 (2006.01)

C09K 8/10 (2006.01)

(52) **U.S. Cl.**

CPC .. ***C09K 8/905*** (2013.01); ***C09K 8/10*** (2013.01)

USPC **507/112**; 507/214; 106/805; 166/292

(57) **ABSTRACT**

Treatment fluids and methods for treating a subterranean formation are disclosed that include introducing a treatment fluid into a subterranean formation, the treatment fluid containing a nanocrystalline cellulose.

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(19) **United States**

(12) **Patent Application Publication**

Bakeev et al.

(10) **Pub. No.: US 2014/0037816 A1**

(43) **Pub. Date: Feb. 6, 2014**

(54) **STABILIZED MULTIPHASE AQUEOUS COMPOSITIONS**

(71) Applicant: **HERCULES INCORPORATED**, Wilmington, DE (US)

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(73) Assignee: **HERCULES INCORPORATED**, Wilmington, DE (US)

(21) Appl. No.: **13/951,944**

(22) Filed: **Jul. 26, 2013**

Related U.S. Application Data

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Publication Classification

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A61Q 19/00	(2006.01)
C09D 7/12	(2006.01)

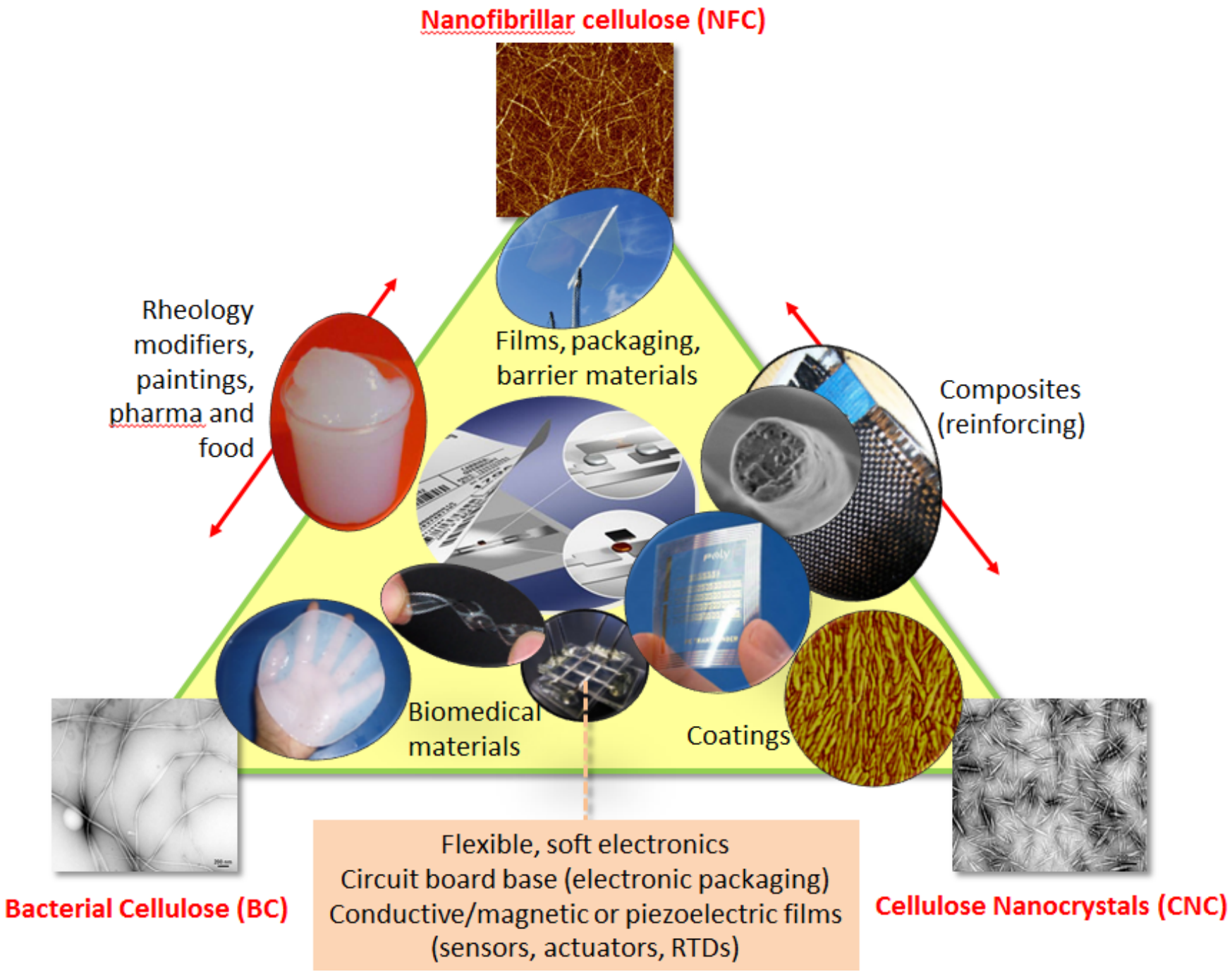
(52) **U.S. Cl.**

CPC ***A23D 7/005*** (2013.01); ***C09D 7/125*** (2013.01); ***A61K 8/731*** (2013.01); ***A61Q 19/00*** (2013.01)

USPC **426/564**; 106/162.8; 524/42; 510/109; 426/602; 426/654

(57) **ABSTRACT**

Aqueous multiphase compositions are stabilized using a blend of cellulose ether and nanocrystalline cellulose. The multiphase compositions can include particulates dispersed in water, oil in water emulsions, foams, and combinations of these systems. The blend can be used to stabilize aqueous paint systems, personal care products such as shampoos and detergents formed as oil in water emulsions, and foaming products such as detergents, shampoos, other personal care products and edible compositions such as whip cream substitutes. Further, this blend can reduce or eliminate the need for surfactants in many of these multiphase compositions.


Nanofibrillar cellulose (NFC)
Rheology modifiers, paintings, pharma and food
Films, packaging, barrier materials
Composites (reinforcing)
Biomedical materials
Coatings
Bacterial Cellulose (BC)
Cellulose Nanocrystals (CNC)
Flexible, soft electronics
Circuit board base (electronic packaging)
Conductive/magnetic or piezoelectric films
(sensors, actuators, RTDs)

Nanocellulose

Identified Market Drivers

- Light-weighting to improve fuel efficient
- Energy Efficiency
- Bio-based materials
- Greener Consumer Products
- Carbon Dioxide targets
- Renewable/compostable