Market Prospects for NanoCellulose

Bruce Lyne

The Royal Institute of Technology

Alberta Biomaterials Development Centre, Feb. 12th 2013

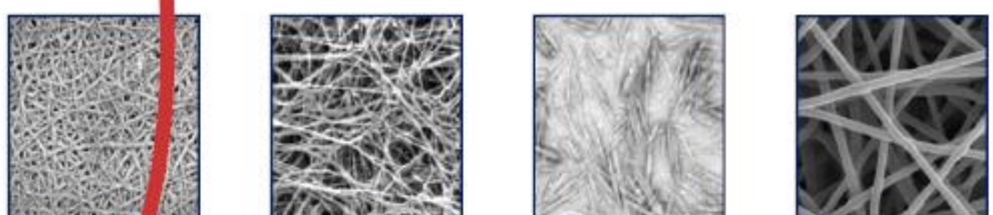
Nanocelluloses – A Class of Nanomaterials

- **Examples of Raw Materials:**

Wood Pulp Bacteria Straw Sugar Beet Banana

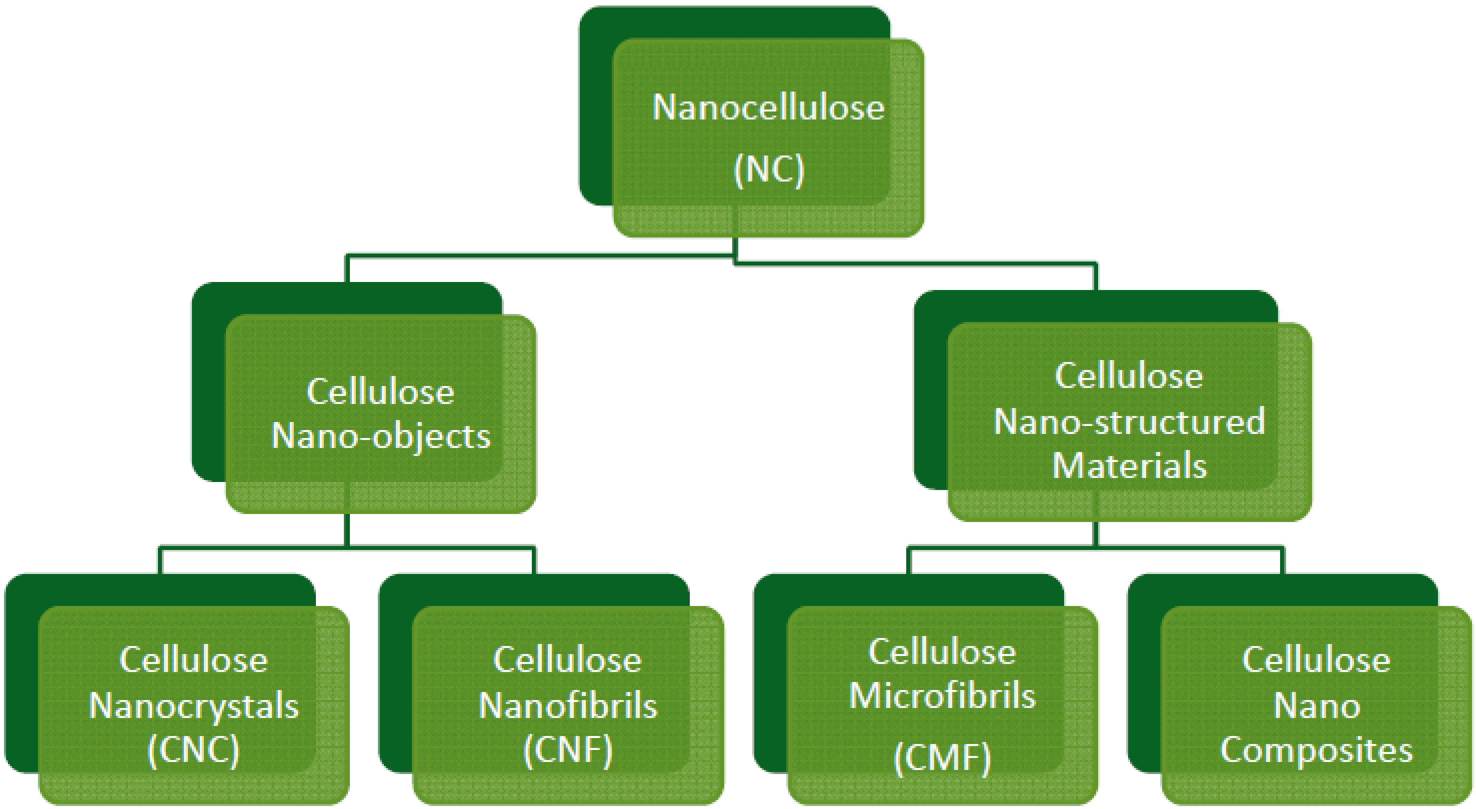
- **Examples of Production Methods:**

Grinding, Homogenizer, Intensification, Hydrolysis / Electrospinning, Ionic liquids

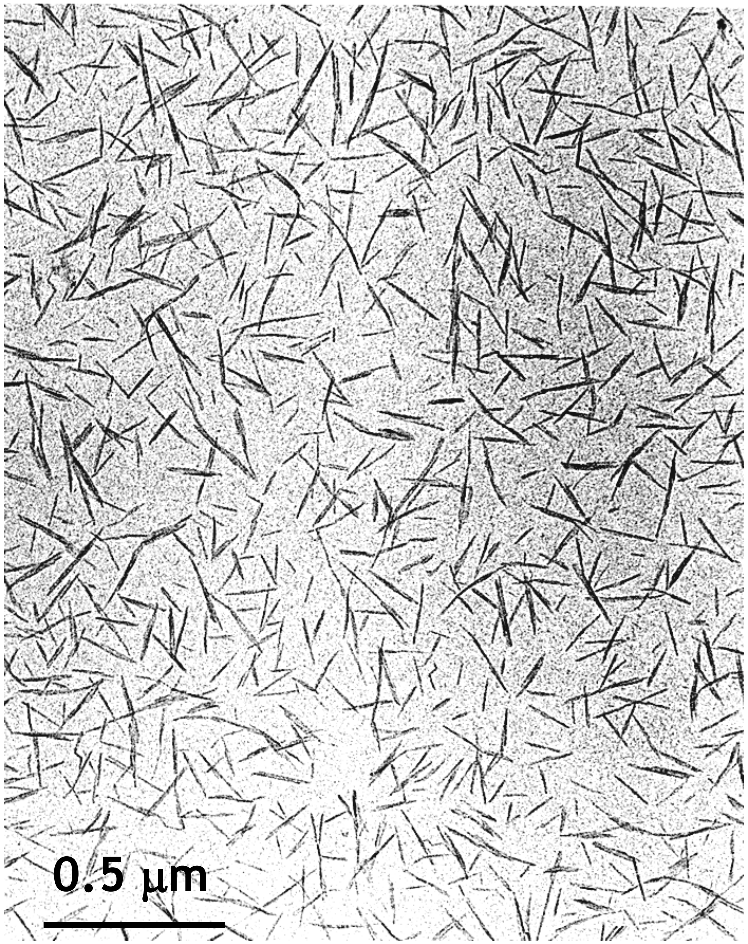


Top-Down / Bottom-Up

Naming Hierarchy for Nanocellulose Materials



Nanocrystalline Cellulose - CNC



TEM image of dilute suspension on carbon grid

- The nanocrystals are made up of **~25 chains** of **13000 glucose units**
- Whisker shaped particles 100-200 nm x 5-10 nm (also called cellulose nanowiskers or CNW)
- Highly crystalline cellulose I with
  Young's modulus: 150 GPa
  Tensile strength: 10 GPa
  (comparable to Kevlar)
- Self-dispersing and chiral nematic in water when liberated from bleached pulp by sulfuric acid hydrolysis
- Nanocrystals have hydrophilic surfaces, but do not swell in water

Revol, J-F; Godbout, L.; Gray, Derek G. *J. Pulp and Paper Sci.*, **1998**, 24,146.

Cellulose Nanocrystal Composites

natural and synthetic polymer matrices:

- Poly-L-lactic acid (NatureWorks™)
- Poly-hydroxyalkanoates
- Cellulose acetate, cellulose acetate butyrate and hemicelluloses
- Silk fibroin ← **Strongest**
- Starch ← **Largest increase in strength (5x)**
- Epoxies ← **Strongest**
- Latexes
- Polyvinyl chloride (PVC) ← **Most rubbery**
- Polysulfones
- Polyvinyl alcohol (PVA)
- Polypropylene
- Polyethylene oxide

Young's modulus: 1-13 GPa
Tensile strength: 2-160 MPa

Courtesy of Emily Cranston

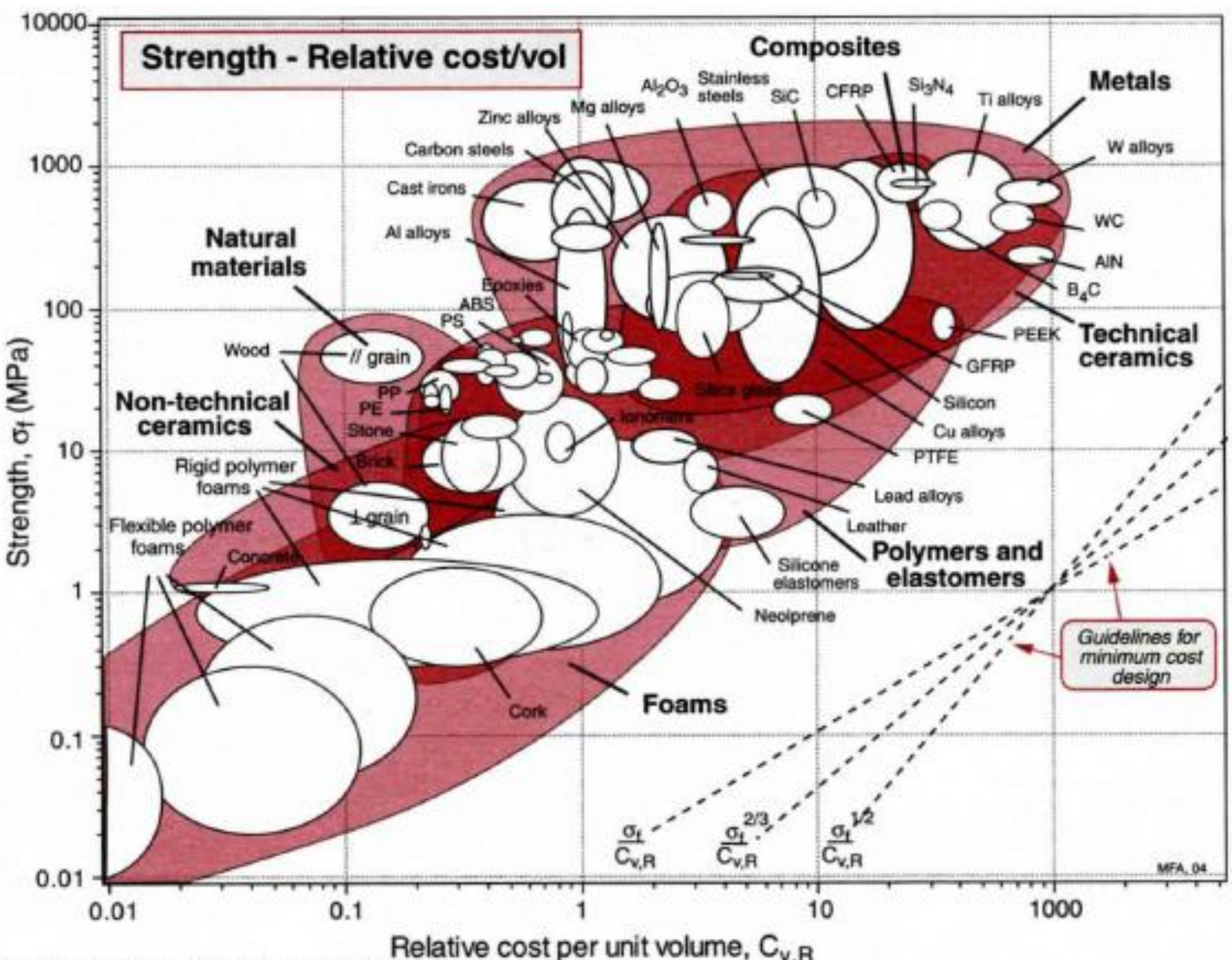
Market Prices (Euro/kg) – Early 2011

Bio-derived plastics have typically been much more expensive but this is gradually changing

PolyEthylenes (PE)	1.30-1.55
PolyStyrenes (PS)	1.75-1.90
Acrylonitrite/Butadiene/Styrene (ABS)	1.90-2.45
PolyCarbonates (PC)	3.10-3.70
Poly(Lactides) (PLA)	1.80 and up (spot 1.25)
Poly(Hydroxy Alkanoates) (PHA)	4.10-4.70
Poly(Butylene Succinate) (PBS)	3.50-4.00
Poly(Butylene Adipate-co-Ter.) (PBAT)	3.30-3.70

Source: Jan Ravenstijn

Carbon Fiber Reinforced Plastics rule!

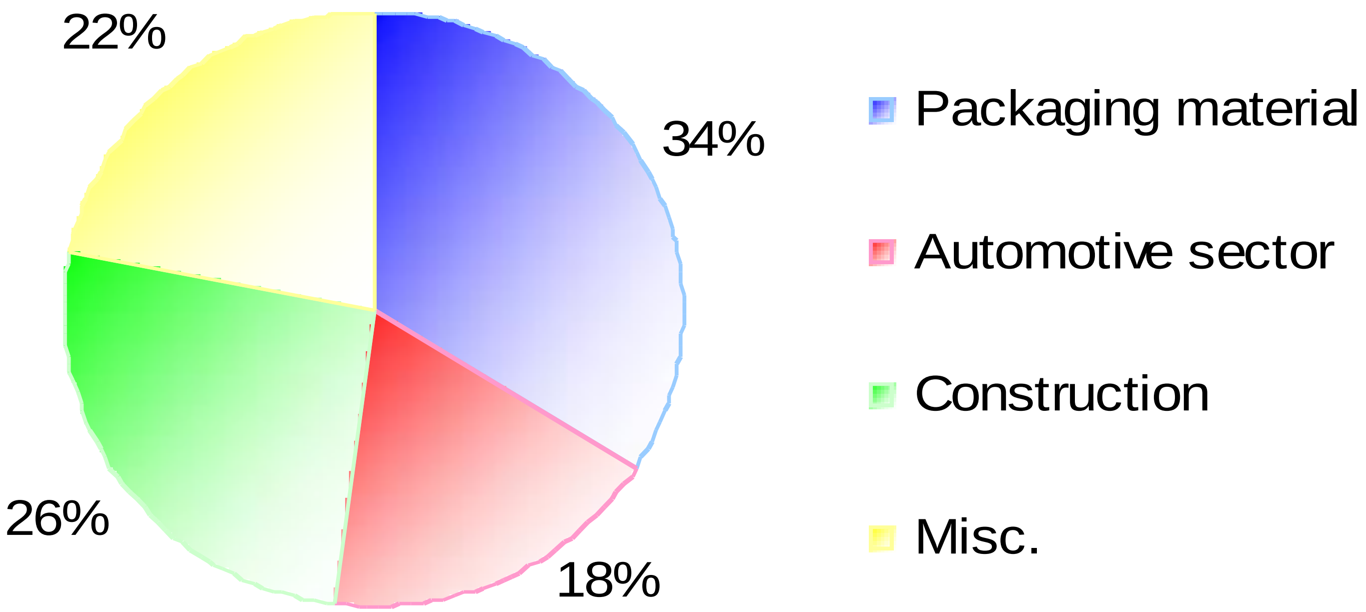


Ashby – Materials Selection in Mechanical Design (2004)

2013 papers on surface modification/grafting

- Compatibilization of NCC with glycidyl methacrylate, xyloglucan, CMC, polyvinylpyridine (PVP) grafted CNC is stable in water at low pH but flocculate at high pH where PVP is uncharged and hydrophobic. This flocculation is reversible. polyNIPAM has also been grafted from cellulose nanocrystals, alone and in conjunction with PVP, to produce thermally responsive and dual thermal + pH responsive nanoparticles
- poly(ethylene glycol) PEG, can improve thermal stability of CNC films
- Quaternary Ammonium Salt
- porphyrin derivatives
- esterification
- CNF treated with CTAB and crosslinked with polyethyleneimine (PEI)
- CNF-sorbitol films
- carboxymethylated CNF is further propargyl-functionalized using the EDC/NHS activation
- green functionalization of CNC with the use of organosilanes

Global Plastic Consumption - Different Sectors

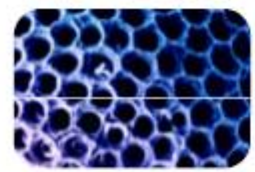


Global Plastic Market around 200Mton
Global plastic consumption by sectors.
Source: Mohini Sain, University of Toronto, Canada

What can we make from CNC?

- Paints, varnishes, coatings
- Films
- Adhesives
- Thermosets
- Thermoplastics
- Reinforced Bio Polymers
- Synthetic fibres and textiles
- Nanocomposites
- Cosmetics and pharmaceuticals
- Optical devices
- Viscosity modifiers and flow aids
- Mesoporous films and membranes
- Catalysts
- Flexible displays
- Printed films
- Hydrogels



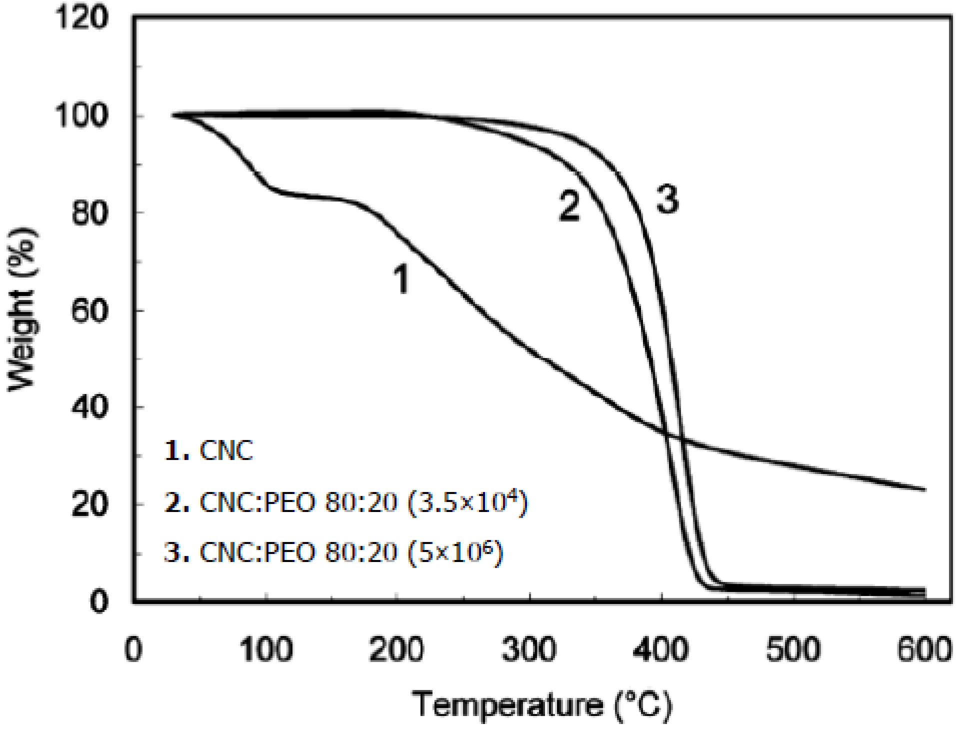

Extruded films

Homogeneous dispersion of CNC

No thermal degradation

Ben Azouz et al., *ACS Macro Letters*, 236 (2012)

Thermal stability of the lyophilizates



Ben Azouz et al., *ACS Macro Letters* , 236 (2012)

Incentives for Manufacturing Industry

- **New source of raw material with wide, largely unexplored range of applications**
  - New products
  - New business opportunities

- **Security of supply**
  - Sustainable renewable resource
  - Availability and price stability
- **Source of “green” materials**
  - Reduced carbon footprint
  - Recyclable
  - Reusable
  - Compostable

Market drivers

- **green** is the real value proposition for switching to nanocrystalline cellulose-based products
- composites must have bio-derived matrix polymers to be **green**
- partner with proactive companies that have publicly declared their intention to use bio-derived materials
- work with industries that sell to the consumer directly e.g. packaging & automobiles
- controlled biodegradability big plus

Market Survey for CNC

- Importance of:
  - sustainable materials
  - green disposal/recycle at end of life
  - clean label/consumer perception
  - biodegradability
  - reduction in weight
  - simplification of structure
  - cost versus current material
  - novel functionality (surface, optical, insulation)

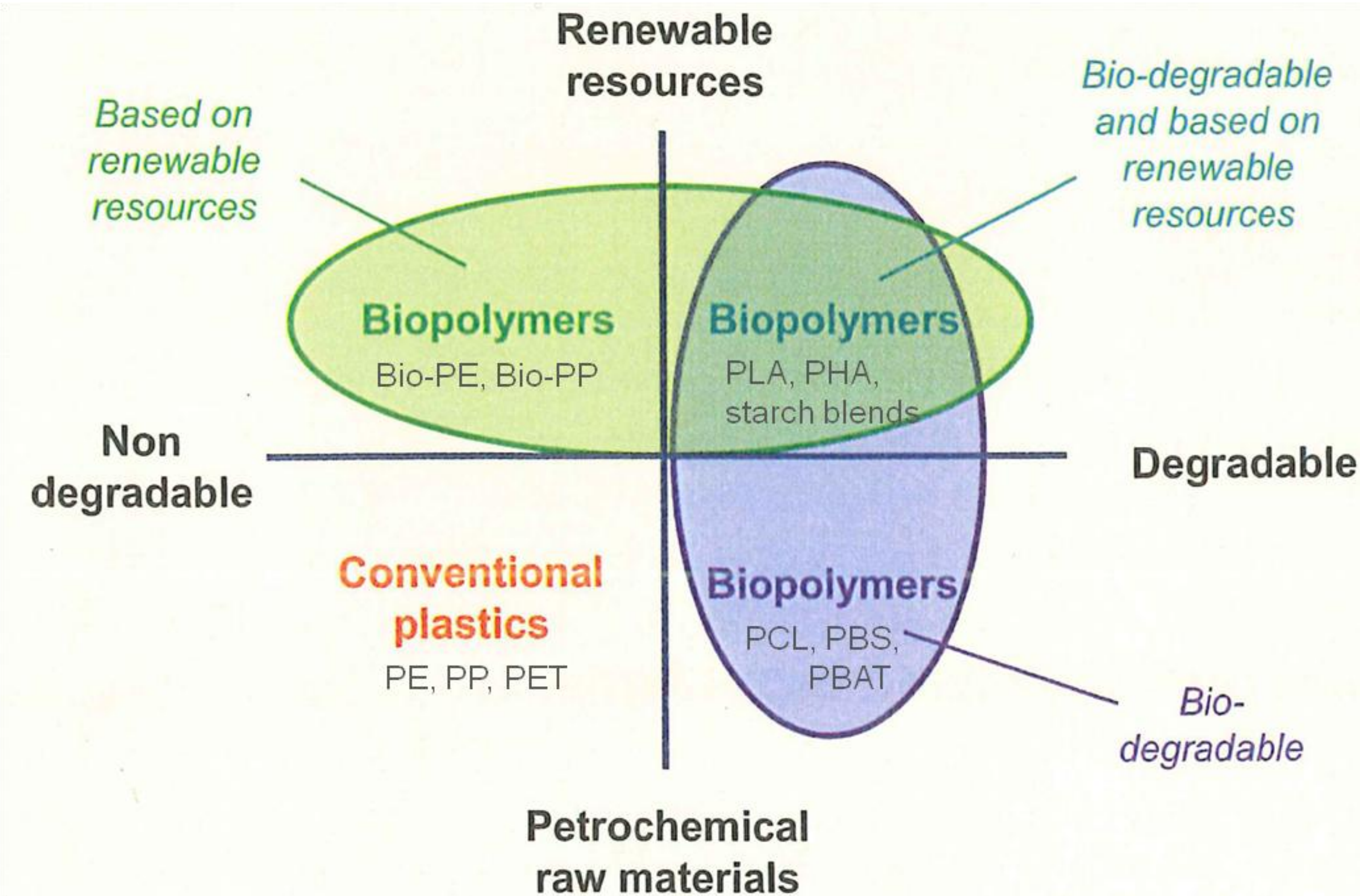
Is There BioProducts Market Opportunities?

Compilation by NRCan and Industry Canada, 2010

PRODUCTS	GLOBAL MARKET POTENTIAL, 2015 (US$ billion)	CAGR (%), 2009-2015 (approximate)
Green chemicals	62.3	5.3
Alcohols	62.0	5.3
Bio-plastic and plastic resins	3.6	23.7
Platform chemicals	4.0	12.6
Wood fibre composites	35.0	10.0
Glass fibre market	8.4	6.3*
Carbon fibre	18.6	9.5
Revenues, Canadian forests product industry	50.0	Neg. or 0-2

CAGR: Compound Annual Growth Rate

Categories of Plastics



Source: Endres H-J and Siebert-Raths A, Engineering Biopolymers, Hanser Verlag, Munich (2011)

PepsiCo's Package Sustainability Strategic Framework

Performance with Purpose

Innovations to make Tomorrow's Packaging Better than Today's

REMOVE	REDUCE	REUSE	RECYCLE	RENEW
• Eliminate waste and inefficiency • Eliminate environmentally sensitive materials and processes	• Optimize designs for efficient use of materials and energy • Develop new technologies to enable improved package system efficiency	• Increase the use of post consumer recycled content • Increase the use of reusable packaging supplies and material delivery systems	• Design packaging systems for efficient recycling • Development of biodegradable and compost-able solutions	• Increase the use of renewable material resources

Foundational Insights and Assessment Tools

- Science Advisory Board
- Metrics and Scorecards
- Life Cycle Assessments
- Analysis Tools
- Process Integration
- Education and Training

Combining the Benefits of Paperboard and Bioplastics

Jaana Keskitalo, Product Manager, Stora Enso Food Service Board

Market Prices (Euro/kg) – Early 2011

Bio-derived plastics have typically been much more expensive but this is gradually changing

PolyEthylenes (PE)	1.30-1.55
PolyStyrenes (PS)	1.75-1.90
Acrylonitrite/Butadiene/Styrene (ABS)	1.90-2.45
PolyCarbonates (PC)	3.10-3.70
Poly(Lactides) (PLA)	1.80 and up (spot 1.25)
Poly(Hydroxy Alkanoates) (PHA)	4.10-4.70
Poly(Butylene Succinate) (PBS)	3.50-4.00
Poly(Butylene Adipate-co-Ter.) (PBAT)	3.30-3.70

Source: Jan Ravenstijn

Opportunities to create proprietary products - packaging

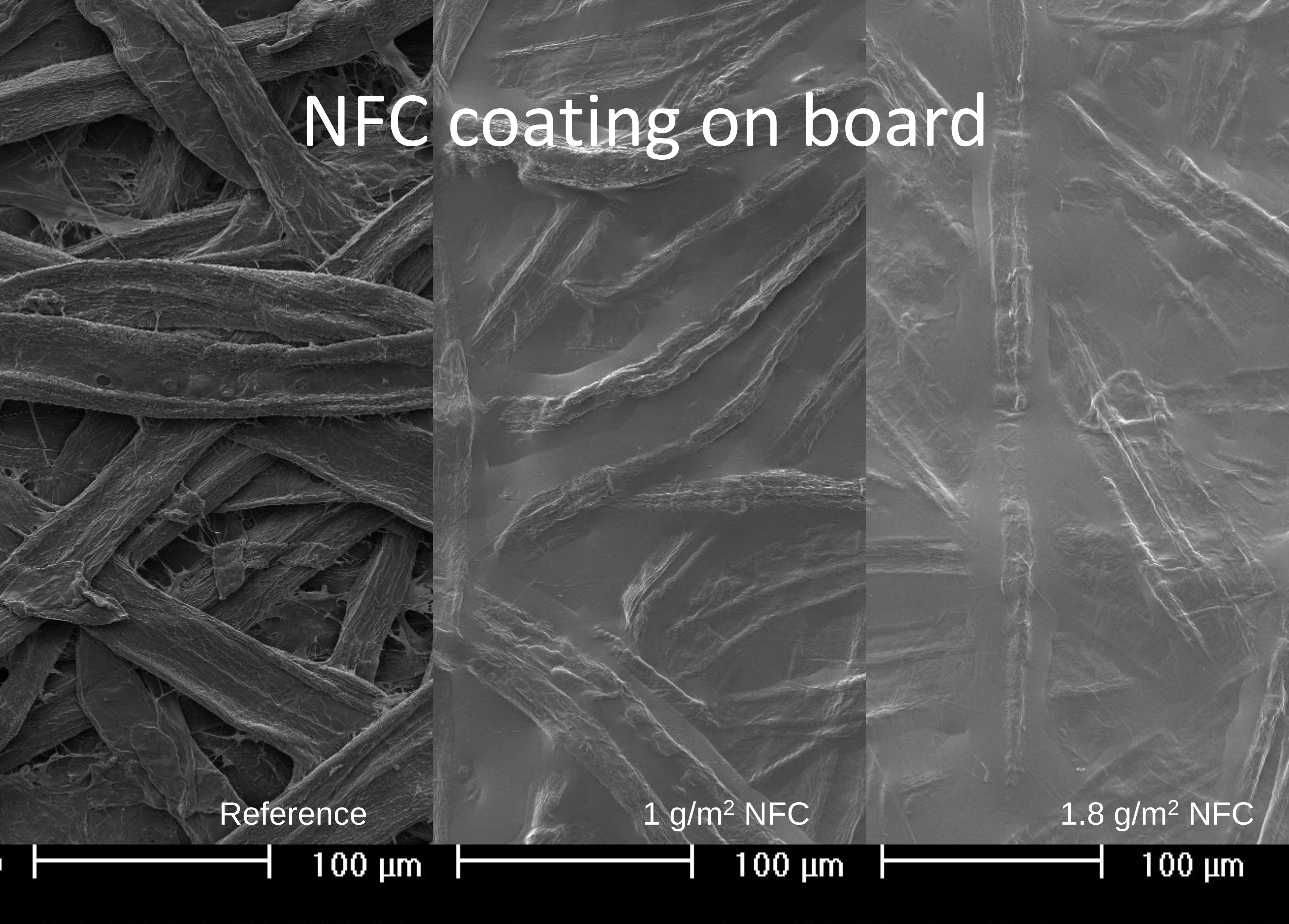
- Biggest potential lies in simplifying the packaging structure to an NCC composite monolayer combining both the strength/rigidity requirements and oxygen/moisture vapor barrier properties. This would facilitate recycling and reduce packaging weight
- Molded NCC-reinforced natural polymer packaging could take forest industry into new packaging sector
- A 10% incursion in these markets via substitution for nonrenewable polymers would require a capacity for NCC composites in the order of 2 million tons in Europe and in the order of 6 million tons the US

Courtesy: David Placket and Istvan Siro

Barrier enhancement with fillers

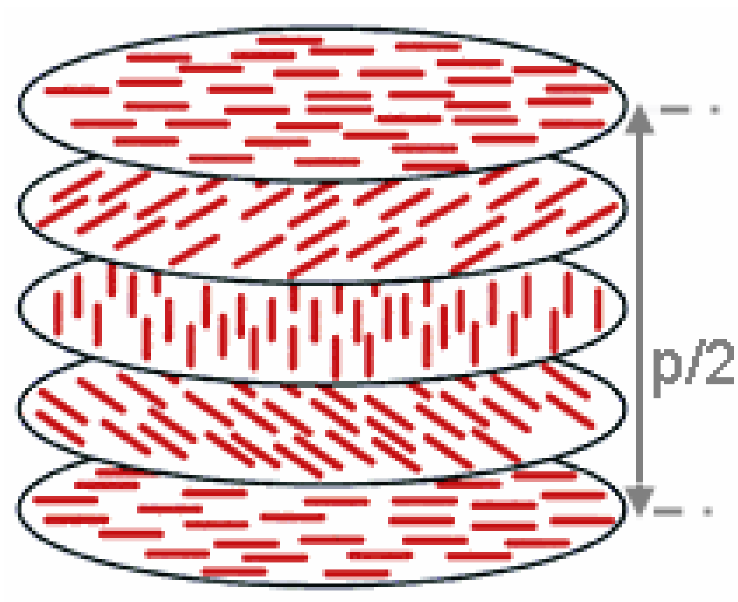
- Cationic Polyacrylamide (CPAM) to adhere the negatively charged TiO2 nanoparticles to nanofibres
- Layered silicates - clays and micas can act as barrier against water vapor in composite films of trimethylammonium-modified nanofibrillated cellulose and 13 different layered silicates
- Nanocellulose mixed with vermiculite nanoplatelets through high-pressure homogenization. The resulting hybrid films are stiff, strong and transparent. The oxygen barrier properties of the biohybrid films outperform commercial packaging materials
- Al_2O_3 coated CNC aerogel composites exhibit improved temperature and oxidation resistance
- CNF and calcium carbonate and CMC

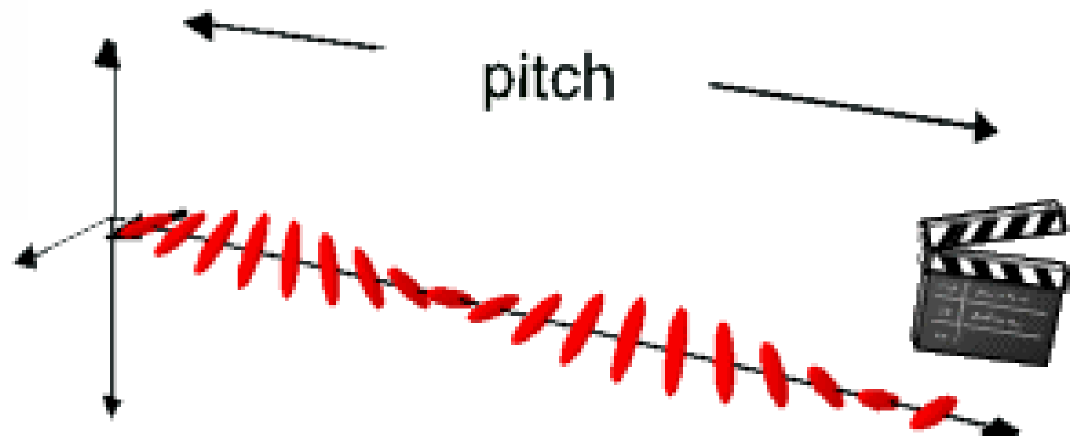
NFC coating on board



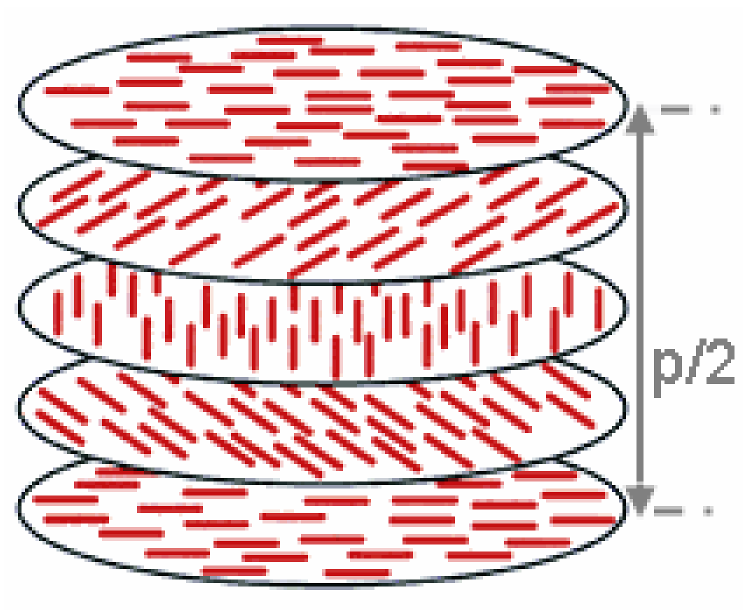
Source: Aulin, C., Gällstdet, M., Lindström, T. (2010). Cellulose 17, 559-574.

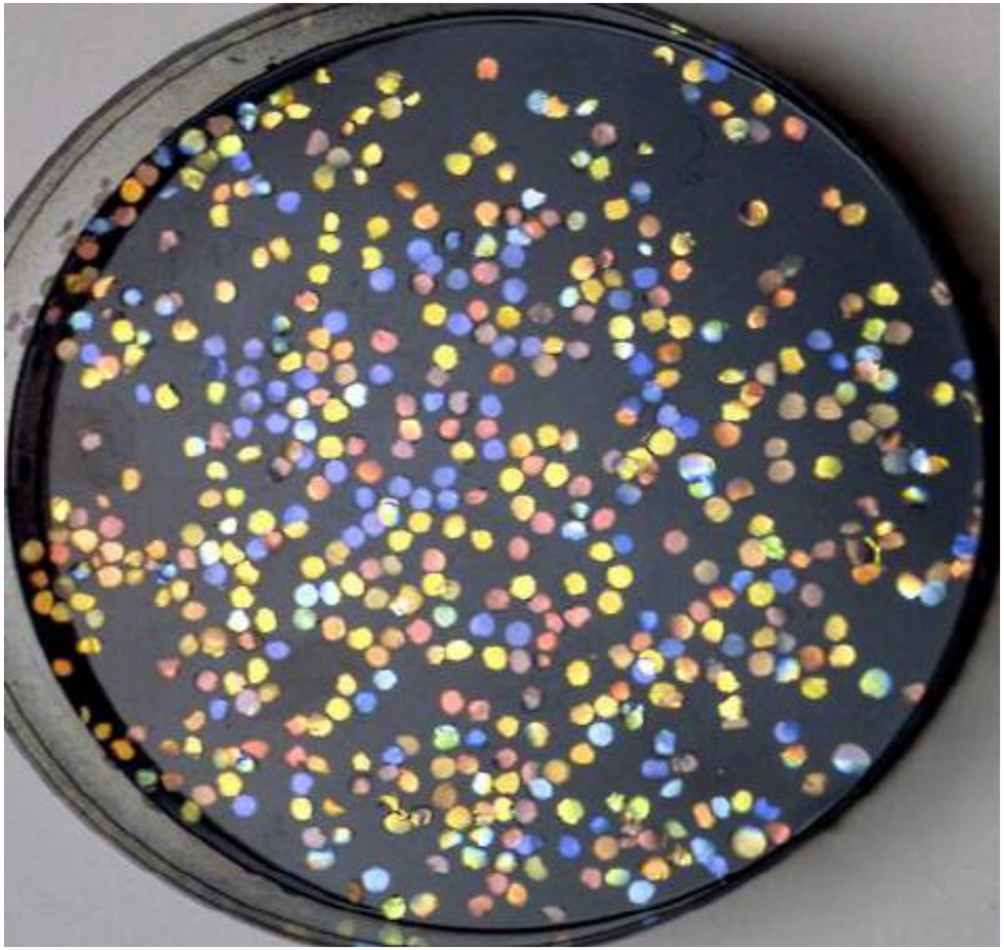
Chiral nematic structure



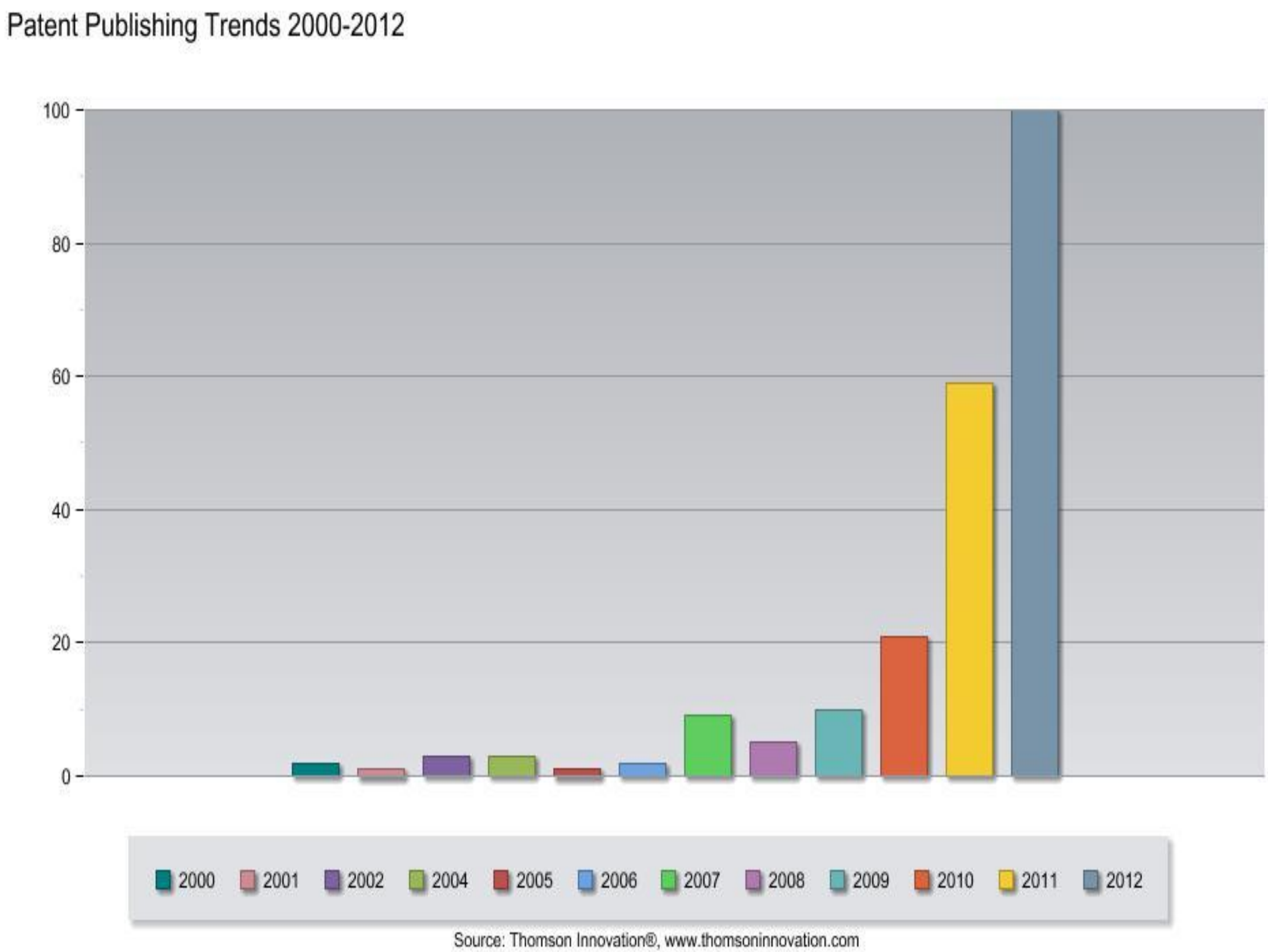


Chiral nematic structure

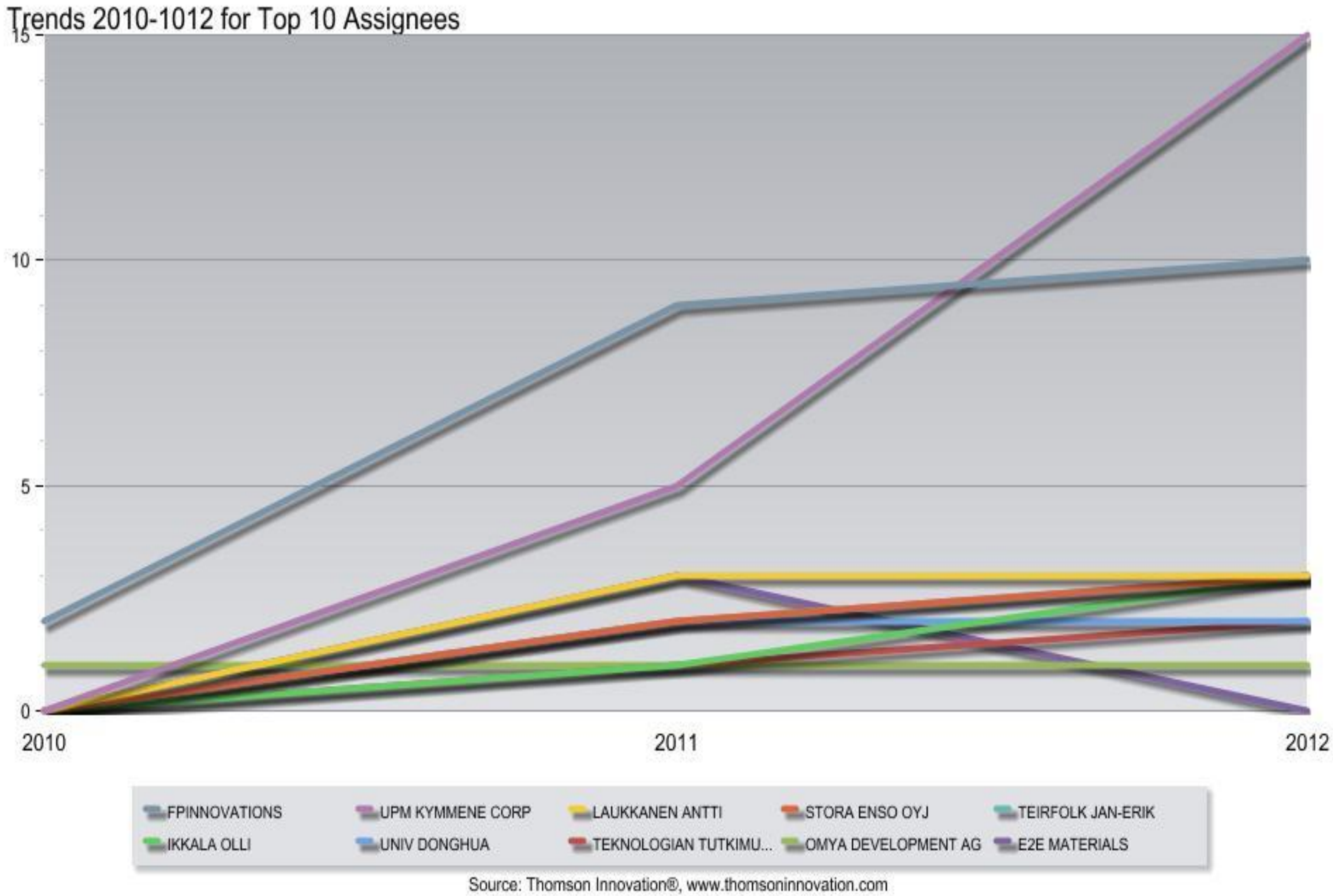




Biggest change is race for patent position



Top assignee for CNC is FPI

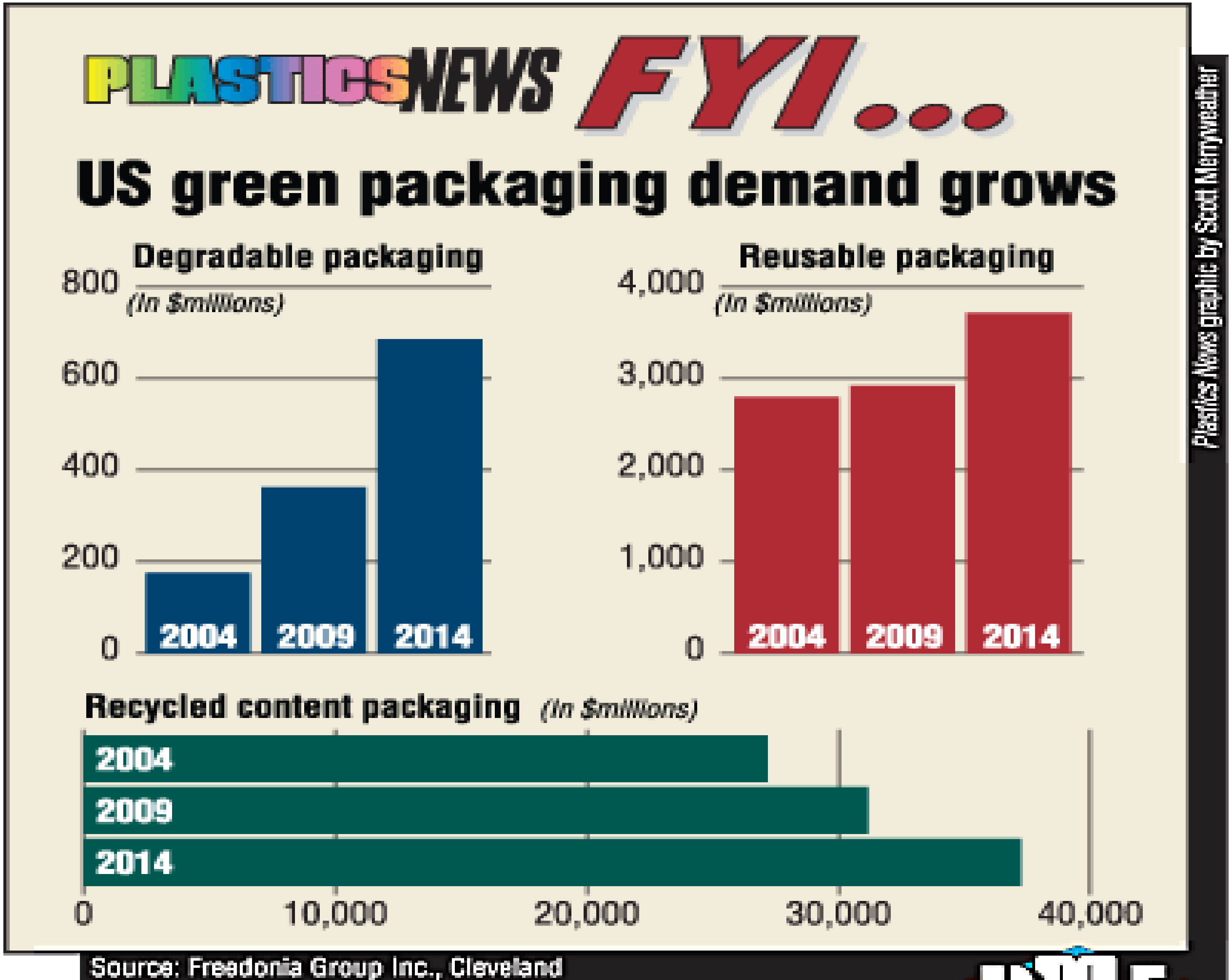


Subjects of Patents

- FPI+UBC+McGill - manufacture of CNC, dispersion of dried CNC, CNC as base for thermoplastic composites and scaffolds, hydrogels, barrier coatings, semiconductor, chiral surfaces, binding drugs, adhesive, controlled color/irredescence, wood coatings, fire retardant coating
- Rhone Poulenc/Rhodia/Danisco - CNC in oil drilling fluid
- AITF - CNC in de-icing fluid/rheology control
- Intelligent Nano - magnetic means of entering cells
- UPM - base for cell culture
- Kruger – coating for fabrics and textiles
- Chalmers – CNC as base for tissue scaffolds
- U of T – transparent conductive coatings
- Shingua – rubber reinforcement

Peer-reviewed articles

- McGill group (Derek Gray and students) 27+ articles
  - Optical, magnetic, grafting, gels, composites, surface forces, characterization
- FPI (Bouchard, Kahn, Salameri, LaCroix, Beck) 19
  - Optical, barrier, functionalized, biodegradable films, chitosan CNC composites, hydrogels, coatings, adhesives
- UBC (Hamad, Shopsowitz, Machlachlan, Burt) 26
  Chiral templating, controlled drug release, scaffolds
- KTH (Berglund, Zhou, Rutland, Bergström) 17
  - NCC composites (PLA, starch, CaCO3), hydrophobic CNC, friction, polyelectrolyte multilayers
- NRC (Luong, Male) NCC functionalization 7
- UNB (Chibante, Yonghao) fabrics 7
- Nottingham (Thielemans) aerogels 4

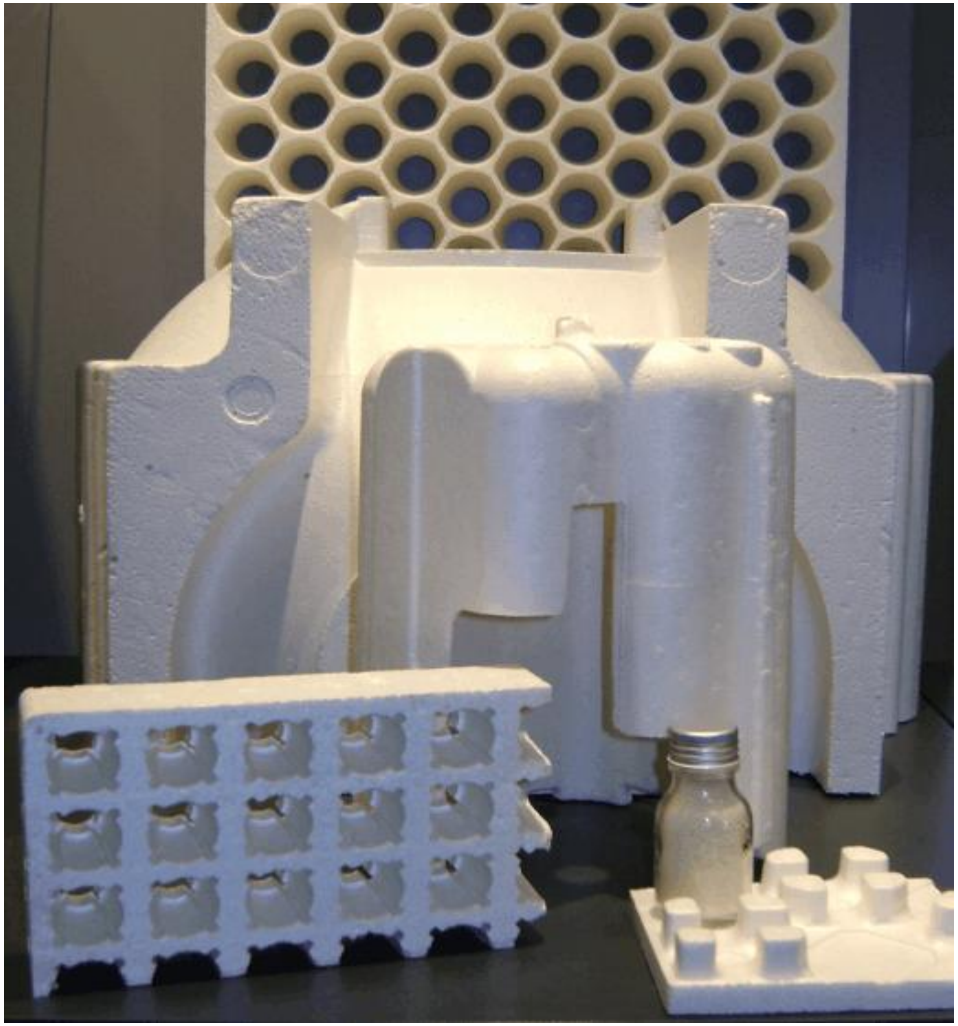


PLASTICSNEWS FYI...
US green packaging demand grows
Degradable packaging
(In $millions)
800
600
400
200
0
2004
2009
2014
Reusable packaging
(In $millions)
4,000
3,000
2,000
1,000
0
2004
2009
2014
Recycled content packaging (In $millions)
2004
2009
2014
0
10,000
20,000
30,000
40,000
Plastics News graphic by Scott Merryweather
Source: Freedonia Group Inc., Cleveland

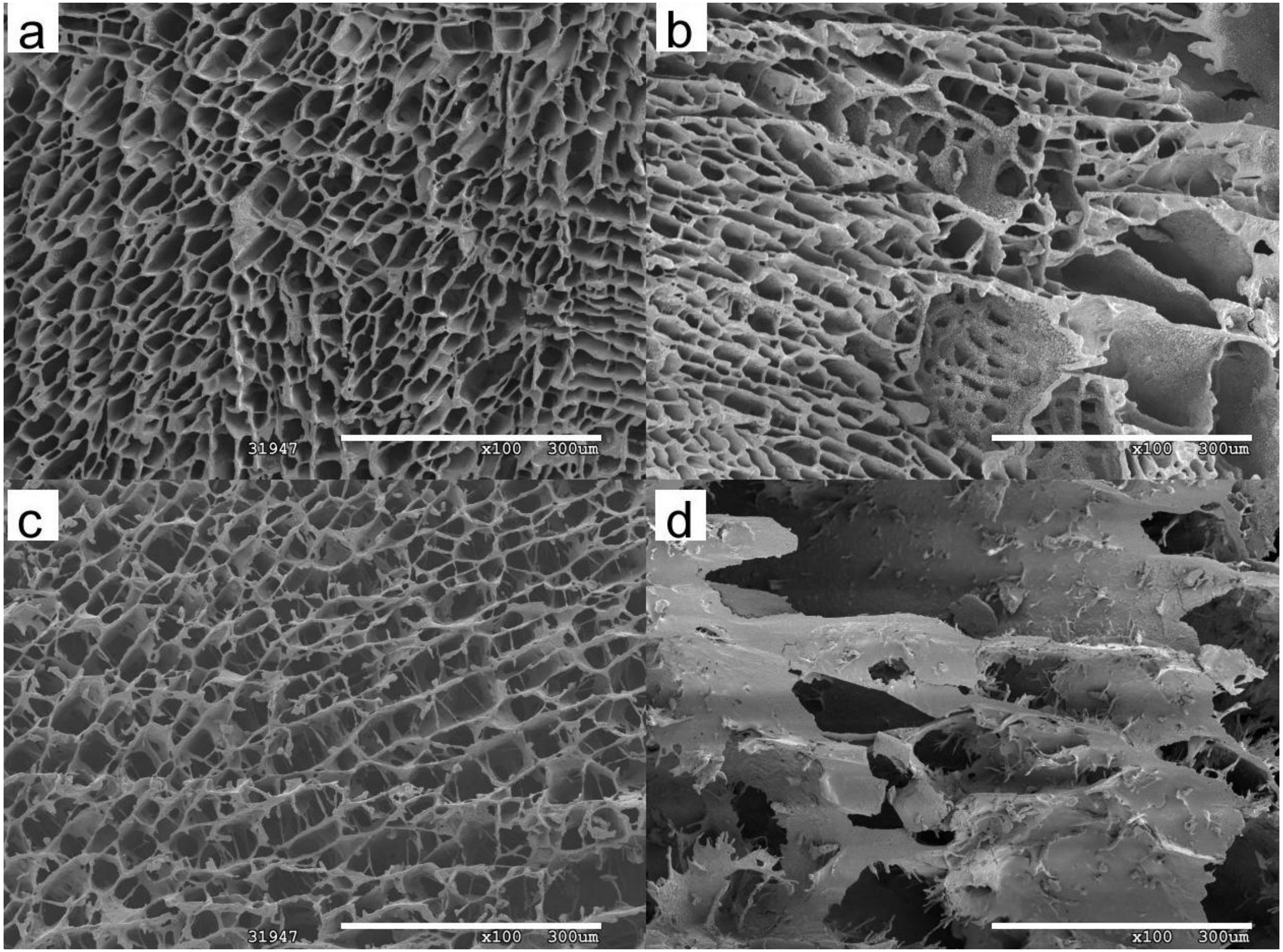
CNC clear barrier films

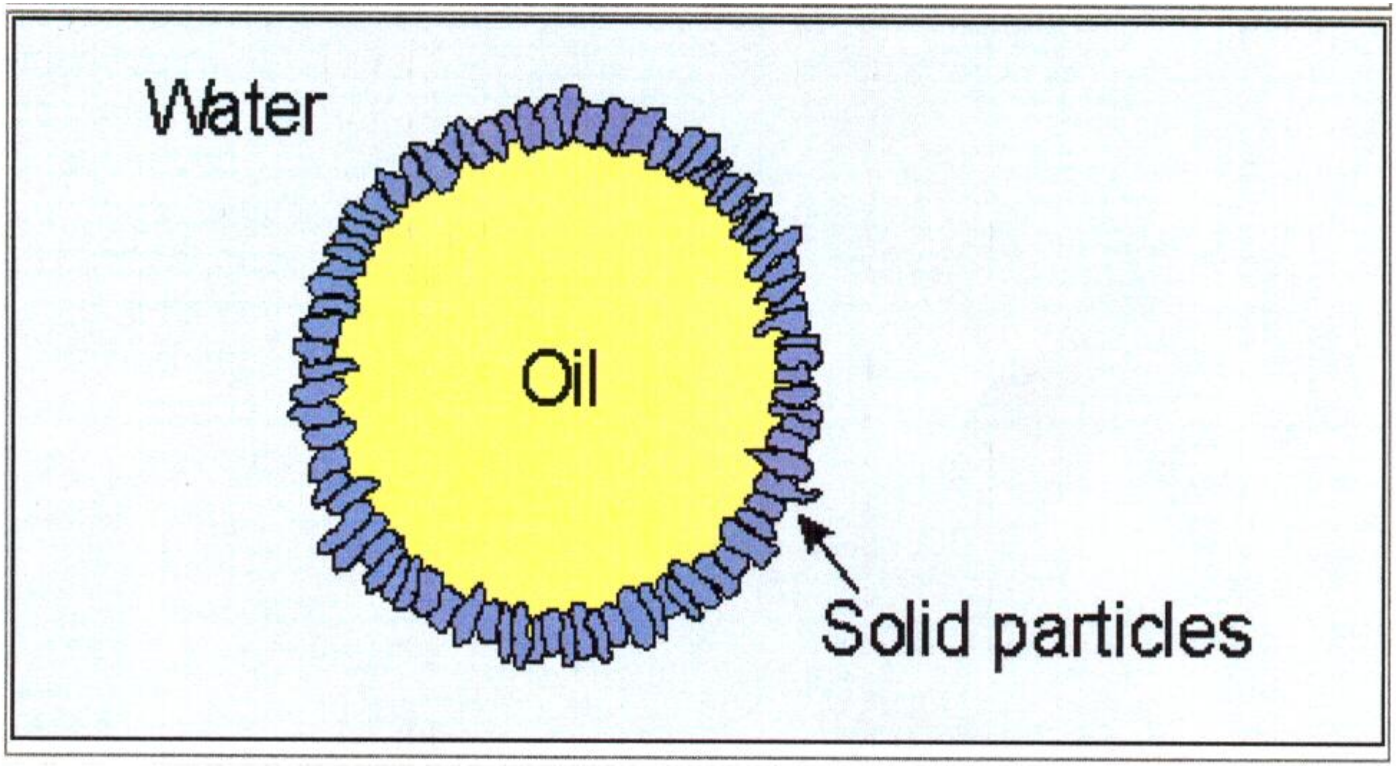
- World transparent barrier film market value has grown 9% during the period 2007-12, 2.9% annually, and is currently valued at $6.7 billion. Smithers Pira forecasts this market to grow over the next five years by 4.2% to reach $8.2 billion

EPS Cushioning Materials



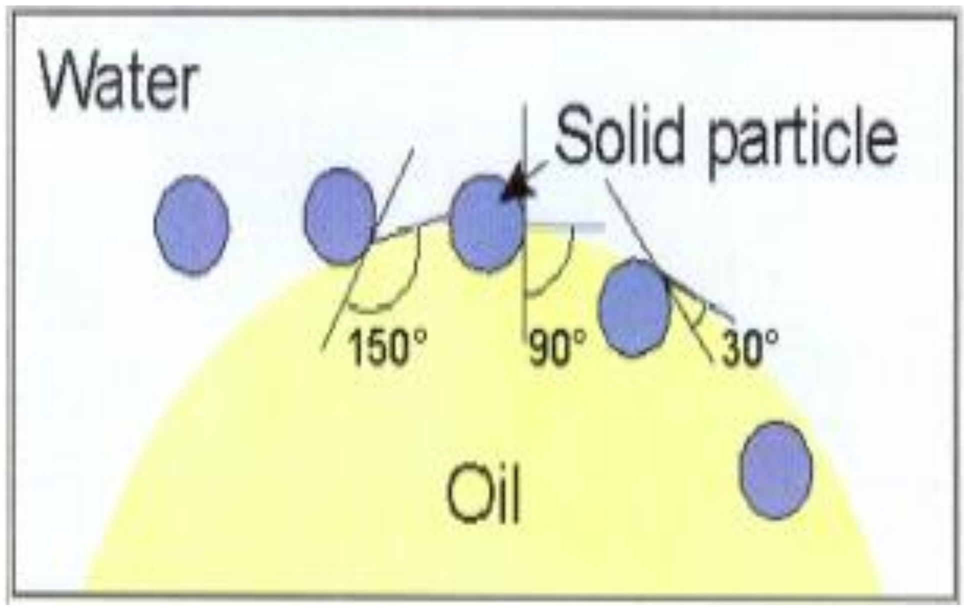
Anna Svagan thesis (KTH 2008) showed starch foams reinforced with MFC could achieve EPS properties, but cell size too irregular



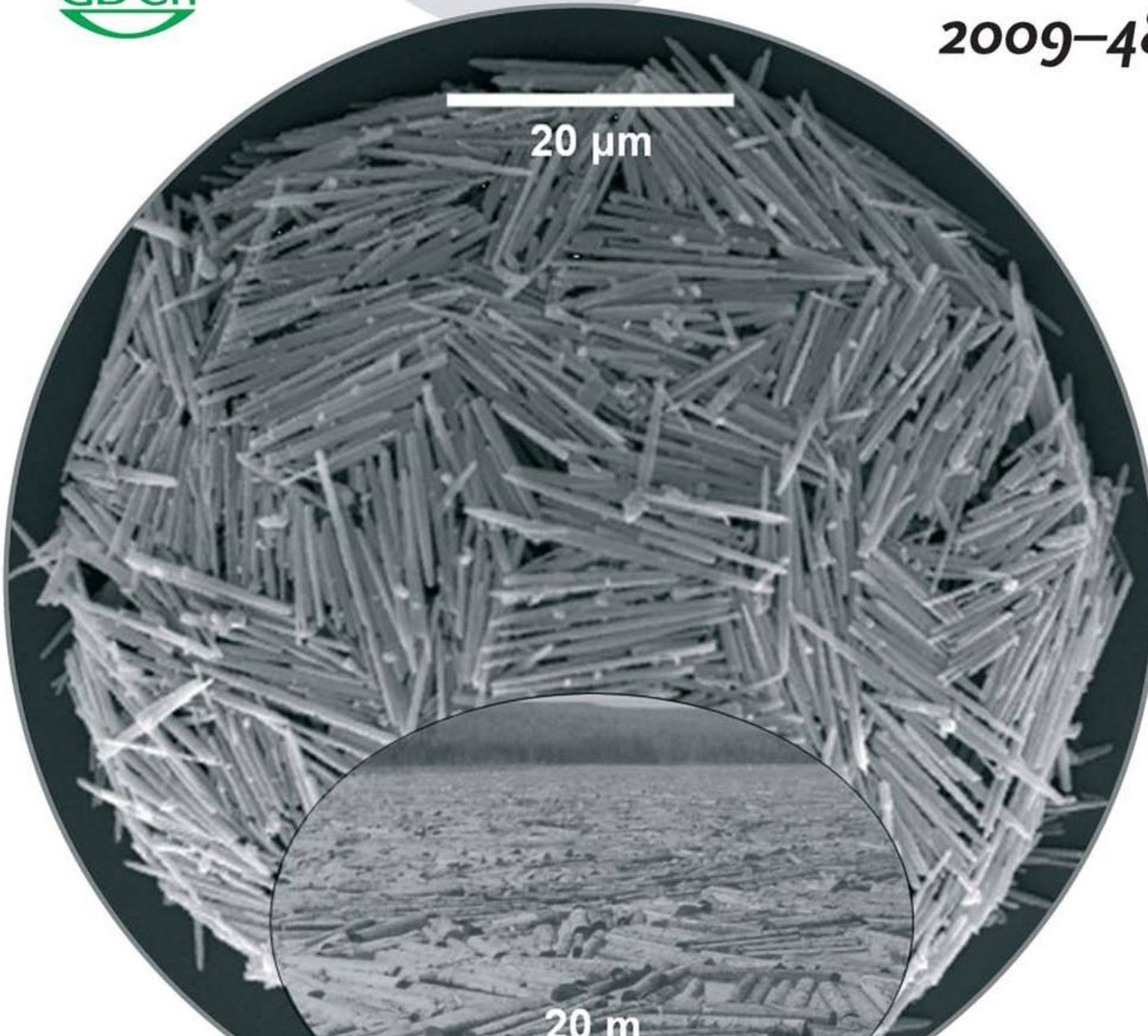


Solid particles stabilizing an emulsion

Particle stabilized emulsions



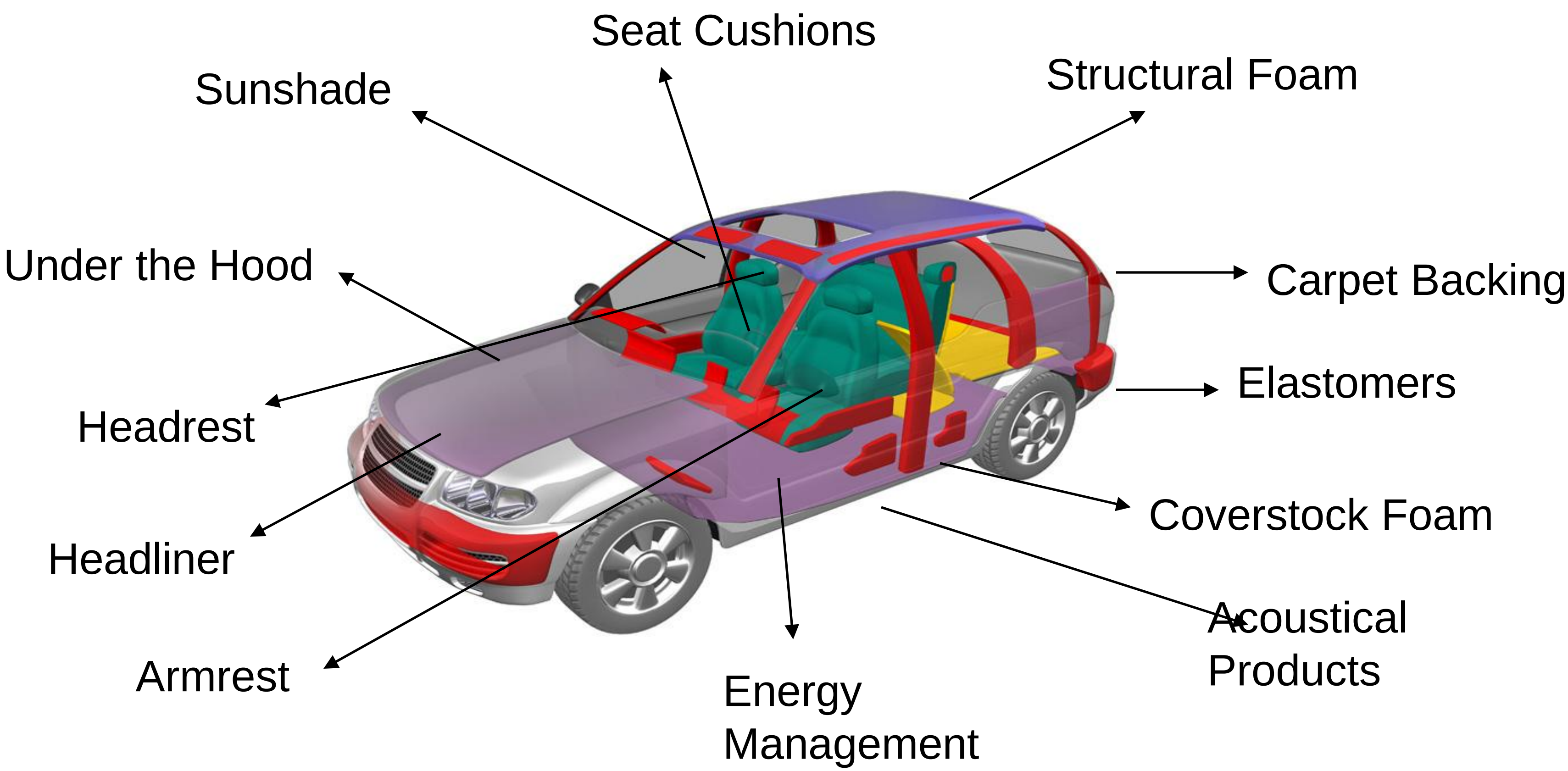
International Edition
GDCh
Chemie
www.angewandte.org
2009–48/2



CNC stabilized/reinforced natural polymer foams

- More than half the market for Expanded Polystyrene (Styrofoam) is in Asia and growing at 7% per year
- EPS for packaging is a 1.6 million ton market, but any substitute must have comparable properties, similar pricing, and be biodegrade at end of use
- UPM Kymmene and Imperial College have used crystalline cellulose to stabilize foams or scaffolds. Andriy Kovalenko from NINT has been modeling CNC foams
- Melodea, a small firm operating in the EU based in Israel with Swedish colaboration are harvesting CNC from papermill sludge and producing reinforced foams

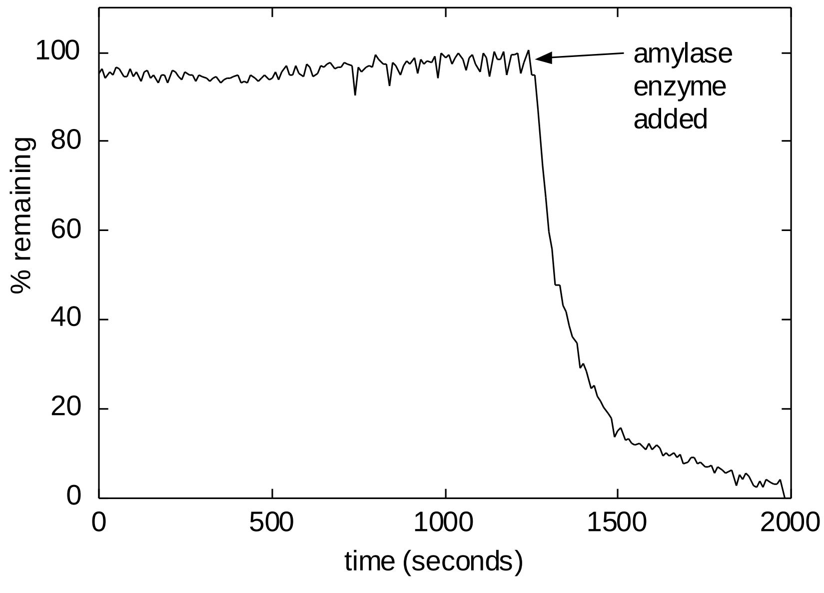
THE OPPORTUNITES FOR NANO TECHNOLOGY



Triggered biodegradation

Accelerated biodegradation assay of modified starch plastics

HM-Starch film

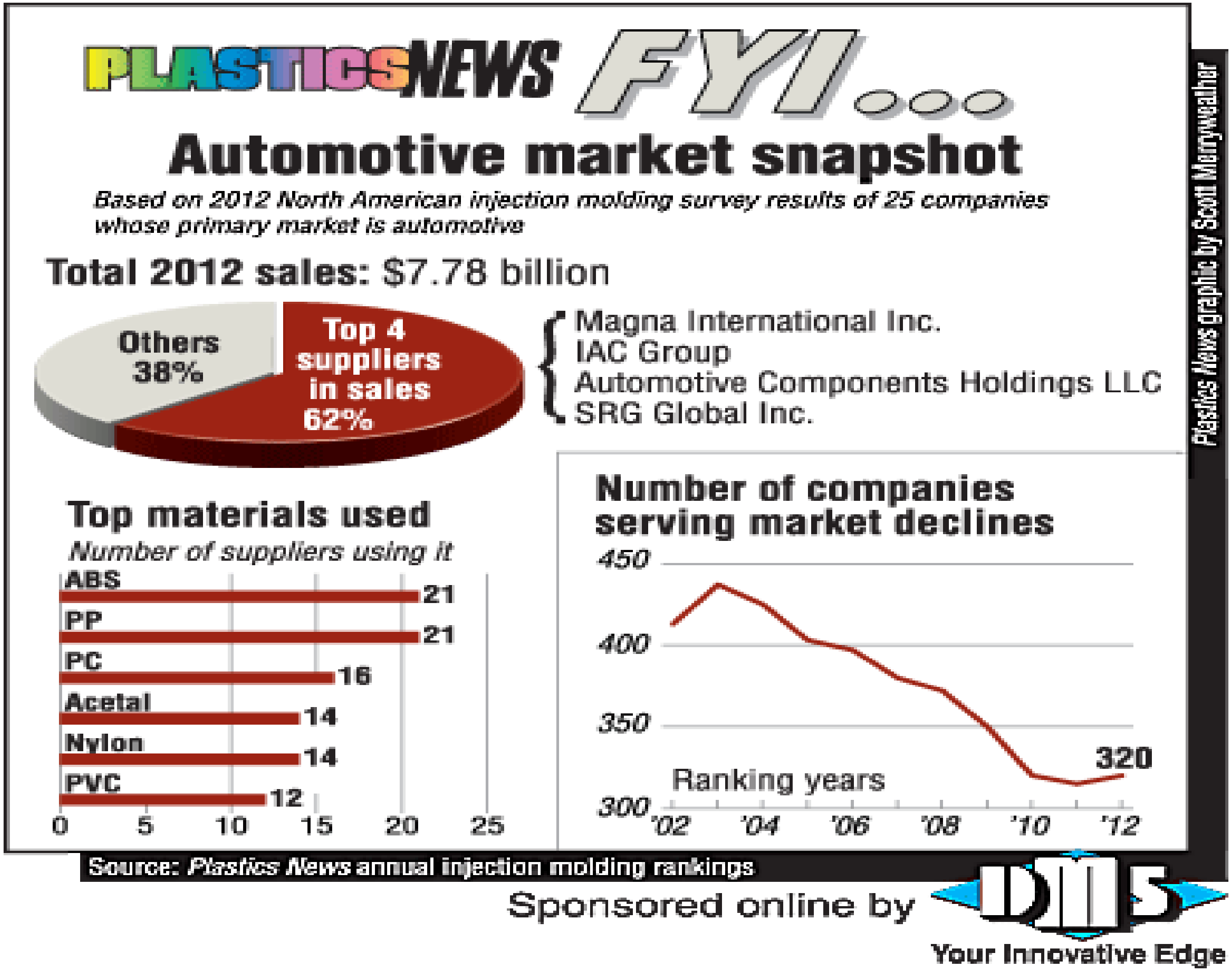


Accelerated testing
0.5 hour test

Result: predicts minimum of 5-50 *µm/yr* thickness reduction of films in soil, depending on soil activity

Automotive foams and extruded polymers for car interiors

- Foam used in automotive globally is 1,7 million tons/year
- ca.150 foam products used in automotive interiors having a wide range of physical attributes
- Substitutes must be biostable under conditions of high humidity and temperature (e.g. a car parked in the sun in Miami)
- While Toyota leads in use of renewables, 100 percent of Ford vehicles built in North America have soy foam in their seat cushions and backs as of 2011, and Ford continues to press their suppliers for components made from renewable materials



Magna is the world's largest supplier of extruded plastic components for the automotive market internationally. Woodbridge is the biggest supplier of foams for car interiors. Both are based in Ontario

NFC gen. 2

2 w-%

NFC gen. 2

7 w-%

Key patents for crystalline cellulose rheology modifiers

- Patent granted to Rhodia in 2001 for amorphous cellulose nano-fibrils used as viscosity modifier in food, cosmetic and detergent products and building materials, and in fluids used in oil extraction
- Patent granted in 2010 to UPM Kymmene for the modified NFC for use in food products, composite materials, concrete, oil drilling products, coatings, cosmetic products, pharmaceutical products and manufacture of paper
- Patent granted to INFRA (INSTITUT NATIONAL DE LA RECHERCHE AGRONOMIQUE) in 2012 for Pickering emulsion e.g. oil in water emulsion such as food composition, cosmetic composition, pharmaceutical composition and phytosanitary composition where the elongated shaped cellulose nanocrystals of the emulsifying particles stabilize the emulsion in a stable manner without surfactant
- Patent granted to AITF in 2011 for aircraft antiicing composition comprising a freezing point depressant and a thickener comprising nanocrystalline cellulose.

Conclusions and recommedations

- Go for green markets where there is a crying customer like replacement of EPS foams and liquid packaging with CNC composite/barriers and that are recyclable and biodegradable
- Exploit Alberta strengths for CNC rheology modifiers in applications like drilling mud, paint, adhesives, and cement
- Partner strategically to compensate for lack of market experience (e.g. in molded packaging) or specific technologies (e.g. polymer extrusion)

Disclosed and Undisclosed (pre-)commercial NFC/NCC production facilities

- **CelluForce (Domtar/FP Innovations) Can. (NCC)**
- **BioVision, Eastern Can. (**Nanocel™ **carboxylated NCC)**
- **Melodea, Israel (NCC reinforced foam with bioresin)**
- **AlPac and AIFT, Western Can. (NCC)**

- **Borregaard,Nor. (NFC)**
- **Rettenmaier, Ger. (NFC)**
- **DaiCel, Japan (NFC)**
- **Nippon Paper, Japan (NFC)**
- **Oji Paper, Japan (NFC)**
- **Stora Enso, Finland (NFC)**
- **UPM-Kymmene (NFC)**
- **Verso Paper, USA (NFC)**

- **2012: At least five other undisclosed companies have declared their intention to launch NFC-production**

Arboranano

MEMBERS

Bell Helicopter Textron Ltd.
CelluForce Inc.
FPInnovations
Kruger Inc.
Marquis Alliance Energy Group Inc.
Nanoledge
NORAM Engineering & Constructors Ltd.
OMYA Canada Inc.
Ontario BioAuto Council
Woodbridge Foam Corporation

INRS – Institut Armand Frappier
McGill University
Queen's University
Université de Sherbrooke
Université du Québec à Trois-Rivières
Université Laval
University of Alberta
University of British Columbia
University of Waterloo
Universtité du Québec en Abitibi-Témiscamingue

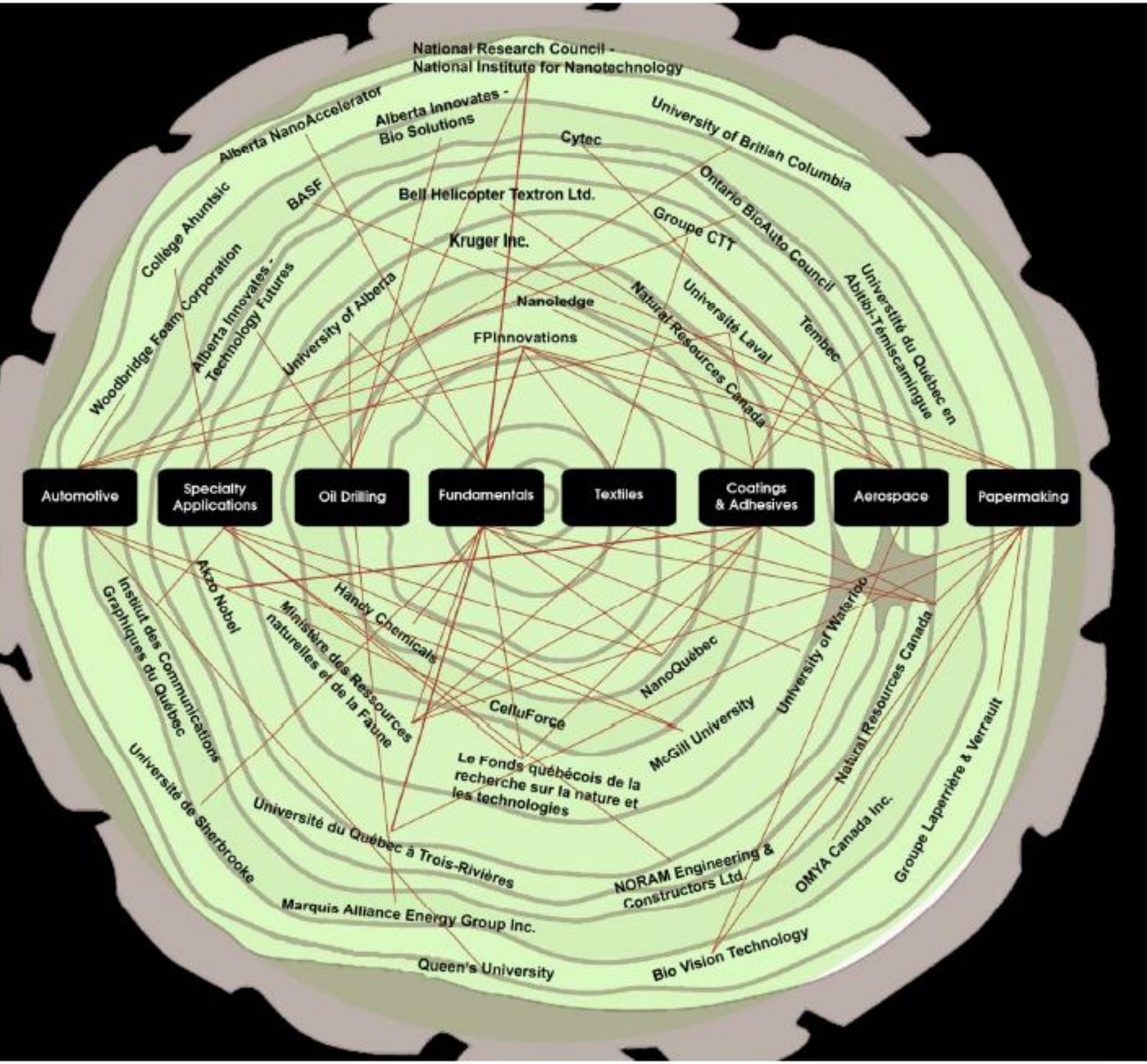
Alberta Innovates - Bio Solutions
NanoQuébec

PARTNERS

Akzo Nobel
Alberta Pacific Forest Industries Inc.
BASF
Bio Vision Technology
Cytec
Groupe Laperrière & Verrault
Handy Chemicals
Tembec
Tissue Regeneration

Collège Ahuntsic
University of Toronto

Alberta Innovates - Technology Futures
Le Fonds québécois de la recherche sur la nature et les technologies (FQRNT)
Ministère des Ressources naturelles et de la Faune (MRNF)
National Research Council - National Institute for Nanotechnology
Natural Resources Canada
Networks of Centres of Excellence of Canada (BL-NCE)
Province of Alberta - NanoAccelerator


National Research Council -
National Institute for Nanotechnology
Alberta NanoAccelerator
Alberta Innovates -
Bio Solutions
Cytec
University of British Columbia
College Ahuntsic
BASF
Bell Helicopter Textron Ltd.
Ontario BioAuto Council
Groupe CTT
Kruger Inc.
Woodbridge Foam Corporation
Alberta Innovates -
Technology Futures
University of Alberta
Nanoledge
FPInnovations
Natural Resources Canada
Université Laval
Tembec
Université du Québec en
Abitibi-Témiscamingue
Automotive
Specialty
Applications
Oil Drilling
Fundamentals
Textiles
Coatings
& Adhesives
Aerospace
Papermaking
Institut des Communications
Graphiques du Québec
Akzo Nobel
Ministère des Ressources
naturelles et de la Faune
Handy Chemicals
NanoQuébec
University of Waterloo
Natural Resources Canada
CelluForce
McGill University
Le Fonds québécois de la
recherche sur la nature et
les technologies
Université de Sherbrooke
Université du Québec à Trois-Rivières
Groupe Laperrière & Verrault
OMYA Canada Inc.
NORAM Engineering &
Constructors Ltd.
Marquis Alliance Energy Group Inc.
Queen's University
Bio Vision Technology

DISTRIBUTION OF FUNDING

7% aerospace

20% automotive

21% forest products

11% oil & gas

3% health

38% varia

Arboranano

DISTRIBUTED BY TARGETED DEVELOPMENT

- Acrylics
- Composites
- Paints
- Coatings/ Sealants
- Epoxies/ Adhesives

7% aerospace

- Cushions
- Headliners
- Headlamps

20% automotive

- Mechanical Paper
- Packaging
- LWC Paper
- Wood Adhesives

21% forest products

- Drilling Mud

11% oil & gas

- Pharmaceuticals
- Personal Care

3% health

- Coatings/Paint/Ink
- Textiles
- Films
- Membranes
- Construction

38% varia

Various Life Cycle and Maturation Stages

Life Cycle	Discovery	Feasibility	Practicality	Application	Production Preparation	Production Preparation	Production Preparation	Production Preparation	Low Rate Initial Production	Production
AFRL TRL	1	2	3	4	5	6	7	8	9	9
NASA TRL	1, 2, 3	4, 5	6	7	7	7	8	9		
TRL	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
IPT Reviews	**Technology Identification**	**System Requirements**	**Initial Design**	**Preliminary Design**	**Critical Design**	**Ground Test Readiness**	**Flight Test Readiness**	**Operational Readiness**	**Production**	**Support**
Certification		Certification Elements Documented	Certification Plan Documented	Certification Plan Approved	Element Validation	Subcomponent Validation	Full Scale Component and Airframe Validation	Flight Validation	Operational Validation and Production Approval	
Application/ Design	Concept Exploration	Concept Definition	Proof of Concept	Preliminary Design	Design Maturation					
Fabrication/ Quality	Fabrication concepts explored	Unfeatured panel fabrication	Feature-based Generic Parts Fabricated	Property - Fabrication Relationships	Production environment readiness				Production rate readiness	
Supportability	Repair requirements identified			Repairs developed for pre-production	Support for recycle/disposal decisions					
Structures & Durability	Preliminary Properties		Initial Properties	Design-To Properties	Prelim. Design Allowables	Design Allowables				
Materials	Lab-Prototype Materials	Prototype /Pilot Materials	Pilot plant materials	Process Control Document	Qualification material made and characterized to specification	Material Approved to Specification			Production Scaleability Validated	Production Material Supplied
Cost/Schedule	Elements Identified	Projected	Rough order of magnitude assessments		Reflects learning curve from qualification and part fab.				Thorough cost and schedule assessment tied to plan	Validate and Update
Intellectual Property/Legal	Patent Disclosure Filed, Legal Issues Identified	Proprietary Agreements in Place	Transition plan includes safety, environmental, intellectual property, and legal issues	Supplier and fabricator discussions	Supplier and fabricator agreements				Supplier and fabricator agreements for production, liability termination agreements	

Technology Readiness

Application Readiness

Production Readiness