Biodegradable polymers; Description, properties and advances

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- Definitions
- Biodegradation
- Biodegradable polymers
- Biodegradable plastics
- Technological advances

Definitions

What is biodegradable ???

- **Degradation:** the irreversible process in which a material undergoes physical, chemical and/or biochemical changes leading to increased entropy as embedded in the second main law of thermodynamics
- **Biodegradation:** degradation catalyzed by biological activity leading to mineralization and/or biomass
- **Biodegradability:** the degree to which biodegradation leads to mineralization and biomass
- **Mineralization:** the conversion of (organic) material to naturally occurring gasses and inorganic constituents
- **Composting:** Biodegradable under industrial composting conditions (defined in EN13432)

Biodegradation

- Recognizable for enzyme systems of bacteria, fungi and yeast
- Properties (T_g, structure, MW, crystallinity etc.)
- Biochemical properties of degradation products
- Dimensional aspects
- Environmental conditions

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Biodegradable polymers

- Biodegradable polymers are polymers that can be broken down by bacteria, fungi or other simple organisms
- Biodegradable polymers can be classified in three groups depending on their origin;
  - Microbial
    - Biotech
  - Naturally occurring polymers
    - Isolation (+ modification)
  - Synthetic biodegradable polymers
    - Based on either renewable or synthetic monomers
    - Polymerization

Microbial origin

- Wide range of materials; polyesters, polysaccharides
- Considerable interest arose when large scale controlled processes were developed
- Applications in pharma, textile, paper, food, cosmetics and plastics industry

Naturally occurring polymers

These polymers originate from nature

- Animal origin
- Marine origin
- Agricultural feedstock

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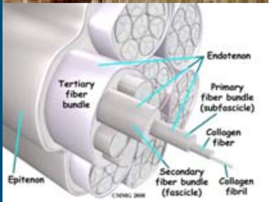
Animal origin: Polypeptides

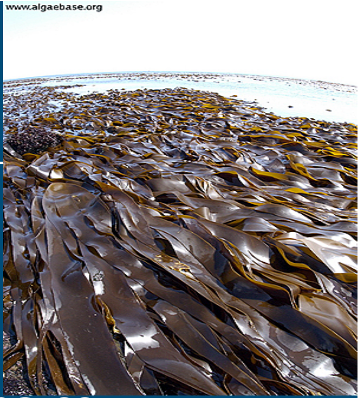
- Mostly neither soluble nor fusable without degradation especially in their natural form
- Wool, Collagen, Gelatin
- Applications in the pharma, biomedical, textile, food industry



Marine origin: Chitin and Chitosan

- Chitin is a polysaccharide found in shells of crabs and lobsters (and insects)
- Chitin is insoluble in its native form but Chitosan, which is partially deacetylated chitin is water soluble
- Biocompatible, have antimicrobial properties and have ability to absorb heavy metal ions
- Applications in the pharma, biomedical, foo cosmetics and plastics industry

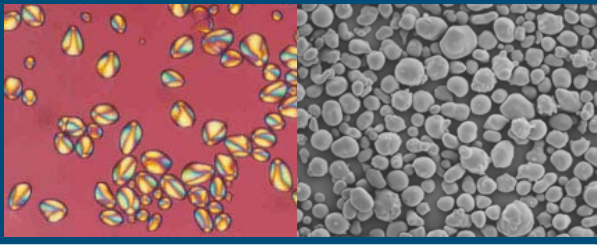
Marine origin: Alginate



- Alginate is a polysaccharide originating from different seaweeds
- Forms insoluble gels in presence of polyvalent cations
- Applications in the pharma and food industry

Agricultural feedstock: Starch

- Produced in the form granules and is combination of two polymers amylose and amylopectin
- Amylose a linear polymer where as amylopectin is branched
- Very abundant polymer
- Applications in food, cosmetics, plastics, paper industry



Agricultural feedstock: Cellulose

- Differs from other polysaccharides in some respects since its molecular chain being very long and consisting of one repeating unit
- Occurs naturally in crystalline state
- It is modified for further application and use (Ethers, esters and acetal)
- Applications in textile, paper and plastics industry

Synthetic biodegradable polymers

Polymers with hydrolysable backbones

- (Aliphatic) Polyesters
  - Polyesters derived from diacids and diols
  - Monomers with both an acid and alcohol group
  - Examples: PGA, PGA/PL, PLA, PCL
- Poly(ester)amides
- Polyurethanes
- Polyanhydrides
- Applications in the pharma, biomedical and plastics industry

Synthetic biodegradable (?) polymers

Vinyl polymers

- Claimed that few exceptions are susceptible to hydrolysis
- Biodegradation requires an oxidation process (oxidisable functional group)
- Biodegradation can be improved by including addition of catalysts to promote oxidation or photo oxidation or both
- PVA is said to be the most readily biodegradable vinyl polymer
- PVAC undergoes biodegradation more slowly
- Application are in the plastics industry, paper industry

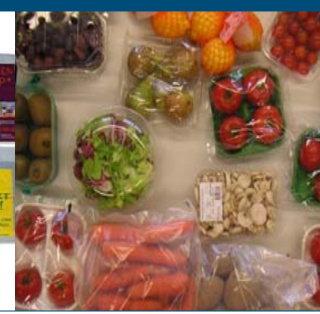
Biodegradable plastics

1. biodegradable polymer +

2. biodegradable additives +

3. material processing



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Biodegradable plastics

Classification

- Cellulose and cellulose derivatives
- Starch based plastics (in particular thermoplastic starch)
- Poly - esters
  - Poly lactic acid
  - Poly caprolacton
  - Poly hydroxy alkanoates
  - other (co)poly-esters
- Industrial protein based materials
- Blends of various biodegradable plastics (in particular thermoplastic starch and poly-esters)

Cellulose/cellulose derivatives

- Good mechanical properties (rather stiff material comparable with polystyrene)
- Material can be capable to withstand boiling water
- Transparent (in most cases)
- Price (> € 4,-/kg)
- Can be processed as delivered, better is drying of the material
- Can be used for injection moulding, sheet extrusion, thermoforming
- Processing temperatures: 190 to 240 °C
- Be aware of thermal degradation during processing

Suppliers/users:

- Mazuchelli SPA, FKUR Kunststoff GmbH, Clarifoil, Wolff Walsrode AG, Albis plastic GmbH, Modiplast

Starch based plastics

- Good mechanical properties (properties vary), and excellent O_2 barrier
- Anti - static
- Films are not completely transparent
- Can be processed as delivered,
- Can be used for film blowing, injection moulding, sheet extrusion (and thermoforming), foam extrusion
- Processing temperatures: 120 to 180 °C

Suppliers/users:

- Novamont Spa, Biopolymer Technologies AG, Biotec GmbH, Plantic Technologies, Biocompound GmbH, Biograde ltd., BioPak.

Poly lactic acid (PLA)

- Good mechanical properties (mechanical properties are comparable with PET)
- Transparent
- Rather cheap in comparison with other biodegradable material (€ 2 - 2.50/kg)
- The material doesn’t degrade at temperatures below 45 °C
- It is sensitive for water during processing
- Can be used for film extrusion (and thermoforming), blow moulding, injection moulding, fibre extrusion
- Processing temperatures: 170 to 210 °C

Suppliers/users:

- Natureworks LLC, Mitsui chemicals, Purac, Biomer, FKUR Kunststoff GmbH, Biopearls, Nestle Oil, Natureplast, Biopak

Synthetic (co)polyesters and poly-ester amides

- Non renewable
- Variable mechanical properties
- Compostable
- Suitable for films and extrusion (in most cases not for injection moulding)

Suppliers:

- BASF, Du Pont, Showa Denko, Solvay, Dow

Combinations

- Improvement of properties (coatings, laminates, wraps)
  - Mechanical properties
  - Water resistance
  - Permeability
  - Visual properties
- Additional functionality
  - Sealability
  - Release of active compounds
- Technical and financial feasibility
  - Price/performance
  - Processing

Technological advances

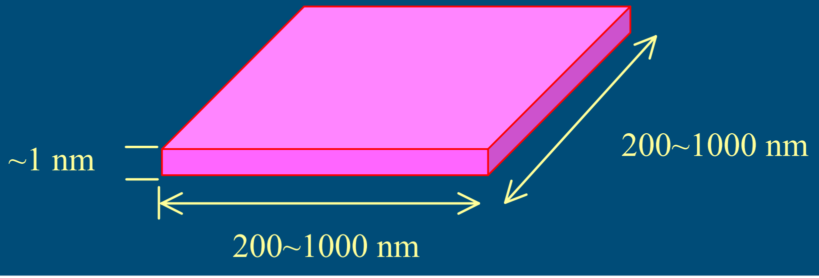
- Composite materials
  - Particles (nano particles)
  - Fibers (nanofibers)
- Nanofoams
- IPNs
- Colloidal particle technology
- Encapsulation technology

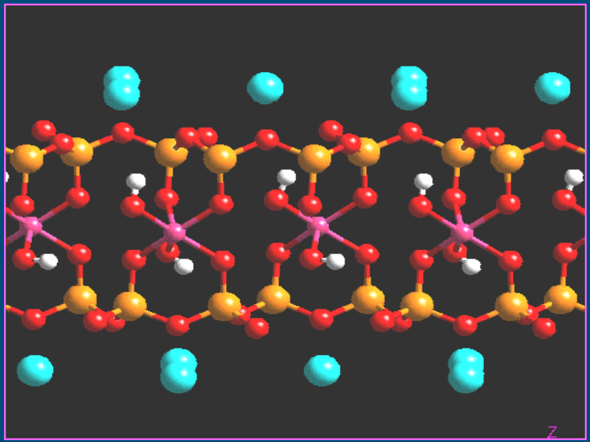
Clay nanocomposites

Clay

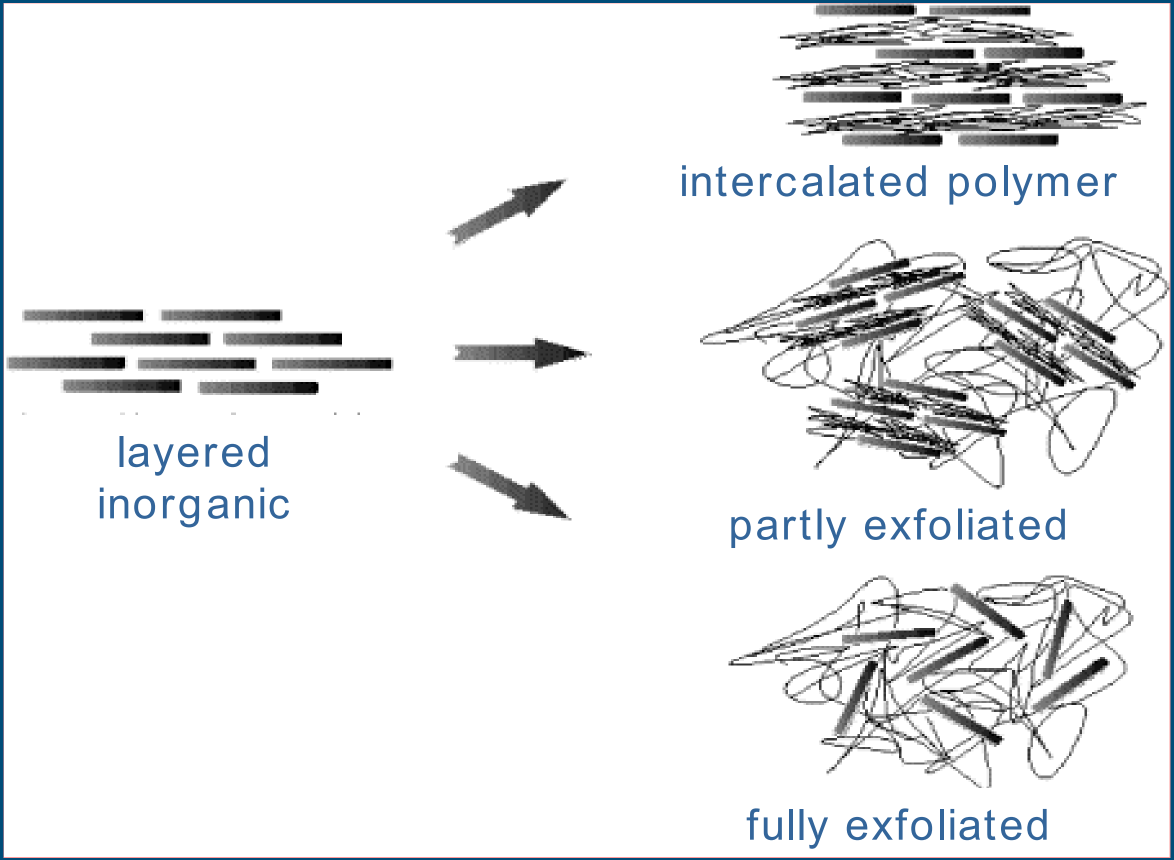
- Natural material
- Layered structure

- E.G montmorillonite
  - thickness 1 nm
  - lateral dimensions 200-1000 nm





How?



intercalated polymer
layered
inorganic
partly exfoliated
fully exfoliated

Background

- Pioneering work by the Toyota group (Nylon/ clay)
- Nano clay, ultra fine layered titane, carbon nanotubes
- Particular interest is the improvement of properties
  - Mechanical properties (tensile and flexural)
  - Permeability
  - Flammability
  - Transparency

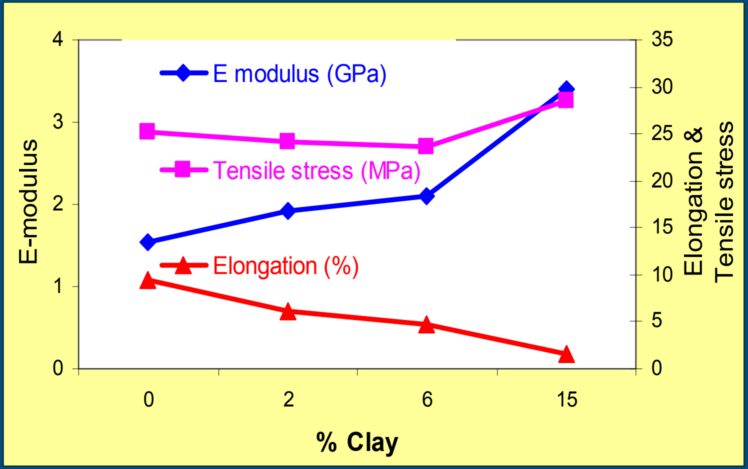
Starch and its nanocomposites

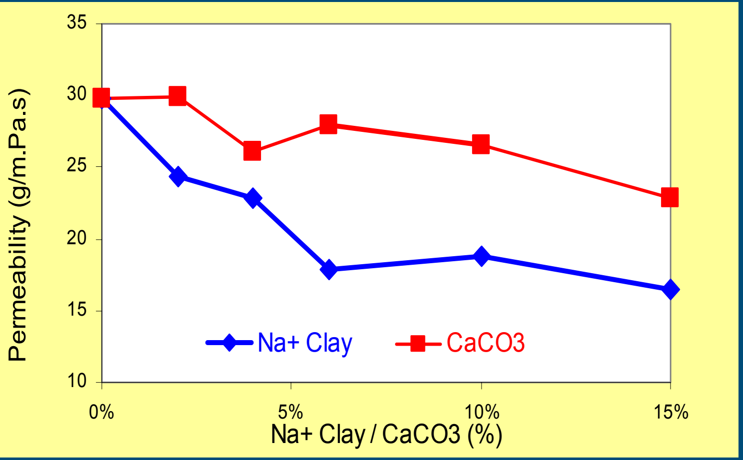
- Commonly melt intercalation technique
- Different types of clays
- Up to 30 %
- Variable degrees of intercalation and exfoliation
- Improvement of both mechanical properties and barrier properties

Starch/nano clay composites

Wet film casting and extrusion

- Relatively easy exfoliation
- Improved mechanical properties
- Improved barrier properties





PLA/nano clay composites

- First reported is the solvent cast method
- Melt intercalation/solvent casting using compatibilisers
- Intercalation/exfoliation
- Improvement mainly on the mechanical properties and biodegradability (faster or slower)
  - HDT
  - Processing

PLA/nano clay composites

- Complete exfoliation is only possible with modified clays
- Processing effects are significant
  - Specific mechanical energy [kWh/ton] does not determine the amount of exfoliation
  - Indication: higher degree of fill in extruder, more exfoliation

Fiber composites

- Proven their value due to their specific properties; high strength, stiffness and low weight.
- Natural fibers are of interest
  - Functional capability
  - Low weight
  - Good interaction with the (polar) matrix
  - Renewable
- Physical and chemical treatments to improve adhesion

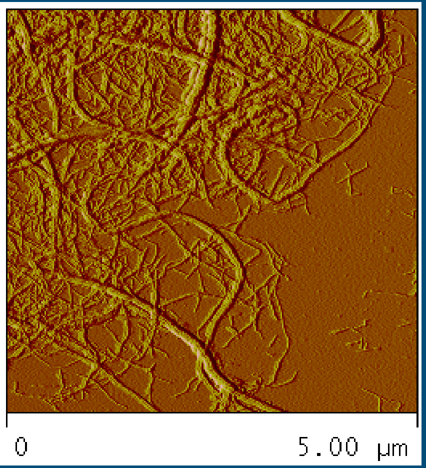
Fibre sources/related processes

- (waste) paper, pulp, potato fibers, wood, hemp, flax, sisal, kenaf, ramie, straw, cocos, bran
- In some cases undesired morphology, color
  - thermo-mechanical processing, milling, bleaching
- Processing
  - pulping, extrusion, (compression) moulding

Extrusion Compounding Technology

Production and characteristics of the MFC

- From bleached sulphite pulp + beating + enzymatic treatment + beating + homogenisation
- 20-30 nm width, 70nm-1µm length



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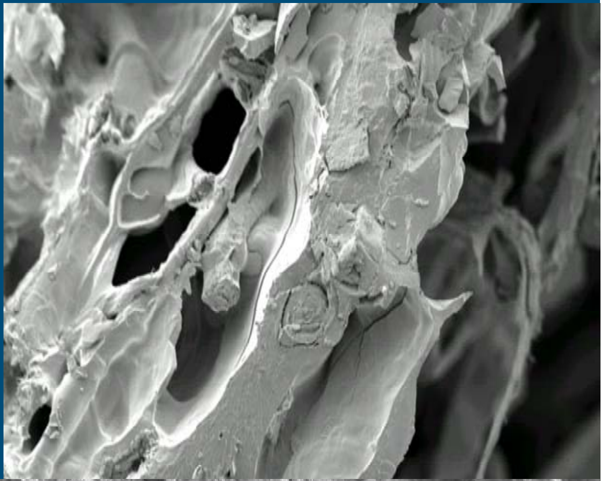
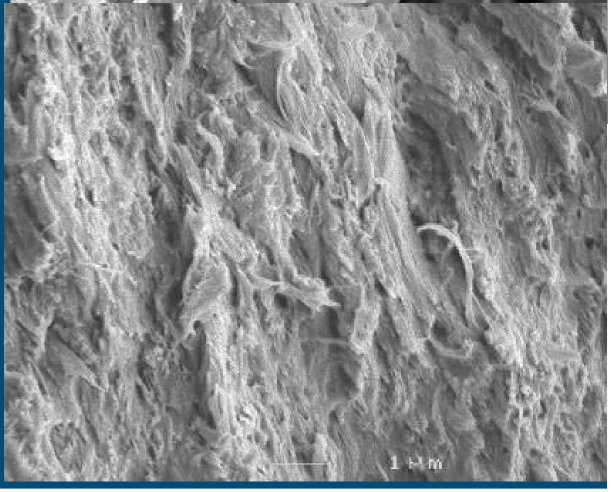
MFC composites

- Combined with nanoclays
  - Variable intercalation and exfoliation
- Solvent cast method
- Melt processing
- Improvements on mechanical properties and permeability

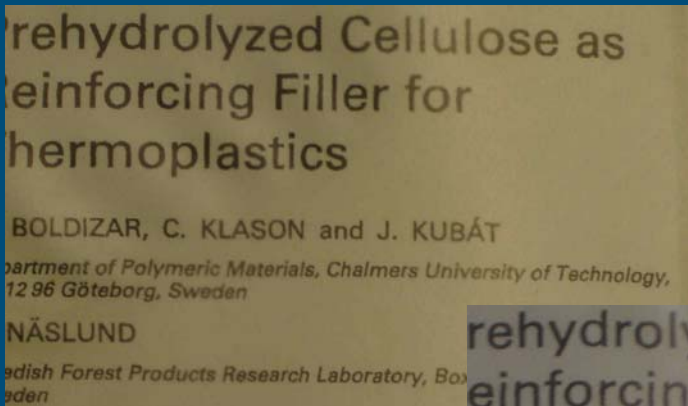




Nano clay and MFC composites

- Starch/amylopectin matrix
- Transparency unchanged
- Improvement on the mechanical properties and permeability remains

Softwood fibres + Nano clay in Starch


rehydrolyzed Cellulose as
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hermoplastics

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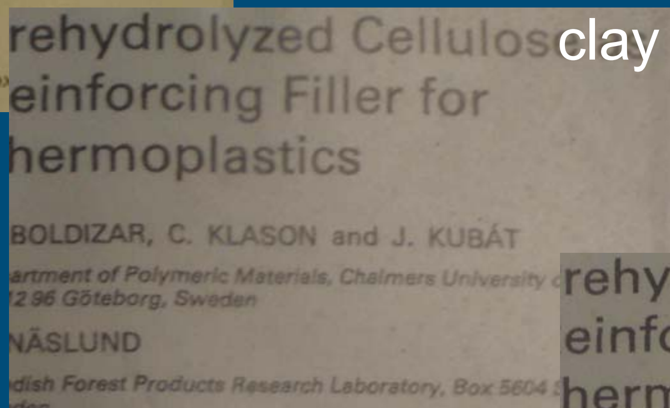
10% fibre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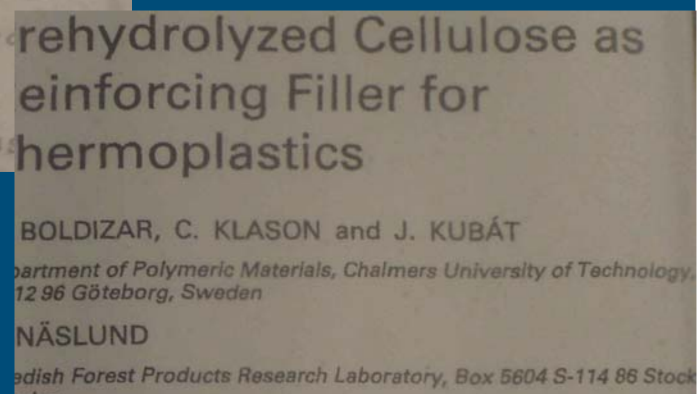
17% fibre + 4% nano clay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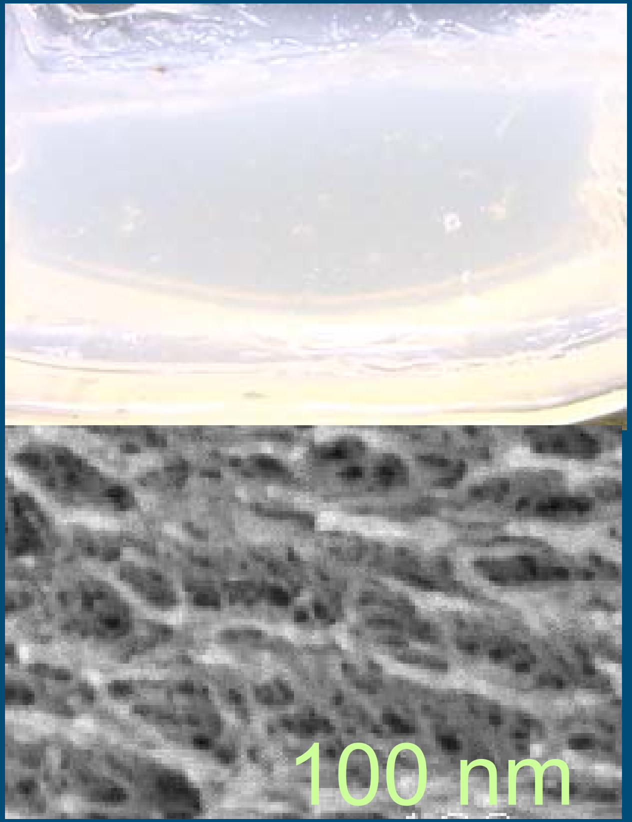
30% fibre

Polymer nanofoam based on polysaccharides

- Highly transparent
- Very light weight
- Good insulating

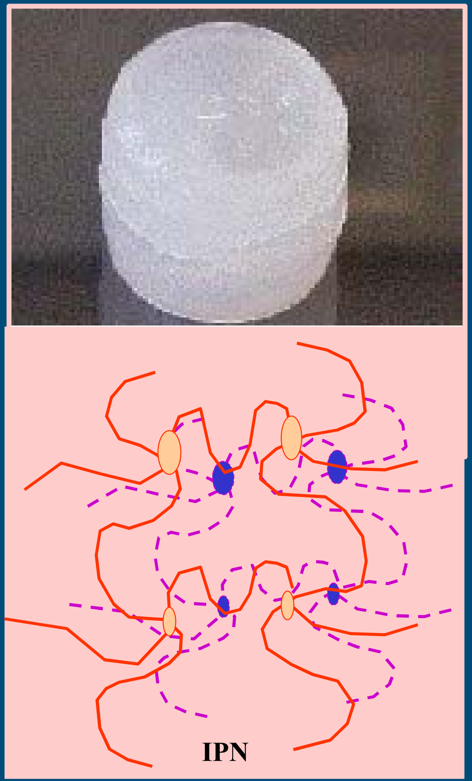
Uses

- Solar cell
- Green house
- Membrane-separation



Carbohydrate IPN's

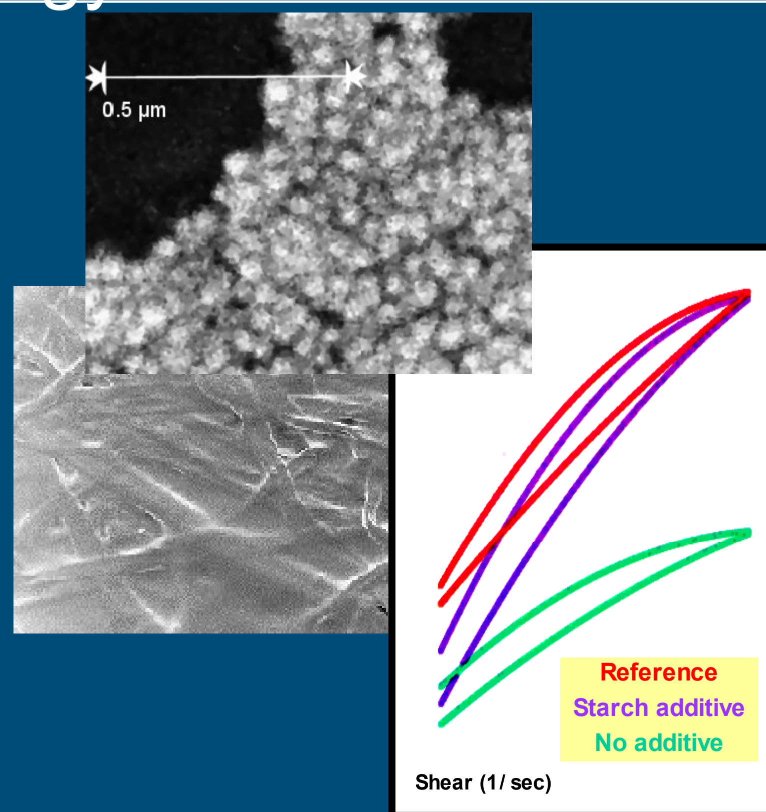
- Advantages:
  - strength
  - less brittle - flexibility
  - low shrinking, sensitivity to solvents / heat
  - less wearing
  - improved compatibility



Colloidal Particle Technology

Looking for new functionalities:

- reduced retrogradation
- low viscosity at high solids
- colloidal stability in water



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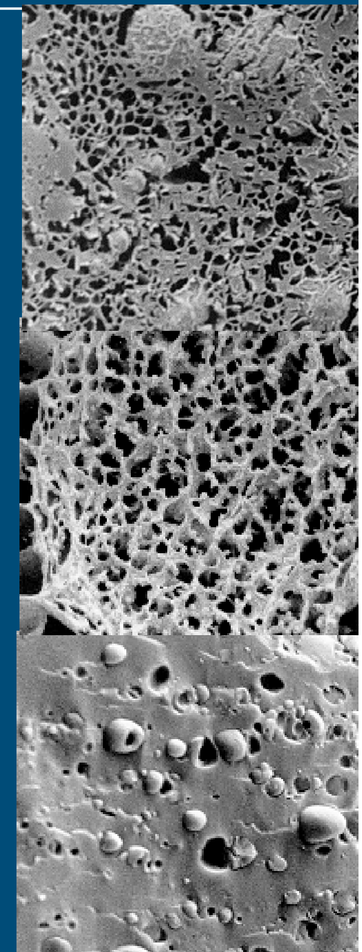
Controlled Release Technology

- Making active compounds available at the wanted location, amount, and time
  - Versatile technology for creating added functionality
  - Can be combined with thermoplastic processing
  - Provides options that are impossible for traditional materials
  - Shaped articles, granules, powder, gels, foams, sheet, flakes



Conclusions

- Biodegradable polymers offer a wide range of properties
- Consumer trends ask for new (food)packaging concepts. Natural polymers can add to the solution or be the solution
- For a successful product development series of positive properties (not only biodegradability) are considered

Acknowledgements

- Sustainpack partners
- A&F colleagues
  - Fibre and paper technology
  - Sustainable chemistry

Thank You!

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