Effects of low-molecular weight additives and aging on rheological properties of chitosan/CN slurries

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n – Chitopack workshop, 17 October 2014, Prague
1. Chitosan /chitin nanofibrils (CN) slurry
   Solid-like and rubber-like behaviour
   CN = strong “gelling agent”

2. Effects of bioplasticizers (glycerol, PEG)
   Delay in the beginning of gelation

3. Effects of metal ions (Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$)
   Ba$^{2+}$ - positive influence on gelation

4. Effects of aging
   Decrease in elasticity

Parts 1 and 2: Carbohydrate Polymers 112, 753-757 (2014)
1. **Processing of chitosan / CN films**
   Transport, mixing (shear rate analysis)
   casting, spraying (yield stress, thixotropy)
   stability, structural recovery (time effects)

2. **Relation to microstructure**
   Rate of self-assembly, strength of physical networks

**Structure ↔ rheology ↔ utility properties**

- mechanical
- barrier
- thermal
Properties of chitosan/CN slurries

- Static chitosan aggregation
- Hydrophobic interactions + H-bond
- Dynamic self-assembly
- Slipping
- Network destruction

Associative polyelectrolyte solution + anisotropic nanoparticles

- Physical network
- Gel point
(1) Investigate effects of bioplasticizers and metal ions ($\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Ba}^{2+}$) on rheological properties of chitosan/CN slurries.

(2) Observe changes in rheological characteristics of chitosan/CN/glycerol slurry during long-time aging.
Materials

**Chitosans:**

a) Giusto Faravalli S.p.A., Italy, $M_w = 1425$ kDa, DA = 20 %

b) HMC+ GmbH, Germany, $M_w = 374$ kDa, DA = 11 %

**Chitin nanofibrils:** (Mavi Sud Srl, Italy), degree of acetylation (DA) = 90 %

**Bioplasticizers:**

glycerol
poly(ethylene)glycol

**Metal hydroxides:**

$Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$
Composition:

(a) Chitosan solution:
   2 wt. % chitosan solution in 2 wt. % acetic acid
(b) Chitosan/CN solution:
   Solution (a) + 0.8 wt. % chitin nanofibrils
(c) Modified chitosan/CN solution:
   1) Solution (b) + 1 wt. % glycerol
   2) Solution (b) + 0.03 wt. % metal hydroxides

Preparation:

Mechanic stirring: 8 h after homogenization at room temperature
Storage: low temperature above 5 °C
Rheometr Physica MCR 501 (Anton Paar, Austria), anti-slipping parallel plates geometry, \( d = 50 \text{ mm} \), measurements at room temperature, pre-shearing 3 s at the shear rate 0.01 s\(^{-1}\)

1. **Steady shear flow**
   - stress controlled experiments – yield stress limits

2. **Small-amplitude oscillatory shear**
   - linear viscoelastic region confirmed at 6.28 rad s\(^{-1}\)

3. **Time dependent experiments**
   - in steady and oscillatory shear
(1) Decrease of the yield stress – destruction of the physical network at a lower stress.

(2) Rubber-like behaviour in the low frequency region only.

(3) Delay in the beginning of gelation.
Effects of metal ions on elasticity of slurries

Storage modulus vs. angular frequency;
Slurry without metal ions, with Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$ ions.
Effects of metal ions on gelation

Storage modulus (■) and loss modulus (▲) vs. time; Chitosan/CN, chitosan/CN/ Ca$^{2+}$, chitosan/CN/Mg$^{2+}$, chitosan/CN/Ba$^{2+}$, chitosan/Ba$^{2+}$(CN absence).
Effect of Ba\(^{2+}\) concentration on gel elasticity

Storage modulus (■) and loss modulus (▲) vs. time; chitosan/CN/Ba\(^{2+}\) (0.03 wt. %), chitosan/CN/Ba\(^{2+}\) (0.01 wt. %) chitosan/Ba\(^{2+}\).
Chitosan /CN/ glycerol slurry - decrease in elasticity
Storage modulus (■) and loss modulus (▲) vs. frequency;
1 day, 6 weeks, 19 weeks of storage
Addition of bioplasticizers to chitosan/CN solutions resulted in the prolongation of self-assembly process in slurries and in the decrease in yield stress.

Presence of Mg$^{2+}$ ions in slurries prolonged and Ba$^{2+}$ ions propagated gelation; effect of Ca$^{2+}$ was not significant.

Elasticity of chitosan/CN/glycerol slurry decreased and solid-like behaviour disappeared during long-time storage. The gelation of the slurry was decimated due to a scission of chitosan chains.

Conclusions
The authors gratefully acknowledge the financial support of the European Union through the grant No. 315233.

Thank you for your attention!