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

Jana Mikešová[a], Jindřich Hašek[a], Galina Tishchenko[a], Pierfrancesco Morganti[b]

[a]*Institute of Macromolecular Chemistry AS CR, v. v. i., Prague 6, 162 06, Czech Republic*
[b]*Mavi Sud Srl, Aprilia, 04011, Italy*

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Content

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)

? Why rheology ?

1. ***Processing of chitosan / CN films***

   Transport, mixing (shear rate analysis)

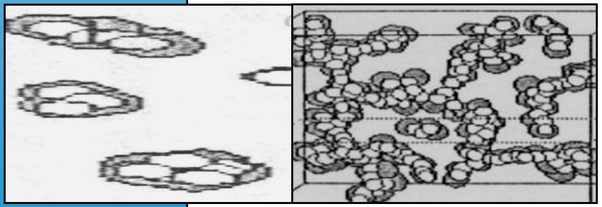
   casting, spraying (yield stress, thixotropy)

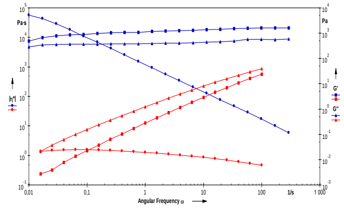
   stability, structural recovery (time effects)

2. ***Relation to microstructure***

   Rate of self-assembly, strength of physical networks

Structure ↔ rheology ↔ utility properties





mechanical

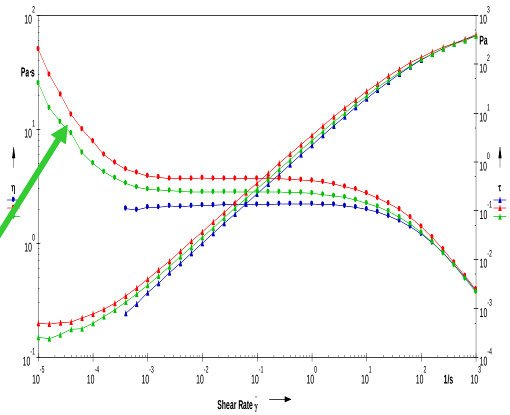
barrier

thermal

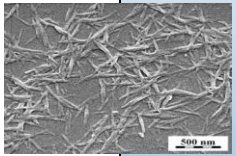
Properties of chitosan / CN slurries

Static chitosan aggregation

Hydrophobic interactions
+
H-bond



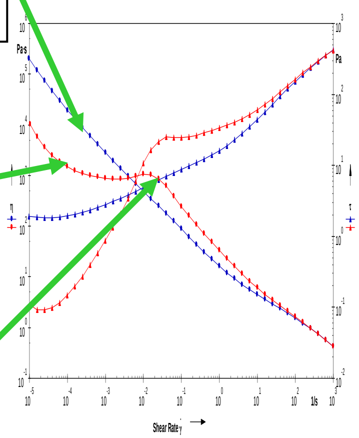
Associative polyelectrolyte solution
+
anisotropic nanoparticles



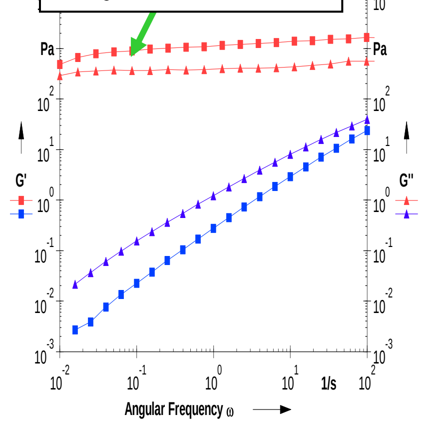
Dynamic self-assembly

Slipping

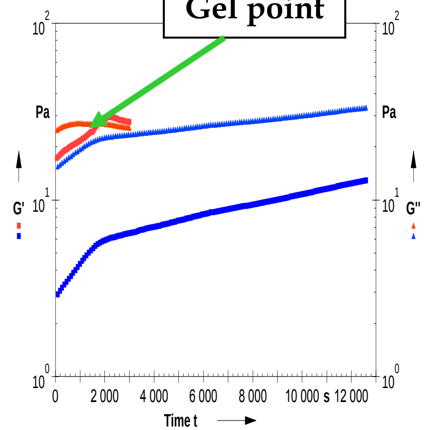
Network destruction



Physical network



Gel point



Aim of the study

(1) Investigate effects of bioplasticizers and metal ions (Ca^{2+}, Mg^{2+}, 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:

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

Solutions

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 ^{o}C

Experimental

Rheometr Physica MCR 501 (Anton Paar, Austria),
anti-slipping parallel plates geometry, d = 50 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

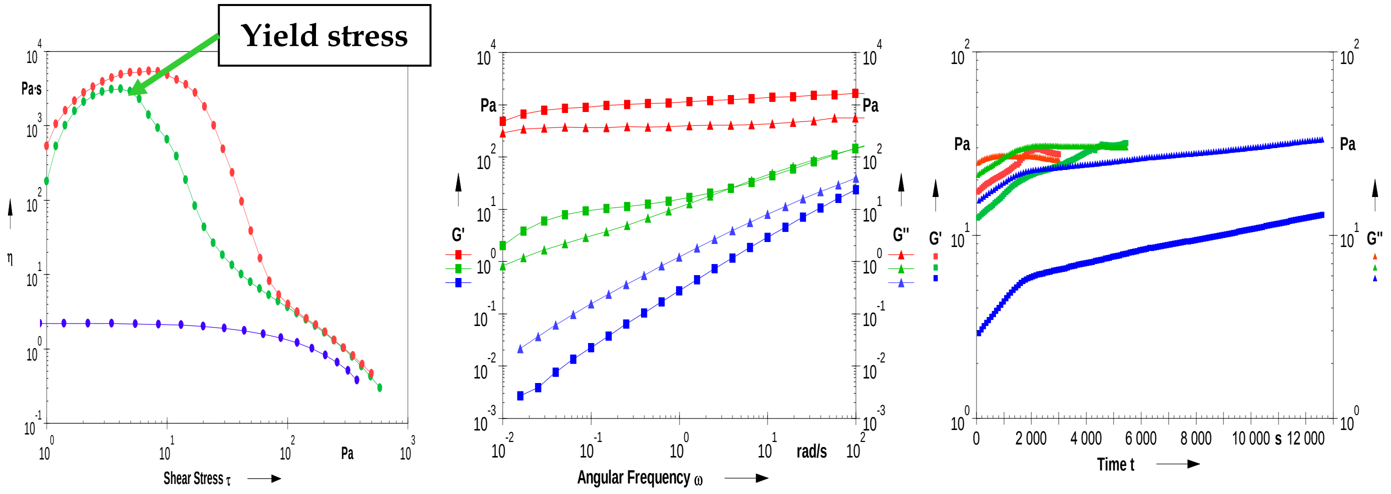
(2) Small-amplitude oscillatory shear

linear viscoelastic region confirmed at 6.28 rad s^{-1}

(3) Time dependent experiments

in steady and oscillatory shear

Effects of bioplasticizers (glycerol)

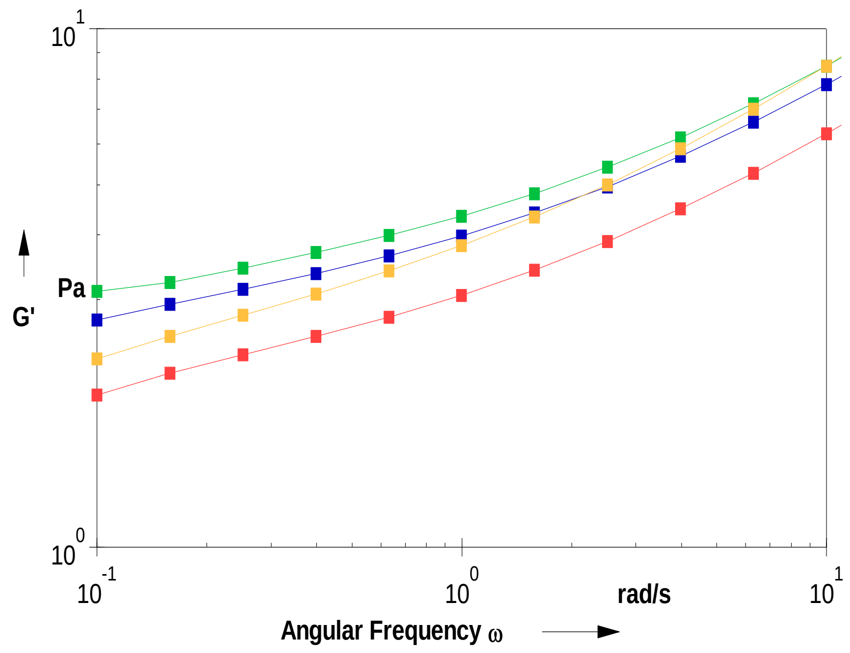


(1) Decrease of the yield stress – destruction of the physical network at a lower stress.

(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

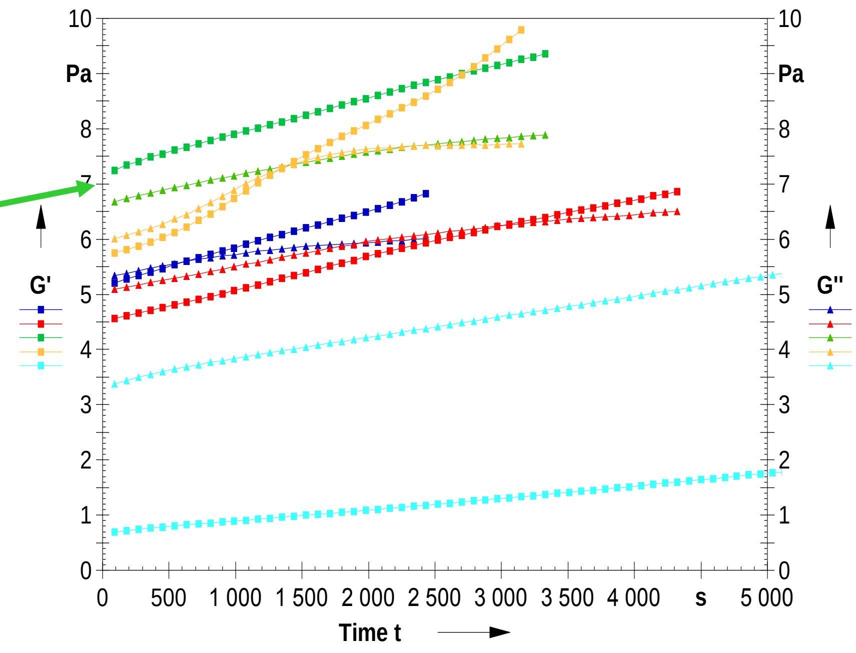


Storage modulus vs. angular frequency;

Slurry **without metal ions**, **with Ca^{2+}**, **Mg^{2+}** , **Ba^{2+}** ions.

Effects of metal ions on gelation

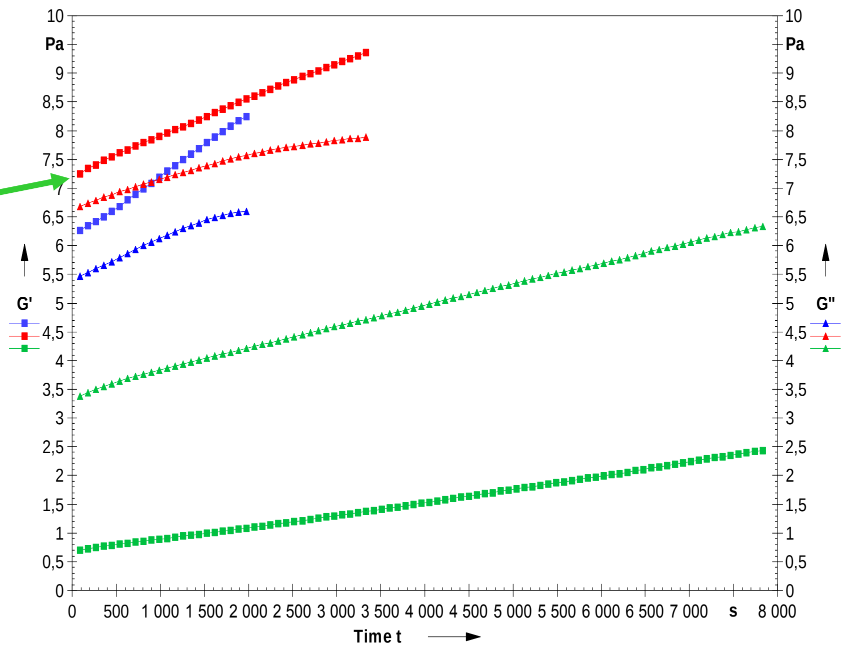
over the gel point



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).

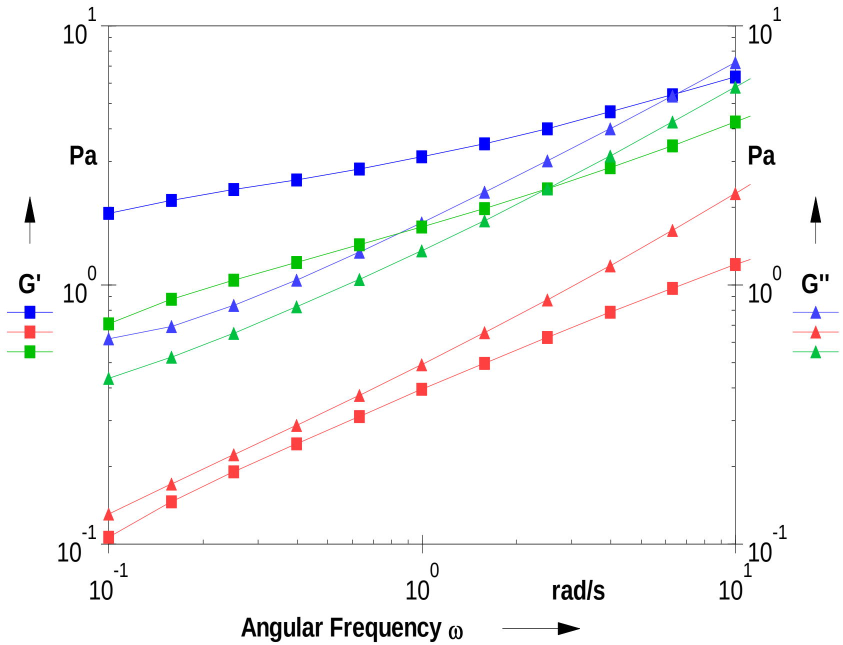
Effect of Ba^{2+} concentration on gel elasticity

stronger network



Storage modulus (■)and loss modulus (▲) vs. time;
chitosan/CN/Ba^{2+} (0.03 wt. %), chitosan/CN/Ba^{2+} (0.01 wt. %)
chitosan/Ba^{2+} .

Aging during storage



Chitosan /CN/ glycerol slurry - decrease in elasticity

Storage modulus (■) and loss modulus (▲) vs. frequency;

1 day , 6 weeks, 19 weeks of storage

Conclusions

(1) Addition of bioplasticizers to chitosan/CN solutions resulted in the prolongation of self-assembly process in slurries and in the decrease in yield stress.

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

(2) 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.

Announcement

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Thank you for your attention !