SINGAPORE INSTITUTE OF TECHNOLOGY

Hydrogels in food science

Dr. Peter HANTZ
guest researcher

UNIVERSITAS BUDAPESTINENSIS DE ROLANDO EÖTVÖS NOMINATA

Foods with gels @ the planet

Chemistry & Physics @ gels

Our R&D

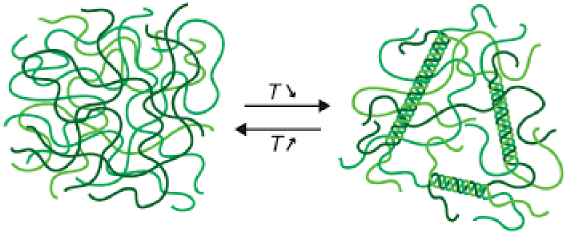
Foods with gels @ the planet

Aspic

skin, bones: **collagen**
triple helix

boiling: collagen → **gelatin**
random coils
soluble

gelling: hydration
heating-cooling
→ triple-helix



Central and Eastern Europe
climate
traditions

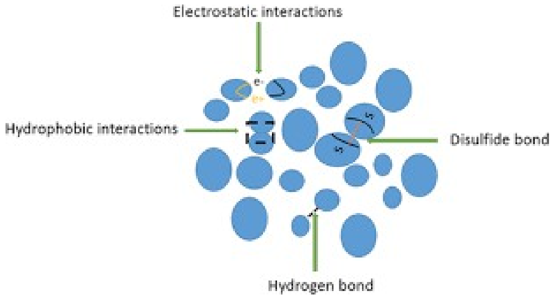
Foods with gels @ the planet

Gummibear

HaRiBo, 1922
gelatin + SUGAR
triple helices / H-bonds

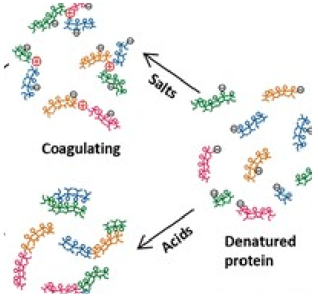
Egg pudding: ovalbumin (albumin/small)

heat: denature
hydrophobic interactions
other links



Tofu: glycinin (globulin/big)

heat: denature
pH: ↓charge → hydrophobic
Me2+: ionic bridges



Bean Curd

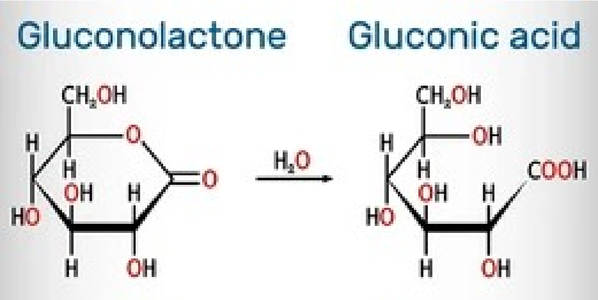
Soya milk - cross-linked

glucono-δ-lactone hydrolysis

slow pH↓

hydrophobic interactions

NOT pressed (no whey liq)



cyclic esther → acid

Foods with gels @ the planet

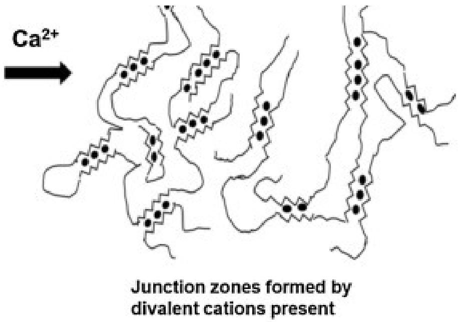
Cyclea barbata gels
Indonesia, Vietnam

heteropolysaccharide backbone
Galacto**uronic acid**
–COO^- groups

Gelling: **high intrinsic Ca2+**
Mech: bit similar to alginate / LM pectin

Anti-insect strategy

Some similarity: black Chinese gelley



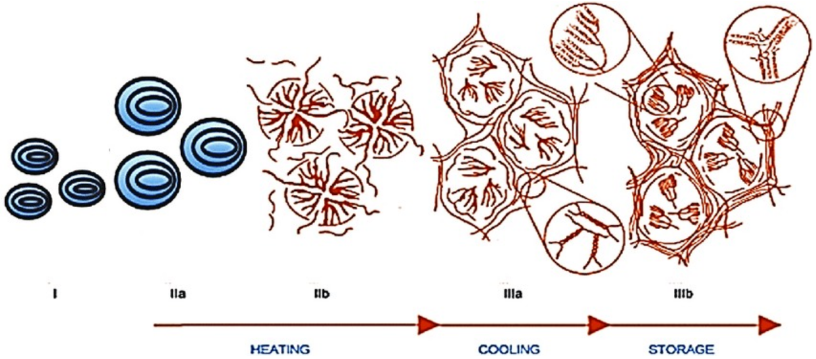
Foods with gels @ the planet

Boba pearls
Taiwan → global

Sago pearls (palm starch)

tapioca: South America → Taiwan
texture-culture
tea @ 1980’s
(suitcase for nothing)

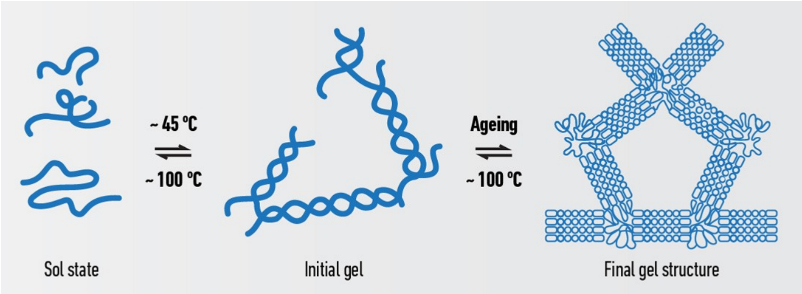
Starch gels: boiled: → gelatinization
cooled: → gelation (→ retrogradation)
hydrogen bonding
entangle



Foods with gels @ the planet

Agar

Japan, 17th century → all over

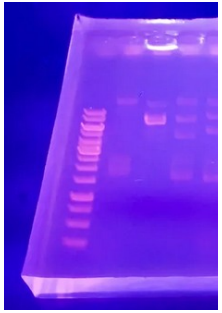


Yōkan

hard agar w red bean paste

Agarose

Uses in biochemistry: DNA gel electrophoresis



Foods with gels @ the planet

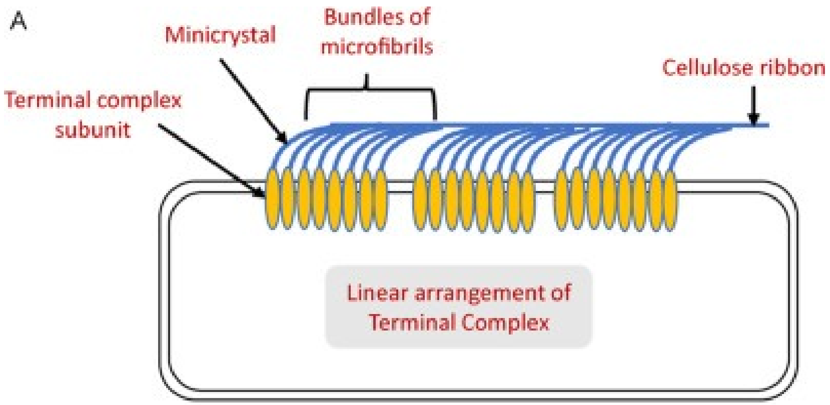
Nata variants
Philippines →


del pina: 18th century
del coco: T. Kalaw-Africa, 1949

Komagataeibacter xylinus: glucose→ cellulose nanofibrils

→ processed biotextiles
cross-linking
plasticizer

Ben Tre, VN



FEEDBACK, DISCUSSIONS

Why boba became a global success?

Space application?
Dietetic applications?

Novel creative foods?

Hydrogels in (micro)biology

Extracellular Matrix (ECM)

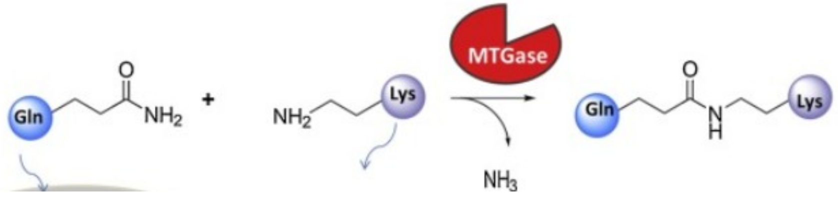
mix: proteins + polysaccharides

collagen + hyaluronic acid (-●o-)

Blood Clot (Fibrin gel)

factor XIIIa

Ca^{2+}-dependent transglutaminase GLU+LYS



Foods: Microbial Transglutaminase

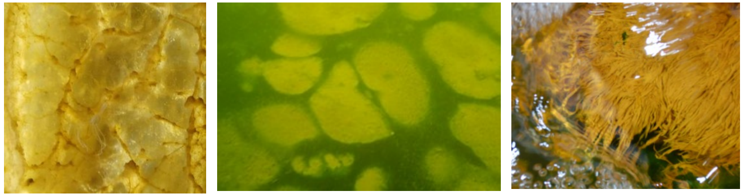
(no Ca^{2+} dep.)

application of MTGase in the food industry

Biofilms

bacteria, diatoms, ...

medicine & <u>environmental science</u>



Lead properties

Polymer, hydrated

→ protein

→ polysaccharide

X vinyl polymers $[-CH_2-CH(R)-]_n$ R is -OH in PVA

X acrylic polymers Vinyl backbone & carboxylic acid

Crosslinking

H-bonding	general:: en.X–H $\delta^+ \cdots$ N or O δ^-	@ **food thickeners**
Helix zones (with H-bonds)	agar(2), gelatin(3), ...	
Ionic	alginate, LM-pectin, soy, ...	
Covalent	proteins :: disulfide, TG-made	
Hydrophobic	proteins:: egg, soy, ...	

Heat

thermo-rev	agar, gelatin, HM-pectin, ...
thermo-irrev	starch, egg
non-thermal gels	Ca-alginate, LM pectin

pH may count!

(Edible)Hydrogels

```
                 Natural Polymers
                        |
          +-----------------------+-----------------------+
          |                                               |
   Polysaccharides                                     Proteins
          |                                               |
   +-----------+-----------+-----------+          +---------+---------+
   |           |           |           |          |                   |
 Plant       Algal      Animal    Microbial     Plant               Animal
 origin      origin     origin     origin       origin              origin
   |           |           |           |          |                   |
 Cellulose   Alginates   Chitosan    Xanthan     Wheat Gluten        Gelatin
 Starch      Agar                    Gellan      Soy protein         Actin
 Pectin      Karragenán              Dextran
 Inulin                              Pullulan
 Guar gum
 Gum Acacia
 Psyllium
```

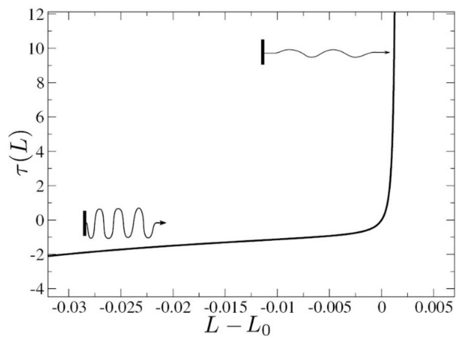
Elasticity

Energetic (Enthalpic, H) Elasticity
bond breaking
↑T → weaker
~ brittle

$$G = H - TS$$

$$F = -\frac{\partial G}{\partial x}$$

Entropic (S) Elasticity
entropy change - “hit-bend”
↑T → stronger (TΔS dominates)
~ elastic



S PVA—tapioca—gelatin—alginate **H**

Plasticizers: ↓ chain interactions: sugar, glycerol...
move more freely
→ entropic & ↓retrogradation

Retrogradation (bread, boba)...
less free movements
→ enthalpic

Design principles of food gels

Yiping Cao[1] and Raffaele Mezzenga[1,2]

https://hydrogeldesign.org

Water miracle

trap > 80-99.9% water
strongly / weakly bound

G minimum
Flory-Rehner eqn.

hitting the network, charges, ...

99.99%
Soccer ball 20cm
Mesh cca. 5m
VM speed cca 500 m/s

Swelling
Hydrophilic groups (-OH, -COOH, -NH2) bind water
Lower crosslinking

Syneresis
Squeezes out water
chains rearrange - more compact

(Aroma) Release

Chewing vs. Static release

Melting? Fracturing?
surface

Aroma-Matrix interactions
H-bounds, ionic, hydrophobic

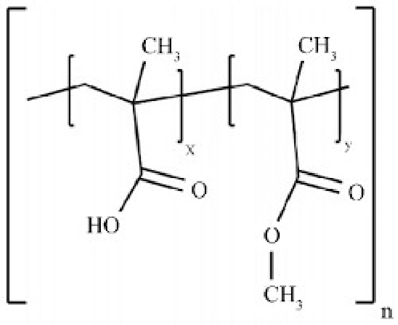
Diffusion

May also reduce Glycemic index (GI)

pH-dependent release

Drug delivery @ a certain segment of the digestive track

Eudragit film coating
pH 1-2: -COOH, neutral
tight
pH 5-8: carboxyl de-protonated
charged → hydrophilic
loose



ester:
passive

Postharvest coatings

↓ moisture loss
↓ O_2 diffusion
↓ spoilage

Apeel Sciences / USA: *Apeel, Edipeel:* polysaccharides + some lipids

FEEDBACK, DISCUSSION AND AWI TIME

Non-hydro gels?
-Si–O–Si- ; ethyl-cellulose, ...

Any further application of hydrogels in your field?

Molecular Gastronomy: Spherifications

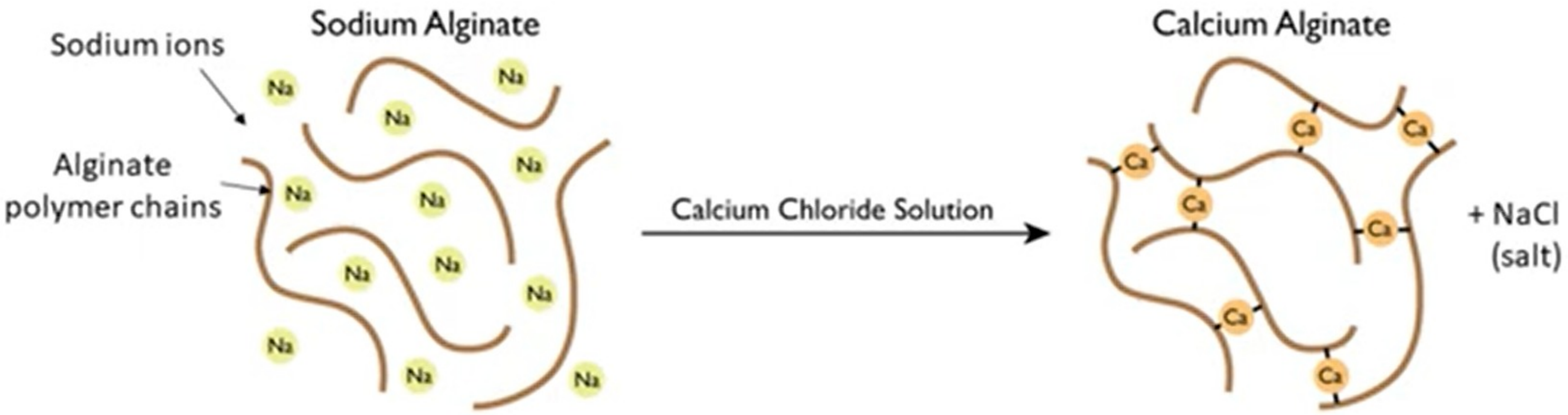
liquid foods are encapsulated in a thin gel membrane

William J. Peschardt
1940

Ferran Adrià
El Bulli Foundation
2003-2005

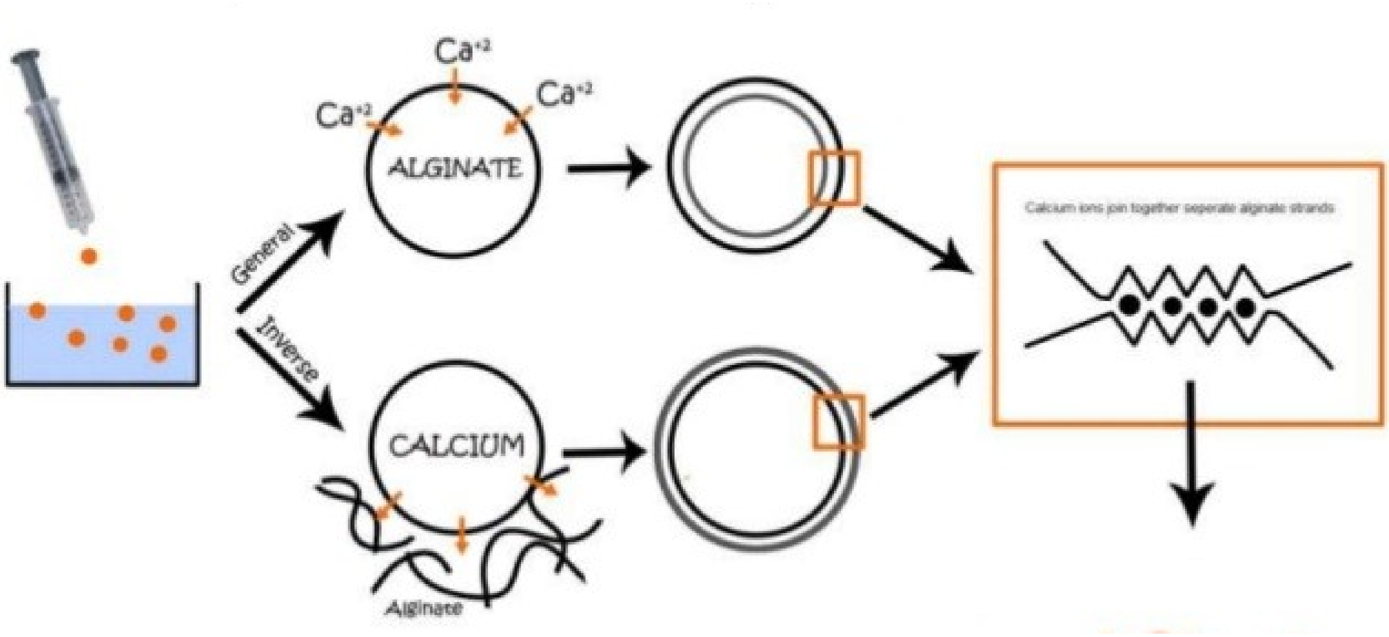
“Normal”: membrane around te delicacy; & gradually solidifies
“Inverse”: membrane persists, doesn't become solid, larger

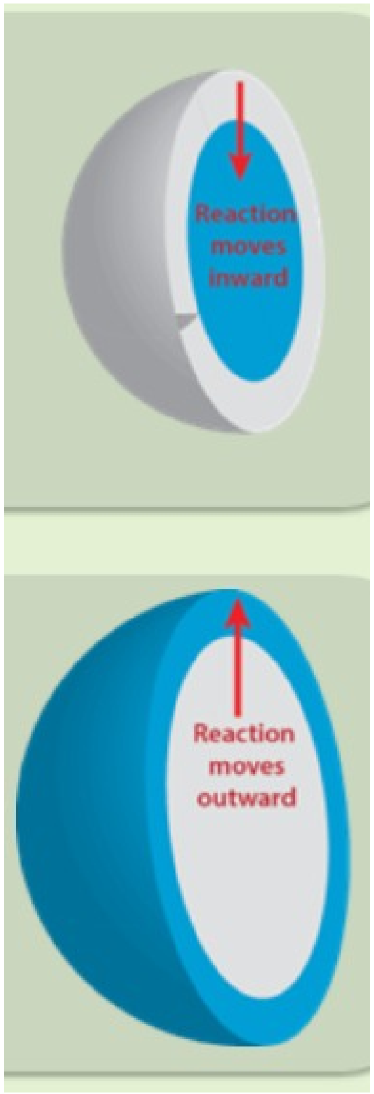
Chemistry behind:



Normal: Alginate drops (liquid)

Inverse: Ca-solution falls (frozen) – shell out





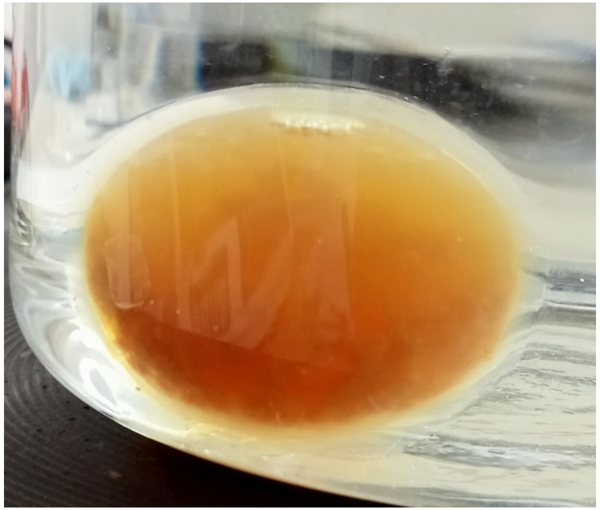
Reverse spherification

- 1L distilled water, 5g Na-alginate. Blend until bubbles rise

- 6g Ca-lactate in 50mL warm water (or directly in the juice).
- 150mL (fruit) juice. Add the Ca-lactate

- Pour fruit-lactate into silicone molds and freeze

- place icy fruit-lactate pieces in alginate.
  After 3-5 minutes, take out and rinse



FEEDBACK, DISCUSSION AND AWI TIME

Your culinary or biotech ideas?

Upcycling BSG/MSG: fiber-boba

BSG / MSG
after starch @ enzyme
20-30% hemicellulose
20-25% proteins

Tapioca Pearls
Anti-retrogradation TP
Ca-alginate pearls

+

BSG/MSG
extras

Added fiber: apple pomace

“Fermenting” with custom ingredients

Tempeh / Koji molds

@ enriched hydrogels / balls

Freedom: choosing ingredients – personalized

Functionality, taste, texture & microbiome

SG+ => salty moromi
SG+ => Maillard reactions

“Nata del Rice”

Intense aeriation @ koji mold liquid substrate

Unknown bacteria & bacterial cellulose
Unknown acid
16S and GC-MS / HPLC

Digression:
phase separation and (reaction-)diffusion in gels

Nucleation and growth:
F bulk & surface term / “barrier”
@ “metastable” domain

cheese holes @ polymer gel

Ice creams@ phase separation
Good & Bad & …

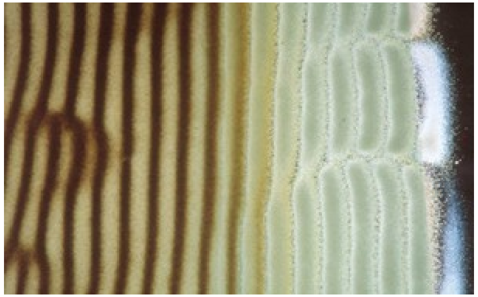
Spinodal decomposition
@ “very unstable” domain

Diffusion Limted Growth:
century egg

Hantz reactions

Article Talk

From Wikipedia, the free encyclopedia



FEEDBACK, DISCUSSION AND AWI TIME

Which enzymes where?

Thanks for your attention!

The knowledge is stored between heads, not inside them.

More info →

peter.hantz.mail@gmail.com
www.hantz.hu
W: +40-722-824515

Gel	Key chemistry	Best use	Heat (<130 °C)	pH stability
Tapioca starch	Entropic starch network	Chewy noodles, pearls	✓	wide range
Gluten dumpling	Protein crosslink network	Boiled dumplings, pasta	✓	acid-sensitive
Rice paper	Starch–fiber matrix	Wrapping, rolling	✓	wide range
Gelatin	Physical protein gel	Cold desserts, gummies	✗	acid-sensitive +
Agar	Ordered polysaccharide	Cuttable gels, cubes	✗	acid-stable
κ-Carrageenan	Ion-stabilized helix gel	Sliceable dairy, meats	✗	acid-sensitive
ι-Carrageenan	Ionic elastic gel	Elastic dairy desserts	✗	acid-sensitive +
Alginate	Ca^{2+} crosslinked gel	Spherification	✓	acid-sensitive +
Pectin (HM)*	Sugar–acid (HM)	Soft fruit gels, jams	✓	low pH only
Soy protein (tofu)	Heat-set protein gel	Tofu, protein curds	✓	acid-sensitive
Gellan (low-acyl)*	Ion-stabilized ordered polysaccharide	Firm gels, films	✓	wide range
Gellan (high-acyl)*	Elastic helical polysaccharide network	Soft elastic gels	✓	wide range
Chitosan	pH-dependent ionic polymer gel	Bioactive, functional gels	✓	acidic only
Pectin (LM)	Ca2+ egg-box crosslinked gel	Low-sugar fruit gels	✓	wide

* = heat required to form the gel,
but once set it does not easily remelt

(Visco)-elasticity

Moduli: response / input

Elastic:

E (Young's modulus) = tensile/compressive stiffness

$\sigma = E\varepsilon$

σ = normal stress

ε = strain, relative deformation

$$\sigma_{ij} = C_{ijkl}\,\varepsilon_{kl}$$

Young E ↔ Shear G

Pure elastic: E and G

Viscous: resistance to flow, SPEED counts

η – viscosity

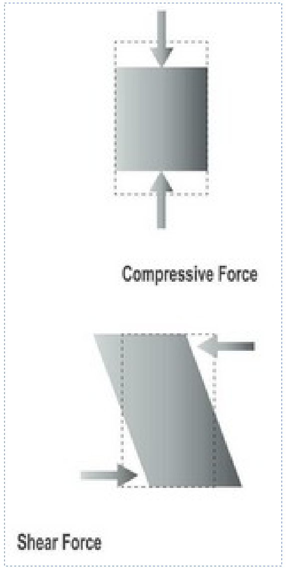
Viscoelastic: E', E'' and G', G'' maybe f(ω)

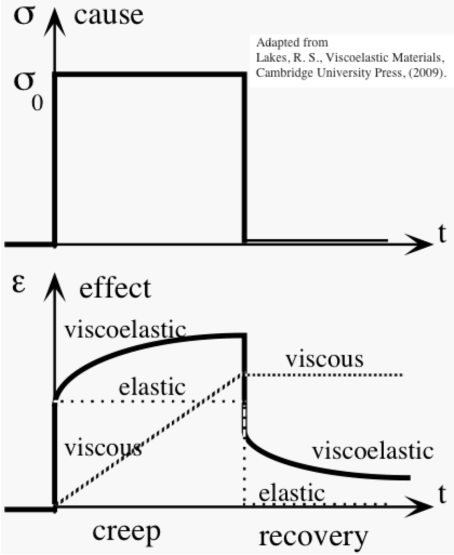
Rheometers work @ SHEAR /practical/

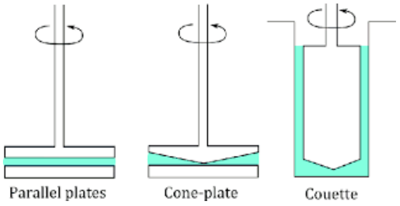
G′ → how springy - "storage"

G″ → how syrupy – "loss"

Viscoelastic solid G′ > G″







A note on storage

1/ Dry

@ pre-gelatinized starch powder + ...

2/ Ready-to-use

Retrogradation @ tapioca

xanthan, glycerol, trehalose

Pasteurization

Boiling + canning

High-pressure pasteurization (HPP)
syneresis?

Alternatives for chewing
Attempts: BBH Unthinkables

Konjaku
Double-network gels:
- konjaku + alginate
- konjaku + kappa-carrageenan

slow aroma release

DISAPPEARING: dry, degrade
NOT sticky

pubs.acs.org/jchemeduc
Demonstration

From Soybeans to Tofu: The Underlying Chemistry

Bingxing Wang,* Qi Wang, Bingli Wang, Songlin Wang, Yongcai Zhang, and Donglin Zhao

Cite This: J. Chem. Educ. 2023, 100, 3724–3730
Read Online

RESEARCH ARTICLE | MARCH 14 2025

Basic spherification as a gelation application in the kitchen: Diffusion coefficient estimation and appearance quality of beverage pearls

Special Collection: Kitchen Flows 2024

Suzan Tireki

Advances in the formation mechanism, influencing factors and applications of egg white gels: A review

Jianwei Zang[a], Yuanyuan Zhang[a], Xiaoyang Pan[a], Dayong Peng[a], Yonggang Tu[a], Jiguang Chen[a], Qingfeng Zhang[a], Daobang Tang[b,**], Zhongping Yin[a,*]

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[b] *Sericultural & Agri-Food Research Institute, Guangdong Academy of Agricultural Sciences/Key Laboratory of Functional Foods, Ministry of Agriculture and Rural Affairs/Guangdong Key Laboratory of Agricultural Product Processing, Guangzhou, 510610, PR China*

Egg White—a Polymer Gel Electrolyte with Exceptionally High Ionic Conductivity

Injamamul Arief, Anatoli Serghei,* Philipp Münzner, Wolf Hiller, Pierre Alcouffe, Philippe Cassagnau, Alexei P. Sokolov, and Catalin Gainaru*

Cite This: ACS Sustainable Chem. Eng. 2024, 12, 11253–11259
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Physicochemical properties of pectin from green jelly leaf (*Cyclea barbata* Miers)

Yuliarti, O.[1,*], Chong, S. Y.[2], Goh, K. K.T[2]

IUCrJ
ISSN 2052-2525
NEUTRON | SYNCHROTRON

Correlated changes in structure and viscosity during gelatinization and gelation of tapioca starch granules

Hsien-Kai Huang,[a] Hwo-Shuenn Sheu,[b] Wei-Tsung Chuang,[b] U-Ser Jeng,[a,b*] An-Chung Su,[a*] Wei-Ru Wu,[b] Kuei-Fen Liao,[b] Chun-Yu Chen,[b] Shing-Yun Chang[c] and Hsi-Mei Lai[c]

Received 13 June 2014

ELSEVIER
journal homepage: www.elsevier.com/locate/tifs

Food hydrogels: Experimental and theoretical aspects relating to their formulation and application

Jaekun Ryu, David Julian McClements*

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REVIEW ARTICLE
https://doi.org/10.1038/s43016-019-0009-x
nature food
Check for updates

Design principles of food gels

Yiping Cao[1] and Raffaele Mezzenga[1,2]

ELSEVIER
journal homepage: www.elsevier.com/locate/pmatsci

Water: The soul of hydrogels

Yue Yuan[a,c], Qianqian Zhang[b,c], Shumiao Lin[a,b], Jinlong Li[a,c,*]

[a] *Key Laboratory of Geriatric Nutrition and Health (Beijing Technology and Business University), Ministry of Education, 11 Fucheng Road, Haidian District, Beijing 100048, PR China*

Five popular misconceptions about osmosis

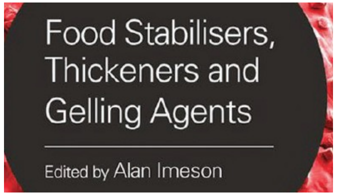
Eric M. Kramer[1, a)] and David R. Myers[2]

1) *Physics Department, Bard College at Simon's Rock, Great Barrington, MA 01230*

Statistical Mechanics of CrossLinked Polymer Networks II. Swelling

Paul J. Flory and John Rehner

Citation: J. Chem. Phys. **11**, 521 (1943); doi: 10.1063/1.1723792



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Review

A review of sodium alginate-based hydrogels: Structure, mechanisms, applications, and perspectives

Hong Wang, Liang Yang*, Yanning Yang

School of Physics and Electronic Information, Yan'an University, Yan'an 716000, China
Shaanxi Key Laboratory of Intelligent Processing for Big Energy Data, Yan'an 716000, China

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Mechanism of starch multi-scale structural in determining the textural properties and formability of starch pearls

Xi Zhao[a], Shixiang Xu[b], Minghao Xu[a], Ye Li[a], Shengyang Ji[a], Fan Wang[a], Zhenjiang Zhou[a], Yuanping Wang[a], Jianfu Shen[a], Baiyi Lu[a,*]

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[b] Goodme Technology Group Co., LTD, Hangzhou 310058, China

Hydrocolloid Gel Particles: Formation, Characterization, and Application

P. Burey, B. R. Bhandari, T. Howes & M. J. Gidley

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Hydrogel beads for designing future foods: Structures, mechanisms, applications, and challenges

Md. Nazmus Saqib[a,b,c,d], B.M. Khaled[e], Fei Liu[a,b,c,d], Fang Zhong[a,b,c,d,*]

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Bacterial cellulose: A comprehensive review

Vincent-Daniel Girard[1,2] | Jérémie Chaussé[1,2] | Patrick Vermette[1]

REVIEW Open Access

A review on superabsorbent polymers: application and recent advances in environmental and economic profiling

Bhavya Surendran V. S.[1], Lohit K. S. Gujjala[2*] and Avanthi Althuri[1*]

Relationship between structure of hydrocolloid gels and solutions and flavour release

Andreas Koliandris*, Angelie Lee, Anne-Laure Ferry, Sandra Hill, John Mitchell

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Received 16 January 2007; accepted 21 February 2007

Different States of Water in Hydrogels?

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Structure and Diffusive Properties of Water in Polymer Hydrogels

Ryo Naohara, Serina Namai, Jun Kamiyama, and Tomoko Ikeda-Fukazawa*

Cite This: J. Phys. Chem. B 2022, 126, 7992–7998 Read Online

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Food structure: Roles of mechanical properties and oral processing in determining sensory texture of soft materials

Yvette Pascua[a], Hicran Koç[b], E. Allen Foegeding[a,*]

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[b] PepsiCo Advanced Research, 7701 Legacy Drive, Plano, TX 75024, United States

Alginate: properties and biomedical applications

Kuen Yong Lee[1,2] and David J. Mooney[1,*]

Fruit reverse spherification
https://www.youtube.com/watch?v=sGlNhTjPBVU

Basic spherification
https://www.youtube.com/watch?v=BeRMBv95gLk
https://www.youtube.com/watch?v=WSRv89CiM-0