Structuration and mechanical properties of gels made from gluten proteins

Mohsen Dahesh, Amélie Banc, Agnès Duri-Bechemilh, Marie Helene Morel, Laurence Ramos

Structuration and Mechanical Properties of Protein Gels Made From Gluten Proteins

Mohsen Dahesh[1,2] , Amélie Banc[1], Agnès Duri[2], Marie-Hélène Morel[2], Laurence Ramos[1]

[1]Laboratoire Charles Coulomb UMR5221, CNRS and Université of Montpellier 2, 34095 Montpellier France

[2]Ingénierie des Agropolymères et Technologies Emergentes UMR 1208, CIRAD, INRA, Montpellier SupAgro, 34000 Montpellier, France

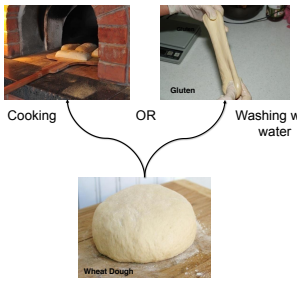
Abstract

Wheat gluten proteins are among the most complex protein networks in nature, due in particular to their poor solubility in water and to their viscoelastic behavior. Gluten networks are often considered as transient networks comprising extensible biopolymer segments of flexible or semiflexible chains between junction points[1]. However, the exact structure of the network, the nature of the junction points and the way it get structured under shear remain to be clarified. Here we report the visco-elastic behavior of model systems composed of gluten proteins near gelation. We build model systems by dispersing in ethanol-water mixtures two major protein groups, gliadins and glutenins, that we have purified from gluten. Rheological properties show a slow evolution over time scales of the order of days of the linear frequency dependence complex modulus of the samples, with a concentration-dependent liquid to solid transition. Interestingly, we find that all data acquired at different protein concentrations and different times after sample preparation can be scaled onto a master curve showing a cross-over from a soft solid behavior at low frequency to a visco-elastic fluid at high frequency. Rheological data are completed by scattering experiments in order to elucidate the complex structure of the materials. For gel samples, the scattering profiles display at small length scales features typical of polymer and evidences at larger length scale a fractal structure that we interpret as being due to the highly disordered state of the junction points. Biochemical assays are also performed to elucidate the origin of the sample aging.

Background

What is gluten?

•Gluten can be defined as the rubbery mass proteins that remain when wheat dough is washed by water to discard starch granules and water-soluble constituents.



•Gluten proteins play a key role in baking quality of wheat product by conferring water absorption capacity, cohesivity, visco-elasticity on wheat dough.

•Gluten contains hundreds of protein components which are present either as monomers or polymers. These proteins can be classified mainly by two broad groups: gliadin and glutenin

1.Monomeric **gliadins** *(15,000<M_w<80,000g/mol)* Viscosityof wheat dough?

2. Polymeric **glutenins** *(150,000<M_w<8,000,000 g/mol)* Elasticity of wheat dough?

•Gluten is like a 'two component glue', in which gliadins can be understood as a 'plasticizer' or 'solvent' for glutenins. A proper mixture of both fractions is essential to impart the viscoelastic properties of wheat dough and the quality of the end product[2].

Motivation

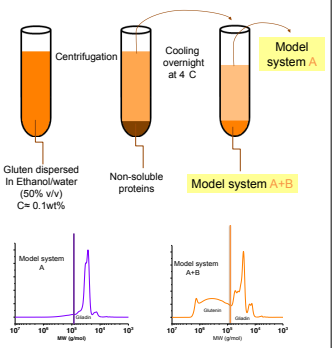
Wheat is the third most-produced cereal in the world after maize and rice. Wheat is mostly used in food industry to make product like bread which is prepared by wheat dough baking.

Gluten plays a key role in the bread making properties of wheat dough and gives the unique visco-elastic properties of wheat dough. Many efforts has been done to reveal structuration and mechanical properties of wheat dough but there is not a firm answer for the moment.

Because of complexity of gluten composition we decided to study the structure and visco-elasticity of purified fractions.

Model systems made from gluten proteins

Protein Purification Protcol



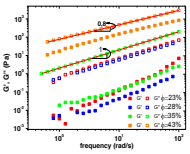
To study gluten complex system, a purification protocol was developed from gluten. Two model systems were obtained.

Model system	Protein fractions [%]	
	Glutenins	Gliadins
A	6.5%	93.5%
A+B	55.5%	44.5%

Rheology of model system A

Pure gliadin (A) dispersion in EtoH/water 40%v/v

Increasing concentration



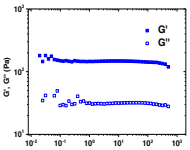
Rheological properties of Model system A was done by measuring complex moduli G´(storage) and G˝ (loss) in the linear regime. It shows viscous behavior (Newtonian) untill certain concentration. After Φ=43% viscolelastic fluid behavior can be observed.

Rheology of model system A+B

(Gliadin+Glutenin) dispersion in EtoH/water 50% v/v

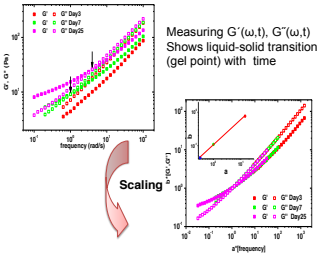
Increasing concentration

Turbid → Opaque → Transparent



Very large range linear regime compared with wheat dough (from 15343 to 10^{-3}) and gluten ($3x10^{-2}$).[3]

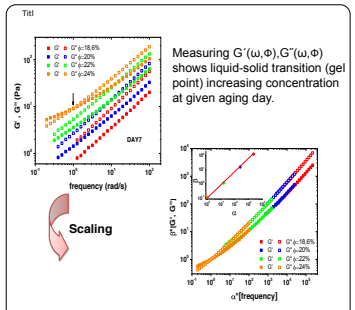
Time evolution



Measuring G´(ω,t), G˝(ω,t) Shows liquid-solid transition (gel point) with time

Collapsed master curve showing scaled G´(ω,t) (closed symbol) and G˝ (ω,t) (open symbols) as functions of the scaled frequency. Inset shows the linear relationship between scaling factors: (a and b)

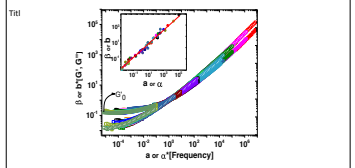
=>Self-similarity in the structure of the network at different aging times



Measuring G´(ω,Φ),G˝(ω,Φ) shows liquid-solid transition (gel point) increasing concentration at given aging day.

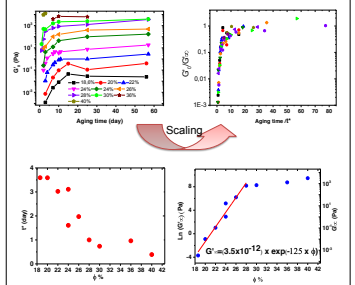
Self-similarity in the structure of the network at different concentrations

Collapsed master curve showing scaled G´(ω,Φ) (closed symbol) and G˝(ω,Φ) (open symbols) as functions of the scaled frequency.Inset shows the linear relationship between scaling factors: (α and β)



Collapsed master curve showing scaled G´(ω,t,Φ) (closed symbol) and G˝(ω,t,Φ) (open symbols) as functions of the scaled frequency.Inset shows the linear relationship between scaling factors: (a , α and b, β)

Low-frequency elastic modulus (G_0´) versus aging time

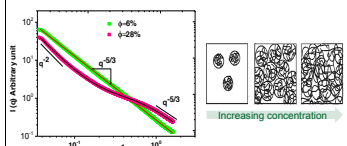


t* charateristic time of gelation

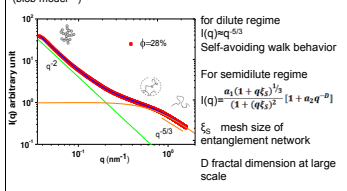
Exponential behavior of G´∞

Structural Study

Small angle X-ray scattering Model system A+B



SAXS data can be fitted with a semidilute polymer solution model (blob model[4,5])

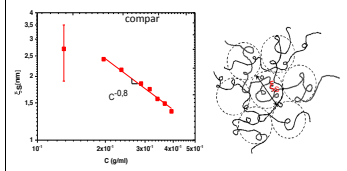


for dilute regime $I(q) \propto q^{-5/3}$ Self-avoiding walk behavior

For semidilute regime $I(q) = \frac{a_1(1+q\xi_s)^{1/3}}{(1+(q\xi_s)^2} + [1+a_2 q^{-D}]$

ξ_s mesh size of entanglement network

D fractal dimension at large scale

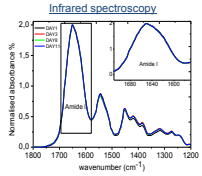


•Length scales ≤ ξ_s = dilute solution behavior for the individual chains.

•Length scales ≥ ξ_s Semidilute polymer behavior .

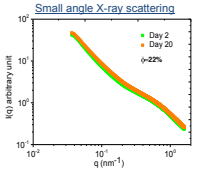
Aging effect study (model system A+B)

Infrared spectroscopy



No change in the secondary structure of the model system A+B with time

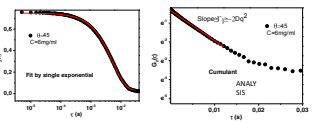
Small angle X-ray scattering



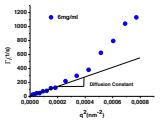
No evolution of SAXS spectra in the range studied. Measurement at q<(0.037nm^{-1}) is required.

Very dilute dispersion of Model system A+B

Dynamic light scattering

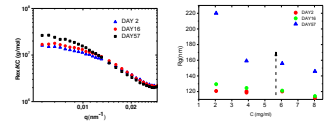


•Monodisperse (γ=0.015 Polydispersity)
•R_H =100 5nm



•Not compact object
•Large q behavior: internal mode of polymer chains[6]

Static light scattering



There is aggregation of the very dilute dispersion with time. It finally leads to macroscopic phase separation.

Conclusion & outlooks

Two model system developed from gluten proteins

Model system A :

Mechanical properties shows Newtonian behavior.

Model system A+B:

- Mechanical properties shows a concentration and time dependent liquid-solid transition (gelation). Moreover frequency-dependent complex moduli (G´,G˝) can be scaled onto a master curve.

=> Self-similarity of the model system with different concentrations and aging times.

- G´ has exponential dependence on Φ untill certain concentration
- Dilute regime structure:
- monodisperse objects with internal dynamic mode (self avoiding walk in good solvent)

Semidilute regime structure

The model system can be described by a semidilute polymer model at small scale and fractal structure at large scale

Outlooks

1. What is respective role of the gliadin and glutenin in the Model system A+B gelation?
2. Is it helpful to study mechanical properties of mixture of model system A and A+B ?
3. What is the structural origin of aging in model system A+B?
4. Shear rheology of model system A+B versus concentration and time is also helpful for structuration study.

References

1. Trevor S. K. Ng et al, J. Rheol. 2008, 52(2), p417-449
2. H. Wieser et , Food Microbiology 2007, 24, p115–119
3. S.Uthayakumaran, et al , Rheol Acta , 2002, 41: p162–172
4. A. N. Falcao, Macromolecules, 1993, 26, p5350-5364
5. Neutron, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter Edited by P.Linder & Th. Zemb, O Glatter - 2002 - Amsterdam: North-Holland.
6. V.Trappe, et al, Macromolecules 1997,30,p2365-2372.