Structuration and mechanical properties of gels made from gluten proteins
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To cite this version:
Mohsen Dahesh, Amélie Banc, Agnès Duri-Bechemilh, Marie Helene Morel, Laurence Ramos. Structuration and mechanical properties of gels made from gluten proteins. International soft matter conference (ISMC), Sep 2013, Rome, Italy. 2013. hal-01601702

HAL Id: hal-01601702
https://hal.archives-ouvertes.fr/hal-01601702
Submitted on 3 Jun 2020

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**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 comprised extensible bipolymer segments of flexible or semiflexible chains between junction points. 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 viscoelastic behavior of model systems composed of gluten proteins near gelation. We build model systems by dispersing in ethanol-water mixtures two major protein groups, gluten and glutenins, respectively. Each group is then purified by gel permeation chromatography, showing a slow evolution over time scales of the order of days of the frequency dependent 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 viscoelastic fluid behavior (Newtonian) 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 rubby mass proteins that remain when wheat gluten is washed by water to discard starch, glutenins and water-soluble constituents.
- Gluten contains hundreds of protein components which are present either as monomers or polymers. These proteins can be classified mainly by two broad groups: gliadins and glutenins.

**Protein Purification Protocol**

1. Monocentric gluten [HF 6000g; pH 5.0-6.0; 0.0005M NaPO4]
   - Trituration wheat dough?

2. Preparative gluten (1000-3000 kDa; pH 5.0-6.0; 0.0005M NaPO4)
   - Elasticity of wheat dough?

- Gluten is a “two-component glue”, in which gliadins can be understood as a “plasticizer” or “solvent” for glutenins. A proper mixture of both fraction assembly impart the viscoelastic properties of wheat dough and the quality of the end-product.

**Motivation**

Wheat is the third most consumed 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 viscoelastic properties of wheat dough. Many efforts have been done to reveal structural and mechanical properties of gluten matrix of wheat dough but there is no firm answer for the moment.

Because of complexity of gluten composition we decided to study the structure and viscoelasticity of purified fractions.

**Model systems made from gluten proteins**

**Protein Purification Protocol**

- Contribution
- Centrifugation
- Washing with water
- Model system A

**Model systems made from gluten proteins**

- Model system A

- Model system A+B

**Measuring G" (ω) G' (ω) shows liquid-solid transition (gel point) increasing concentration at given aging day**

**Aging effect study on model system A+B**

- No change in the secondary structure of the model system A+B with time
- No evolution of SAXS spectra in the range studied. Measurement at 4050nm is required.

**Rheology of model system A**

**Data gelation parameter Dependence 1/9**

**Increasing concentration**

**Rheological properties of Model system A**

- was done by measuring complex moduli G' (storage) and G" (loss) in the linear range.
- It shows viscous behavior (Newtonian) until certain concentration. After φ>43% viscoelastic fluid behavior can be observed.

**Rheology of model system A+B**

**Gluten+Glutenin dispersion in 50% v/v Ethanol**

**Increasing concentration**

**Very large range linear regime compared with wheat dough** (from 35340 to 10^5) and gluten (2x10^11)

**Time evolution**

- Measuring G" (ω), G' (ω) shows linear evolution (gel point) with time

- Measuring G" (ω) G' (ω) shows liquid-solid transition (gel point) increasing concentration at given aging day

- Collapsed master curve showing scaled G (1/ω) (closed symbol) and G (1/ω) (open symbol) as functions of the scaled frequency 

- shows the linear relationship between scaling factors (a, b, β, γ)

- Use frequency elastic modulus G(1/ω) versus aging time

- Collapsed master curve showing scaled G (1/ω) (closed symbol) and G (1/ω) (open symbol) as functions of the scaled frequency 

- shows the linear relationship between scaling factors (a, b, β, γ)

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- Collapsed master curve showing scaled G (1/ω) (closed symbol) and G (1/ω) (open symbol) as functions of the scaled frequency 

- shows the linear relationship between scaling factors (a, b, β, γ)

- Use frequency elastic modulus G(1/ω) versus aging time

**Structural Study**

- Small angle X-ray scattering model system

- Very dilute dispersion of Model system A+B

**Dynamic light scattering**

- Dynamic light scattering

- Molar mass (M) Polydispersity (P)

- 4θ = 90° Shear
t

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

**Conclusion & outlook**

Two model system developed from gluten proteins

- **Thermal properties**
  - Mechanical properties shows a concentration and time dependent liquid-solid transition (gelation). Moreover frequency dependent complex moduli G(ω) G"(ω) can be scaled onto a master curve
  - Self-similarity of the model system with different concentrations and aging times
  - G" les exponential dependence on ω until certain concentration
  - β is a regime on scale
  - Monodisperse objects with internal dynamic mode (self avoiding walk in good solvent)

**Simulation regime studies**

The model system can be described by a semi-dilute polymer model or small scale and fractal structure at large scale

1. What is the respective role of the gliadins and glutenins in the model system G" (ω) gelation
2. It is helpful to study mechanical properties of mixture of model system A+B and A+B
3. How to choose the scheme of aging in model system A+B
4. Show rheology of model system A+B versus concentration and time and also helpful for struculation study

**References**