Plasticization Regimes in Biopolymers

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Motivation

• Proteins
  – Renewable feedstock
    • Abundant, readily separated in waste stream, chemically versatile molecules

• Glycerol plasticization: simple, tried and true technology
  – easy processing, enhances properties
  – Not fully understood
Technical approach
Glycerol effect on secondary structure

Amide II peak position of FK films made with varied %Glycerol

XRD patterns of FK films made with varied %Glycerol
Protein plasticization with glycerol

Dehydrated protein

Glycerol

Net change in secondary structure
FTIR Amide I peak

XRD patterns of FK films made with varied %Glycerol
Using %Glycerol > c*
**Modulus vs. Glycerol - ***

- **Elastic Modulus, $E$ (GPa)**
  - $10^{-3}$
  - $10^{-2}$
  - $10^{-1}$
  - $10^0$
  - $10^1$

- **Molar ratio, (mol glycerol/mol protein)**
  - $10^{-3}$
  - $10^{-2}$
  - $10^{-1}$
  - $10^0$

- **Glycerol content, %(w/w)**

- **Molar ratio, (mol glycerol/mol protein)**

- **Elastic Modulus, $E$ (GPa)**
  - $10^{-3}$
  - $10^{-2}$
  - $10^{-1}$
  - $10^0$

Legend:
- FK
- LA
- WG

Graphs show the relationship between elastic modulus and molar ratio, as well as glycerol content.
Sensitivity to plasticization vs. cysteine content and number polar side chains*

(Sensitivity)

Range \[ \frac{I(1660)+I(1650)}{I(1625)} \]

No. Polar side groups

Chain fraction Cysteine
Thermodynamic model

\[ E \propto \rho \frac{RT}{Me} \]

\[ \rho \propto \frac{1}{[\text{Glycerol}]} = \text{v.weak dep.} \sim \text{const.} \]

\[ Me \propto \frac{[\text{Glycerol}]}{[\text{Cys}]} \]

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\[ \Leftrightarrow E \propto RT \frac{[\text{Cys}]}{[\text{Glycerol}]} \]
Modulus at $c^*$ is function of cysteine content

\[ E \propto RT [Cys] \]

$R^2 = 0.90$
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Questions?

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