Thermal Analysis of Polysaccharides
Mechanical Methods

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Topics Covered

• Introduction to polymer viscoelasticity
  – Examples
    • Thermal transitions in polysaccharide containing sweets, cellulose powders and solutions of ethyl cellulose

• Rapid viscosity analyser
  • Temperature induced swelling of particulates
    – Examples
      » xanthan gum and cellulose particles
Stress Relaxation Experiment

Force

Time

Rubber

Bread dough
Response of high molecular weight amorphous polymer

Log force or Log modulus (G(t) in shear)

Transition zone
Plateau
Glassy state
Terminal zone

Relationship to zero shear viscosity

\[ \eta_0 = \int_{-\infty}^{\infty} tG(t) d \ln t \]
What has this to do with temperature?

log force or log modulus ($G(t)$ in shear)

Measured at a single time after deforming sample

Transition zone

Plateau

Glassy state

Terminal zone

Temperature
Time Temperature Superposition

The Oscillation Experiment

\[ \gamma = \gamma_0 \sin(\omega t) \]

\[ \sigma = \sigma_0 \sin(\omega t + \delta) \]

Resolve stress into components in phase with strain and 90° out of phase

\[ \sigma = \sigma_0 \cos \delta \sin(\omega t) + \sigma_0 \sin \delta \cos(\omega t) \]

“in phase” component

“out of phase” component
Some parameters from the oscillation experiment

Shear Storage Modulus \[ G' = \frac{\sigma_0}{\gamma_0} \cos \delta \]

The *storage modulus* is given by the ratio of the amplitude of the component of the stress *in phase with the strain* to the strain amplitude. \( G' \) gives the proportion of the energy supplied to the system which is *stored elastically* during each cycle of oscillation.

Shear Loss Modulus \[ G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \]

The *loss modulus* is given by the ratio of the amplitude of the component of the stress *90° out of phase with the strain*. For a given strain \( G'' \) gives the proportion of the energy supplied to the system which is *dissipated during viscous flow* during each cycle of oscillation.

Loss tangent \[ \tan \delta = \frac{G''}{G'} \]
Response of high molecular weight amorphous polymer

Dependence of real part of dynamic modulus on frequency mirror image of stress relaxation modulus on time. High frequencies correspond to short times.

Where $G'$ changes slowly with frequency behaviour more elastic. Energy dissipation low and $G''$ less than $G'$.
Master curve of storage and loss modulus, and their ratio (\(\tan \delta = G''/G'\)) as a function of frequency, polymer concentration and molecular weight, and temperature at the terminal zone (I), plateau (II), glass transition (III), and glassy region (IV).

Dynamic Mechanical Thermal Analysis (DMTA))

- Extensively used to characterise synthetic polymers
- Good for solid samples
- Not fundamentally different from oscillatory rheometry in rotation
- Examples
  - Gummy sweets
  - Cellulose powder
Dynamic Mechanical Thermal Analysis (DMTA)

bending mode

![Diagram of Dynamic Mechanical Thermal Analysis]

Dimensions:
- 5-8mm
- 1-2mm
- ~20mm
Gum tested in single cantilever bending mode
Determination of Tg from DMTA for Gellan Based Gum

Onset $E' = -34^\circ C$

Peak $\tan \delta = -10^\circ C$

Peak $E'' = -31^\circ C$

Data of Marcin Deszczynski
Master curve of storage and loss modulus, and their ratio ($\tan \delta = \frac{G''}{G'}$) as a function of frequency, polymer concentration and molecular weight, and temperature at the terminal zone (I), plateau (II), glass transition (III), and glassy region (IV).
“Amorphous” Cellulose Powder

• Attempt to measure mechanically, glass transition of small quantities of ball milled cellulose powder

• Mechanical measurements of transition much more sensitive than calorimetric measurements

DMTA – Pocket Technique
DMTA – Ball Milled Amorphous Cellulose
Glass Transition of Amorphous Cellulose and Starch

![Graph showing temperature vs. water content for different samples of cellulosic materials.](image)
Association in Ethyl Cellulose Solutions on Heating

Original observation from Jena group on cloud point observed after heating at indicated temperature for five minutes. Can solution rheology follow this transition?

Is rheology consistent with visual observation?

2% Ethyl Cellulose Random Substitution

(1Hz, 2% strain 1°C/min⁻¹)
Is rheology consistent with visual observation?

2% Ethyl Cellulose Regular Substitution
Large Differences in Cloud Point

Sample were held at these temperatures for 5 minutes.

Observations from University of Jena
Rapid Viscosity Analyser
Typical Viscosity Response to the Pasting Experiment

Viscosity

Increase due to granule swelling

Decrease due to granule disruption under heat and shear

Temperature

Set back primarily due to network formation as a result of amylose retrogradation
“Pasting” Curve for Physically Modified Xanthan (2% xanthan 0.4 %NaCl)

Data of Fuad Hajji and Woroud Alsanei
Effect of Preheating in the Rapid Viscosity Analyser on Viscosity Development of Cellulose Particles in LiCl/Urea/Water Solutions

Data of Dr. Ivana Tatárová
References


Thank you for listening