The University of Nottingham

Biopolymer Solutions

Thermal Analysis of Polysaccharides

Mechanical Methods

John Mitchell

STEP ITN

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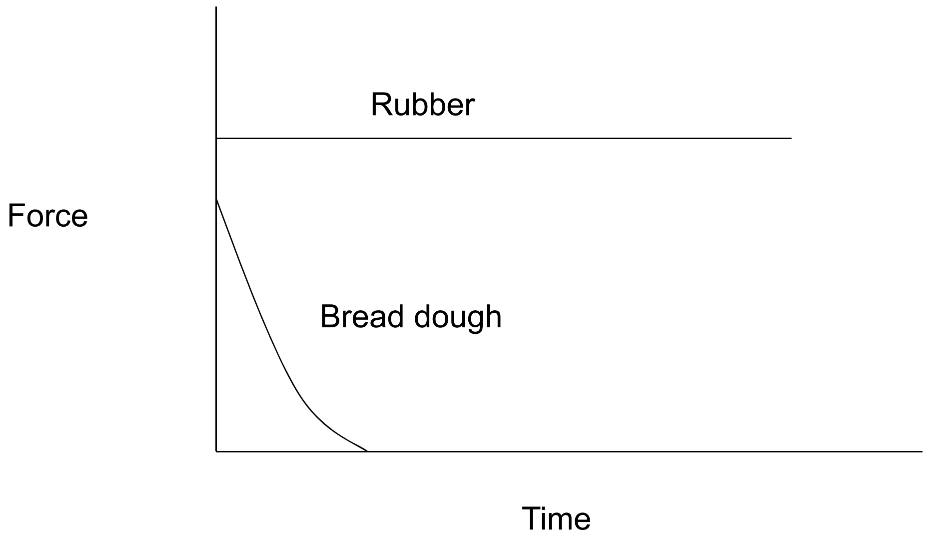
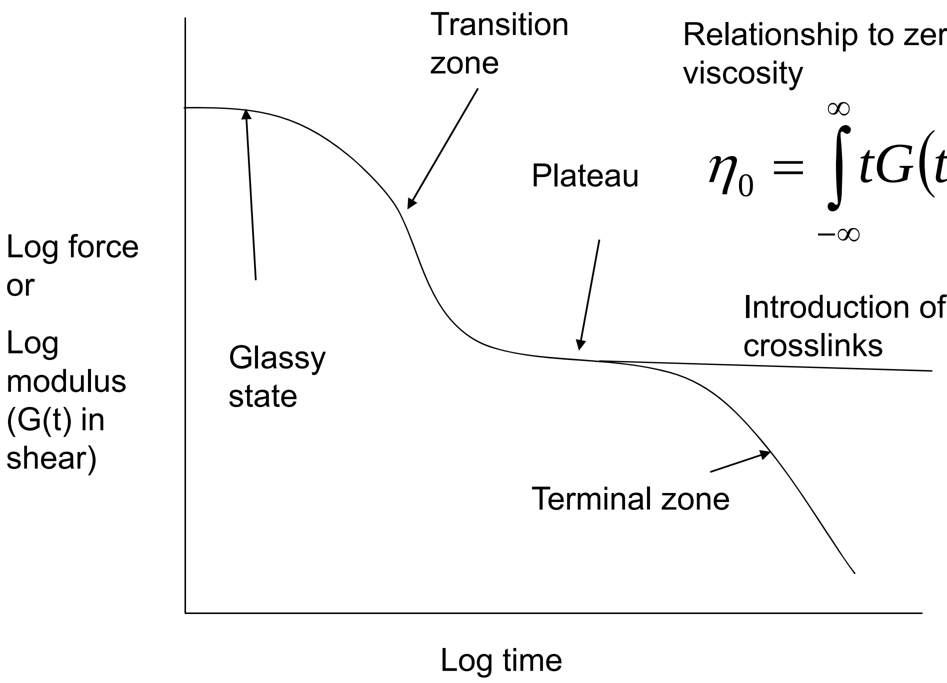
Topics Covered

- 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



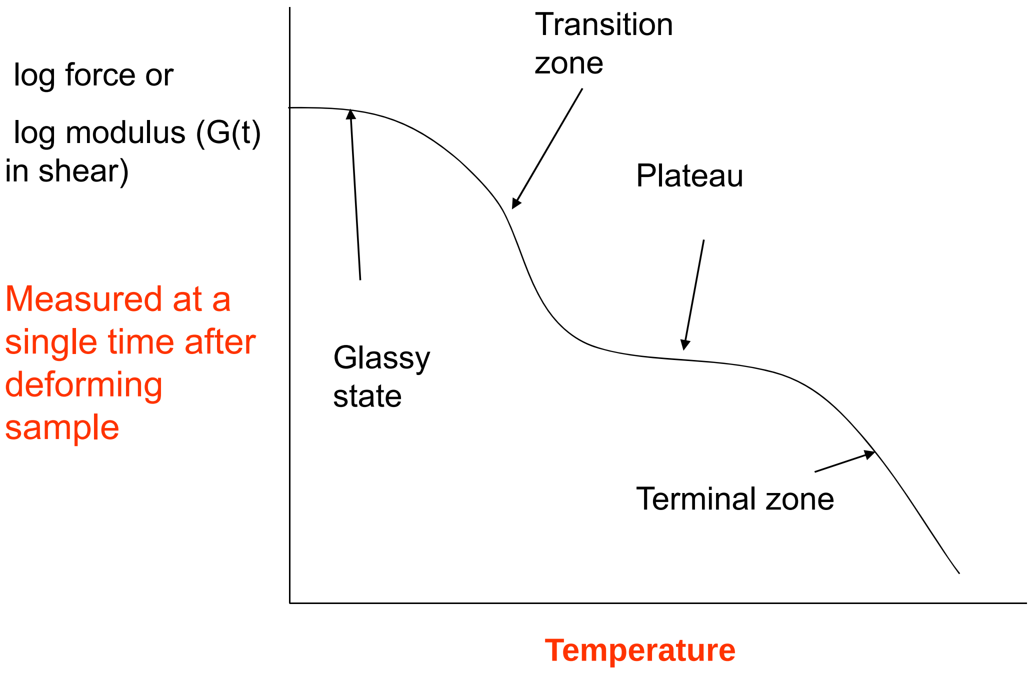
Response of high molecular weight amorphous polymer



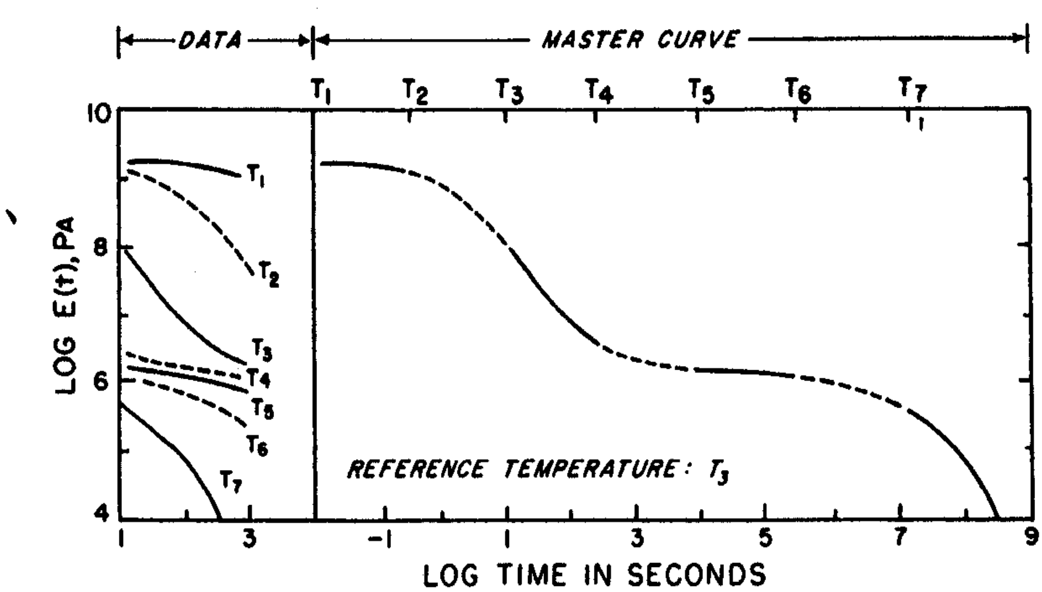
Relationship to zero shear viscosity

$$\eta_0 = \int_{-\infty}^{\infty} tG(t)d\ln t$$

What has this to do with temperature?

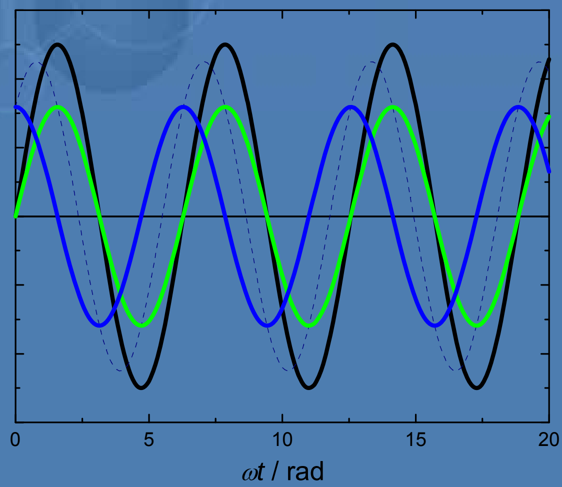


Time Temperature Superposition



An Introduction to Polymer Viscoelasticity: Aklonis, J.J. and MacKnight, W.J. (1983) Wiley-Interscience page 44

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

$$\sigma = \underbrace{\sigma_0 \cos\delta \sin(\omega t)}_{\text{"in phase" component}} + \underbrace{\sigma_0 \sin\delta \cos(\omega t)}_{\text{"out of phase" component}}$$

“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 *90^0 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.

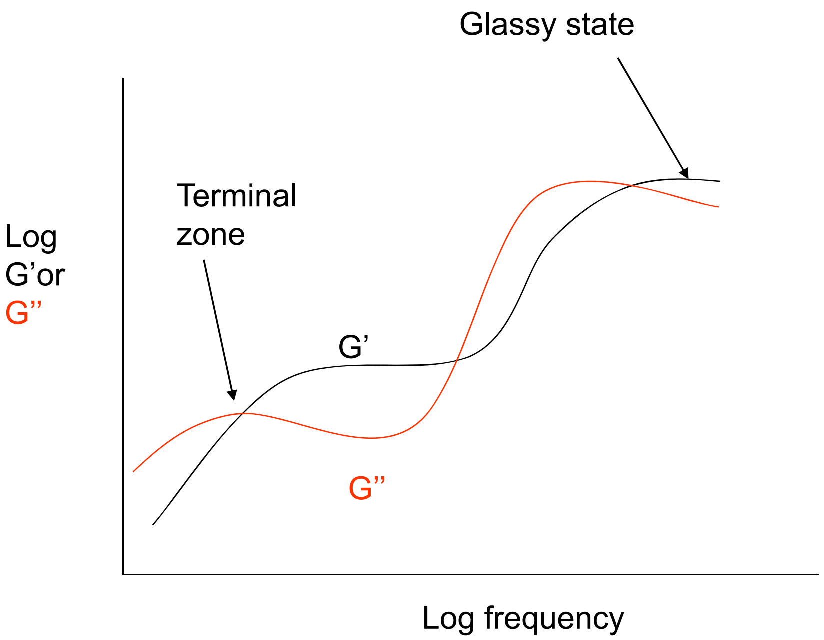
Loss tangent $\tan\delta = G''/G'$

- - (8)

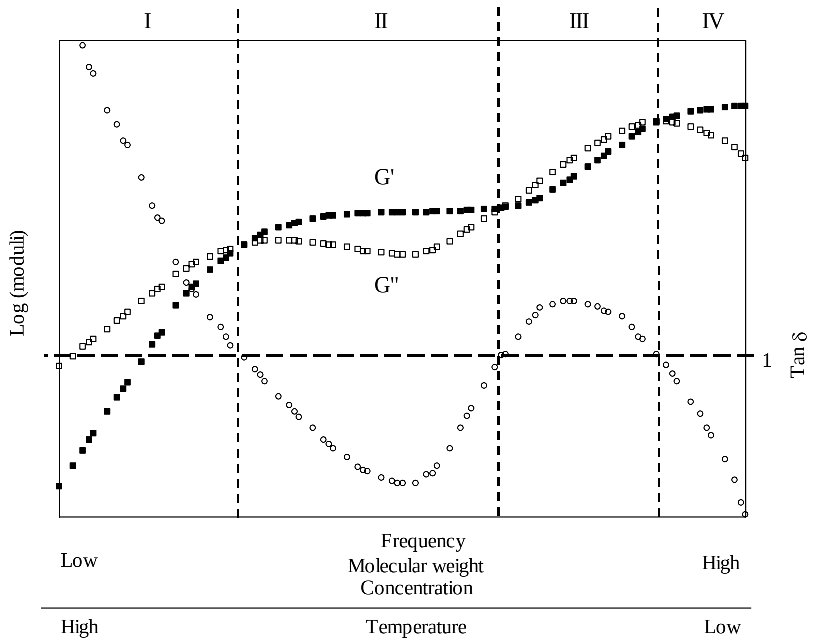
Response of high molecular weight amorphous polymer

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 δ = 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).



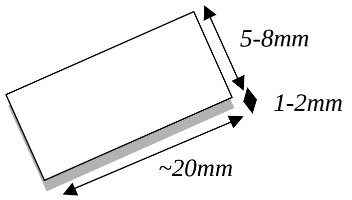
Kasapis, S p 235 in Functional Properties of Food Macromolecules Edited Hill, S et al., (1998) Aspen, Maryland

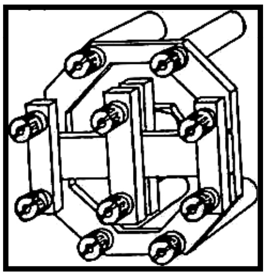
Dynamic Mechanical Thermal Analysis (DMTA))

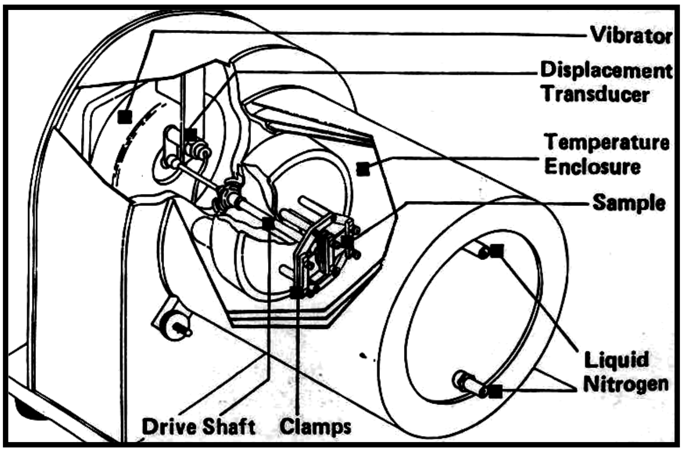
- Extensively used to characterise synthetic polymers
- Good for solid samples
- Not fundamentally different from oscillatory rheometry in rotation
- Examples
  - Gummy sweets
  - Cellulose powder

Dynamic Mechanical Thermal Analysis (DMTA)

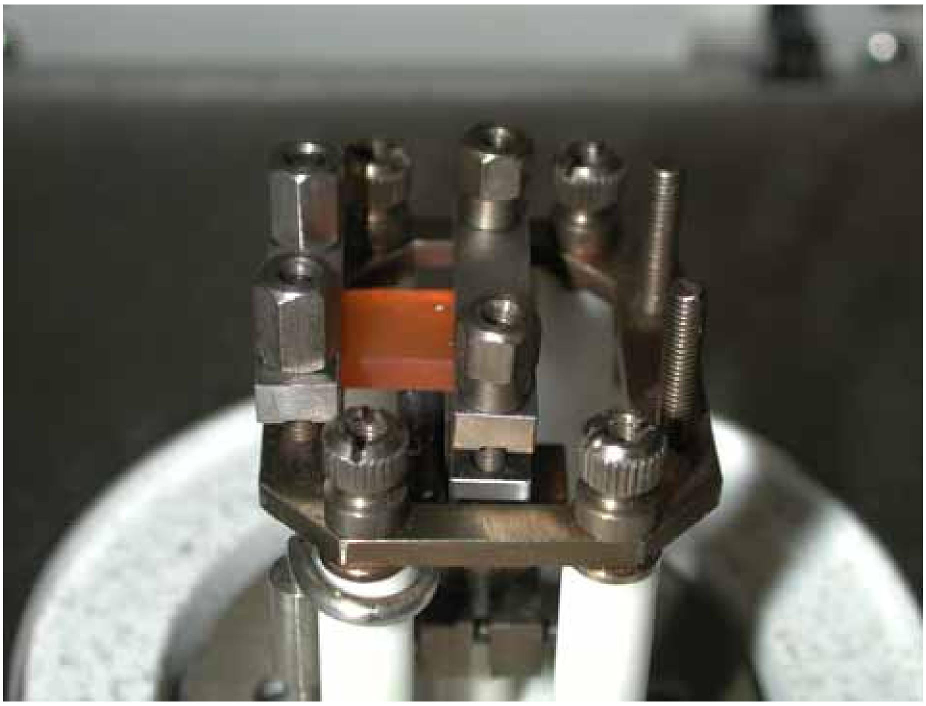
bending mode



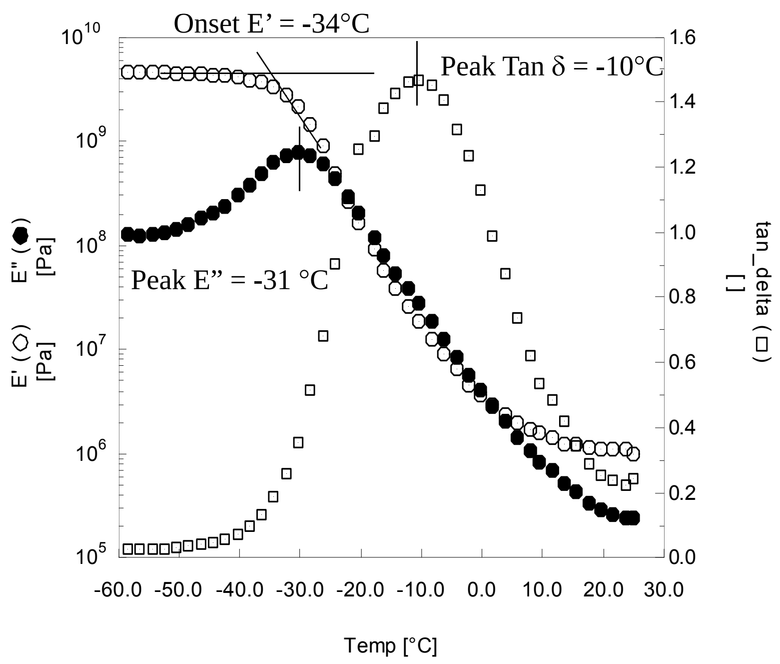




Gum tested in single cantilever bending mode

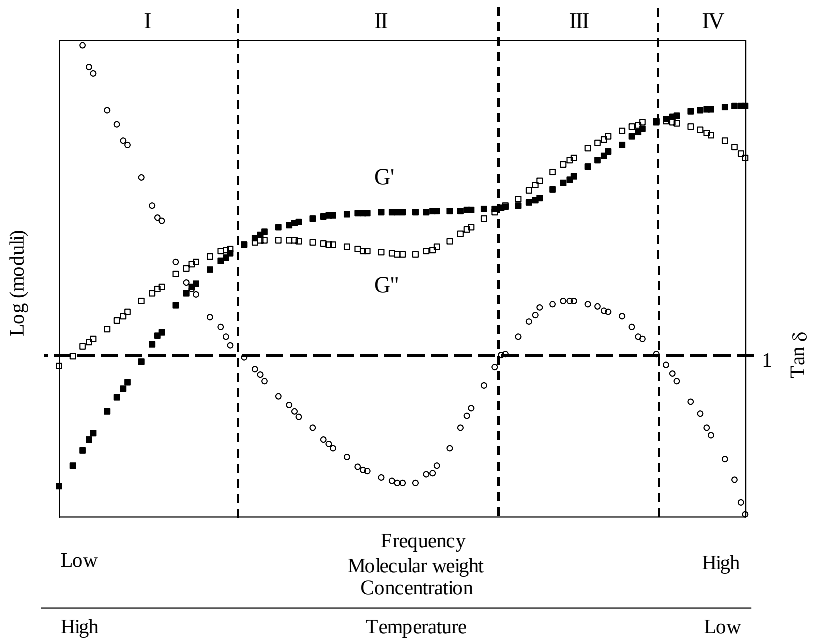


Determination of Tg from DMTA for Gellan Based Gum



Data of Marcin Deszczynski

Master curve of storage and loss modulus, and their ratio (tan δ = 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).

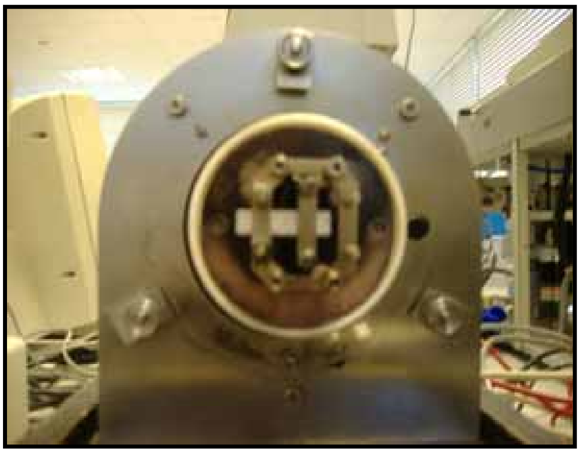


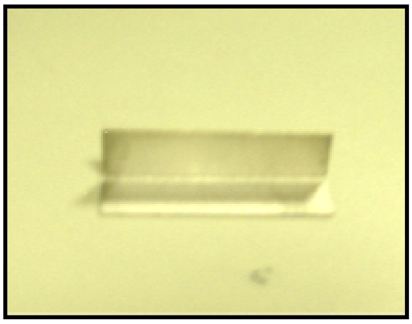
“Amorphous” Cellulose Powder

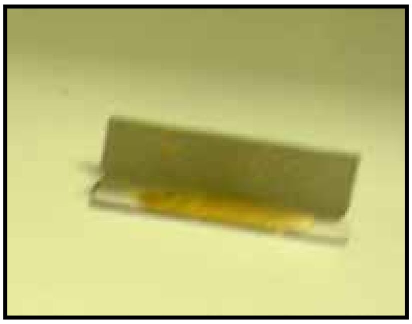
- Attempt to measure mechanically, glass transition of small quantities of ball milled cellulose powder
- Mechanical measurements of transition much more sensitive than calorimetric measurements

Paes, S ,Sun, S, MacNaughtan, W, Ibbett, R., Ganster, J., Foster TJ. and Mitchell, J.(2010) Cellulose 17, 693-709

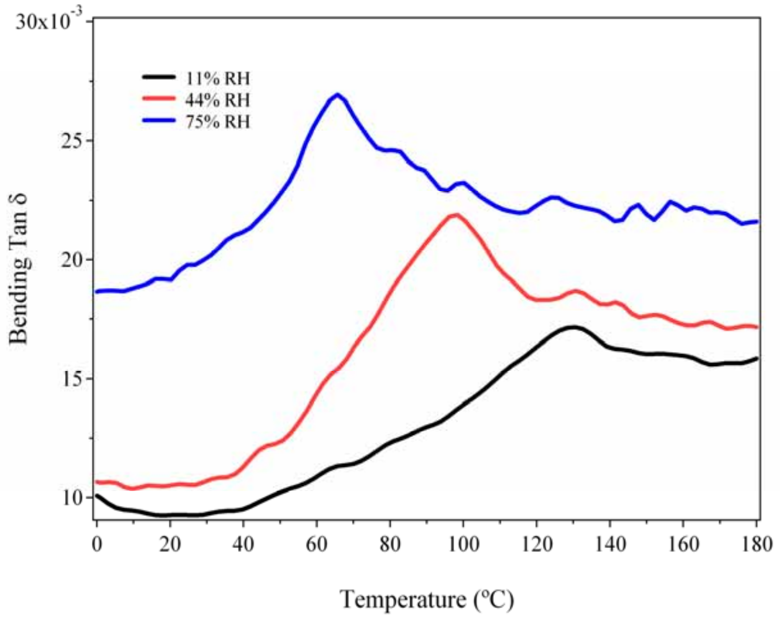
DMTA – Pocket Technique



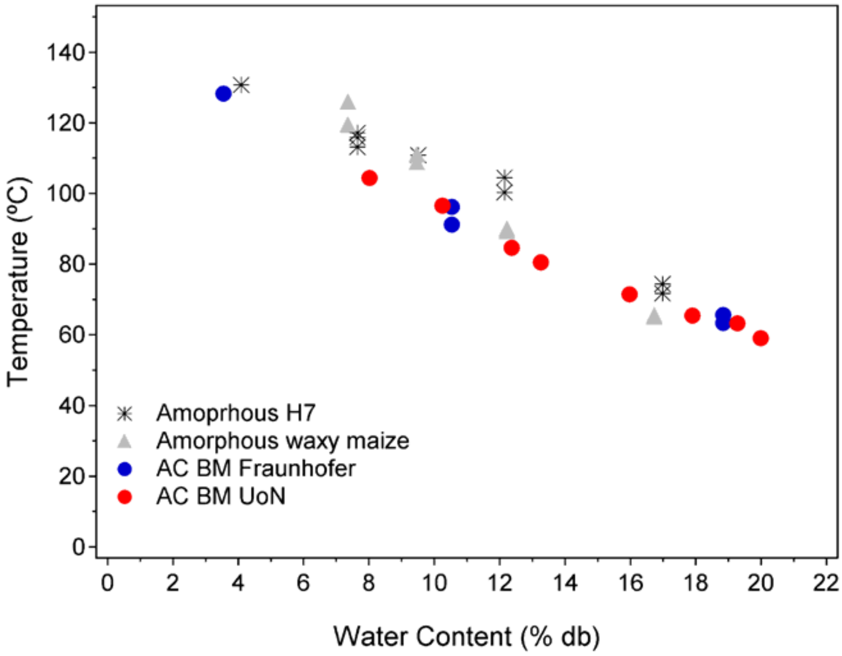




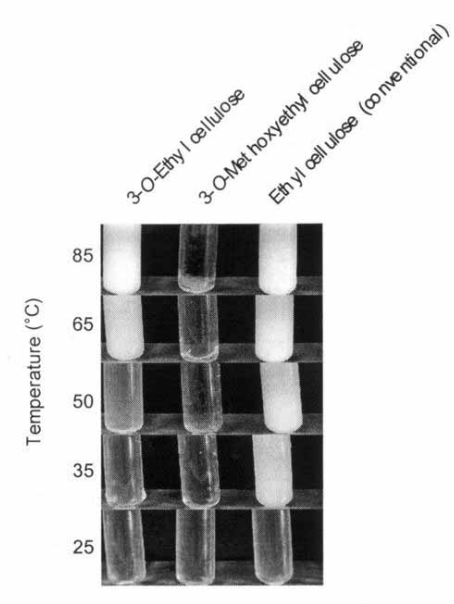
DMTA – Ball Milled Amorphous Cellulose



Glass Transition of Amorphous Cellulose and Starch



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 transtion?

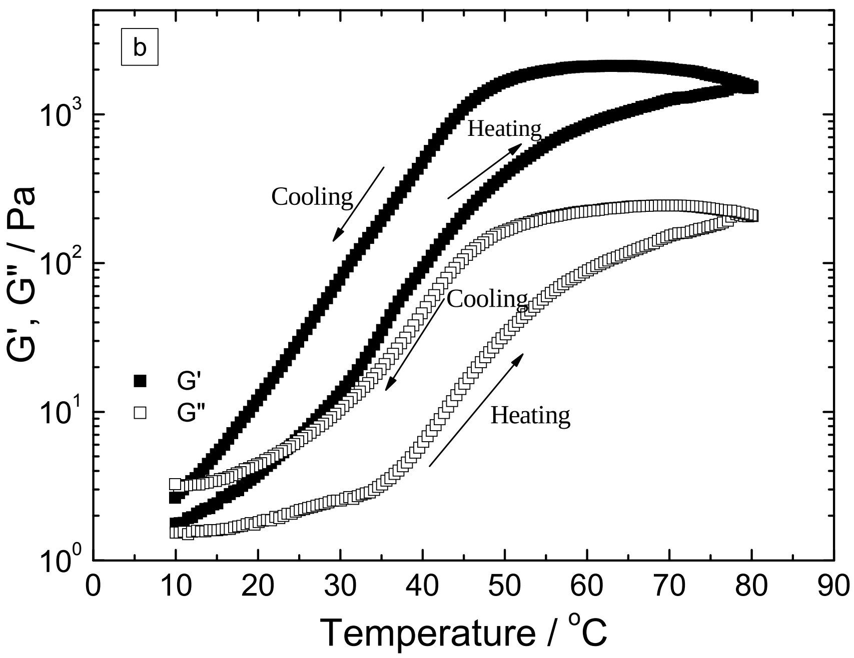
Sun, S., Foster, T., MacNaughtan, W., Mitchell, J., Fenn, D., Koschella, A. and Heinze, T. (2009) Journal of Polymer Science Part B Polymer Physics 47, 1743-1752

European Polysaccharide Network Of Excellence

Is rheology consistent with visual observation?

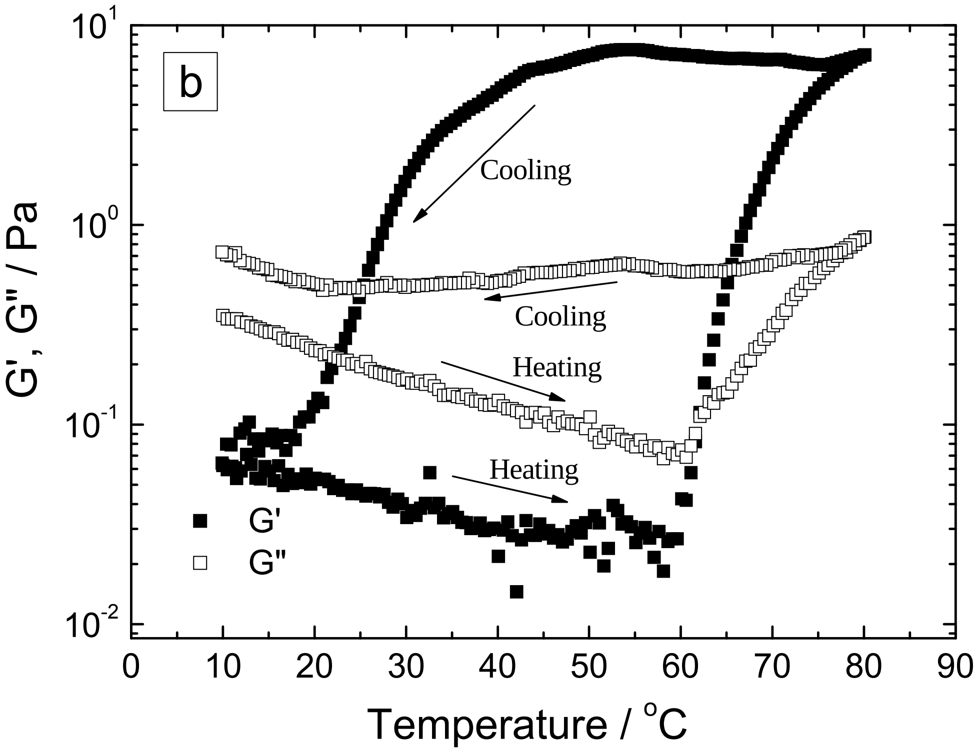
2% Ethyl Cellulose Random Substitution

(1Hz. 2 % strain 1^{O}Cmin^{-1})

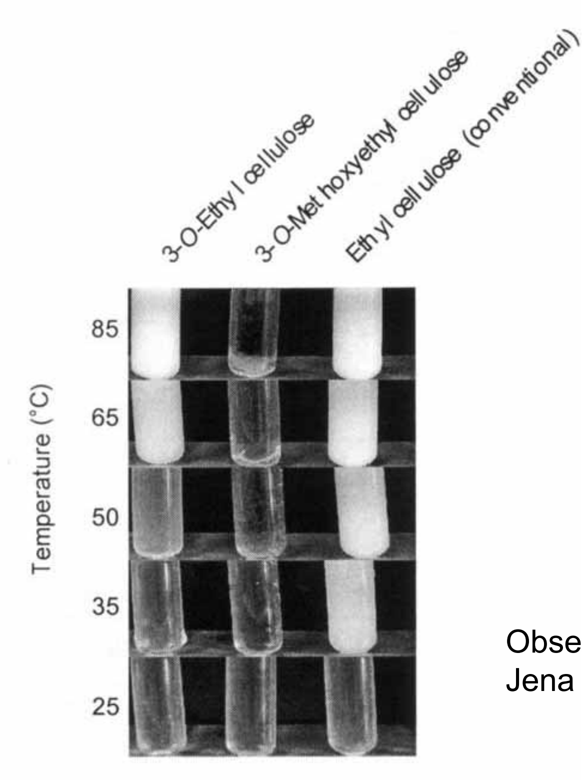


Is rheology consistent with visual observation?

2% Ethyl Cellulose Regular Substitution



Large Differences in Cloud Point

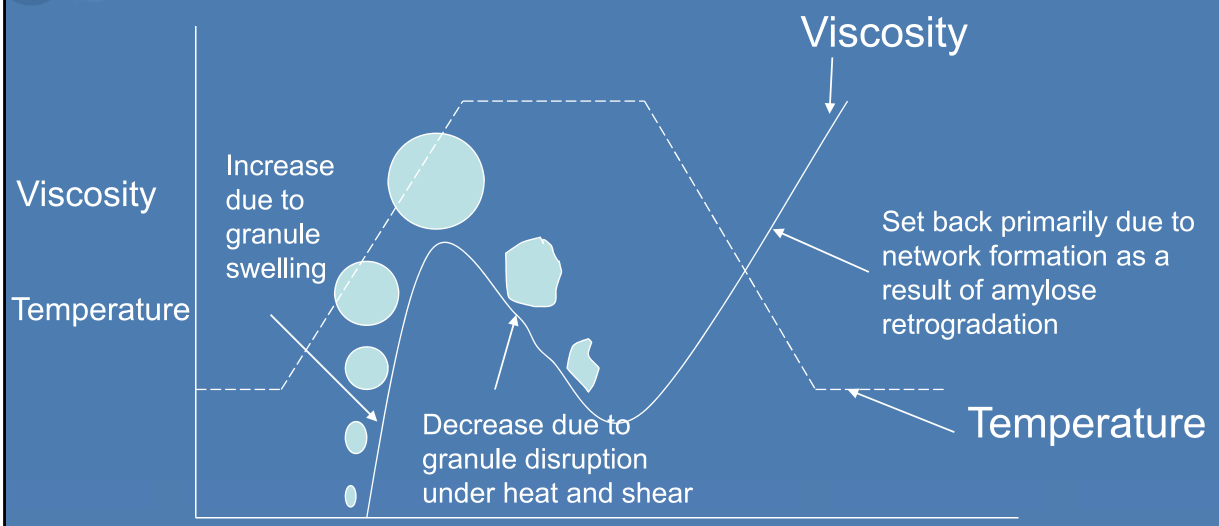


Sample were held at these temperatures for 5 minutes.

Observations from University of Jena

Rapid Viscosity Analyser

Typical Viscosity Response to the Pasting Experiment



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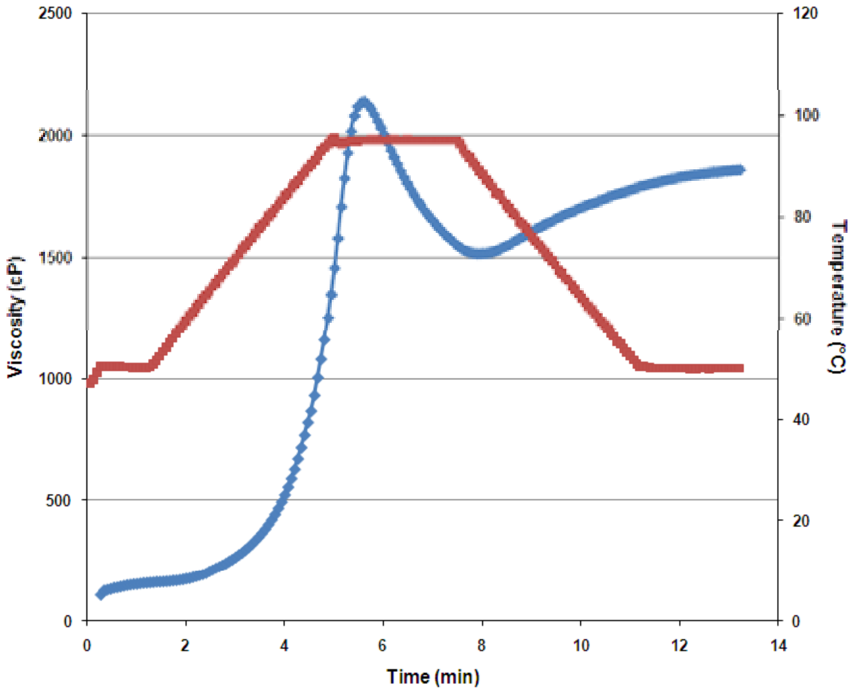
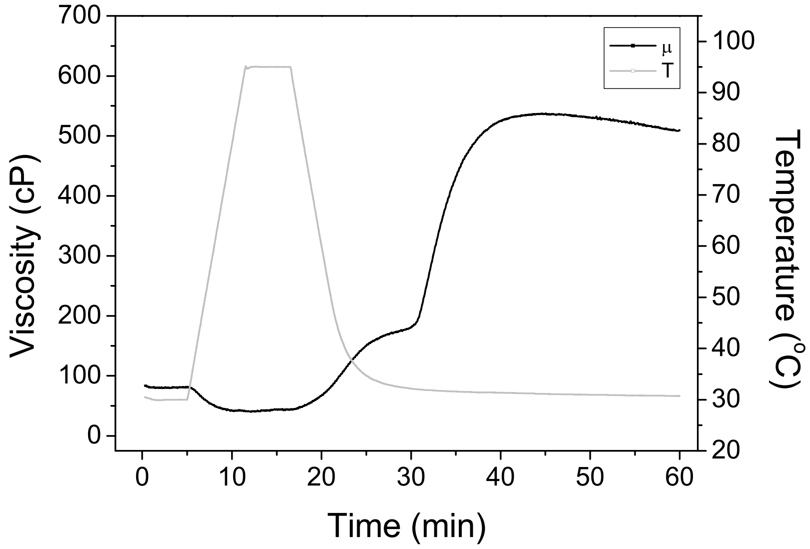
"Pasting" Curve for Physically Modified Xanthan (2% xanthan 0.4 %NaCl)



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

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Dynamic Mechanical Analysis: A Practical Introduction: Menard K.P. (1999) CRC Press

An Introduction to Rheology. Barnes, H.A., Hutton, J.F. and Walters, K. (1989) Elesevier, Amsterdam

Viscoelastic Properties of Polymers 3rd Edition: Ferry, J.D. (1980) Wiley

Thank you for listening