Rheological And Dielectric Characterization of Thermosetting Polymers

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Outline

- Introduction
- Oscillatory parallel plate rheometry
- Dynamic dielectric measurements
- Simultaneous dynamic mechanical/dielectric measurements
- In-situ cure monitoring
- Summary

Rheology

- Everything flows
- The observed properties depend on the time-scale of the deformation

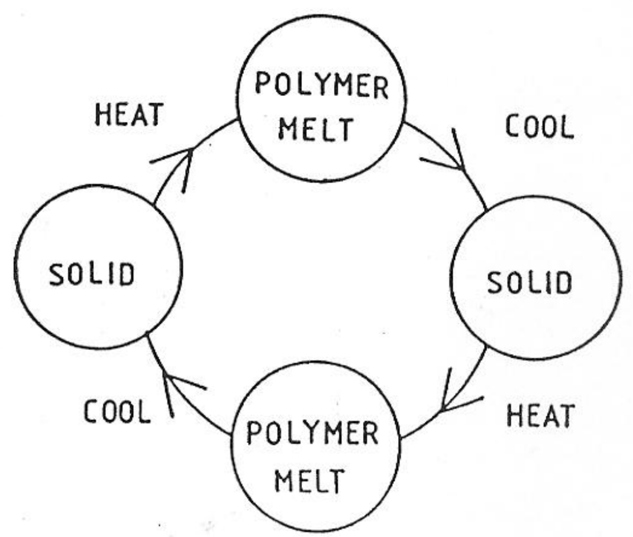
  Glass ⟶ Newtonian Liquid
- Polymer melts are called "memory fluids"
  - Properties depend on the deformation history
  - Memory fluids exhibit both liquid-like and solid-like properties
- Hence the term ***Viscoelasticity***

Viscoelasticity of Polymer Melts

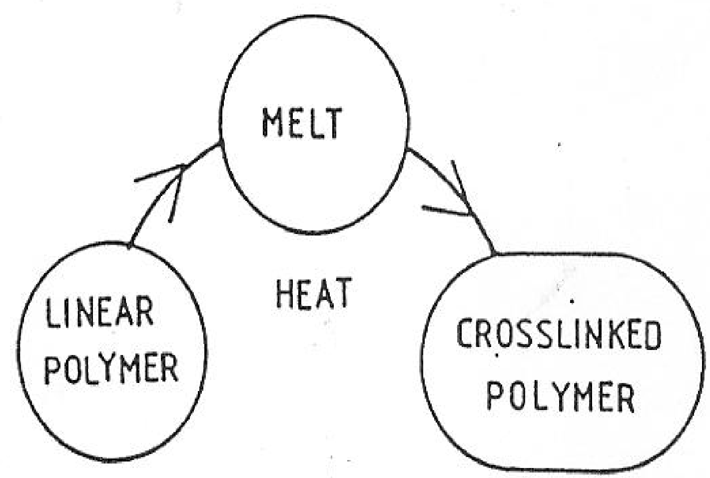
- Short deformation times lead to ***elastic*** solid behavior
- Deformation at a constant rate for a time which is long compare to the memory time (relaxation time) leads to ***viscous*** behavior
- Think about "Silly Putty"
  - How does it deform at short times?
  - Does it flow?

Thermoplastics versus Thermosets

Thermoplastics
-polymer chains not linked together
-reprocessible by melting



Thermosets
-polymer chains are crosslinked
-cannot be reprocessed

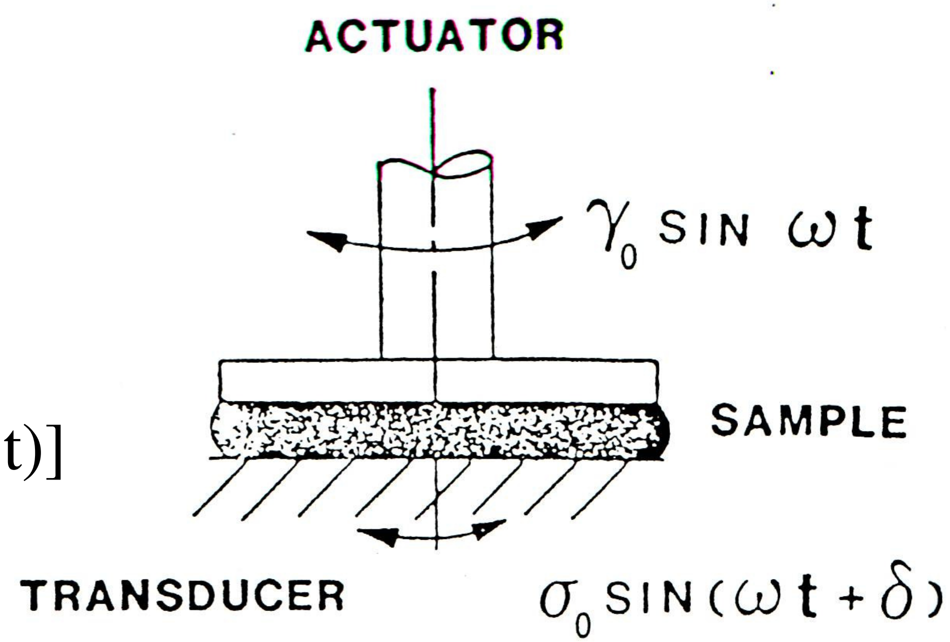


Rheology of thermosetting polymers is determined by the curing conditions

Parallel Plate Geometry

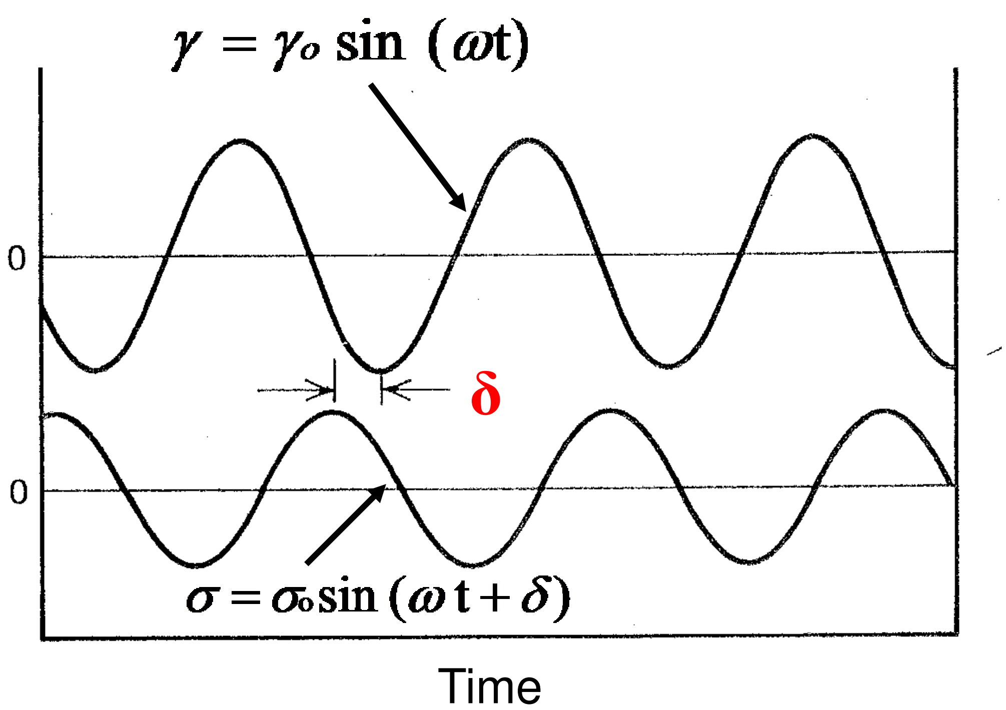
For small strain amplitude, time-independent polymers (linear viscoelastic regime):

$$\sigma = \gamma_0 [G' \sin(\omega t) + G'' \cos(\omega t)]$$



Plates enclosed in temperature-controlled oven for curing studies

Oscillatory Rheometry



Measure both elastic and viscous components

The dynamic storage modulus G' and the dynamic loss modulus G" can be calculated:

$$G' = (\sigma_o / \gamma_o) \cos \delta$$

$$G'' = (\sigma_o / \gamma_o) \sin \delta$$

From the dynamic moduli, the viscosity may be calculated:

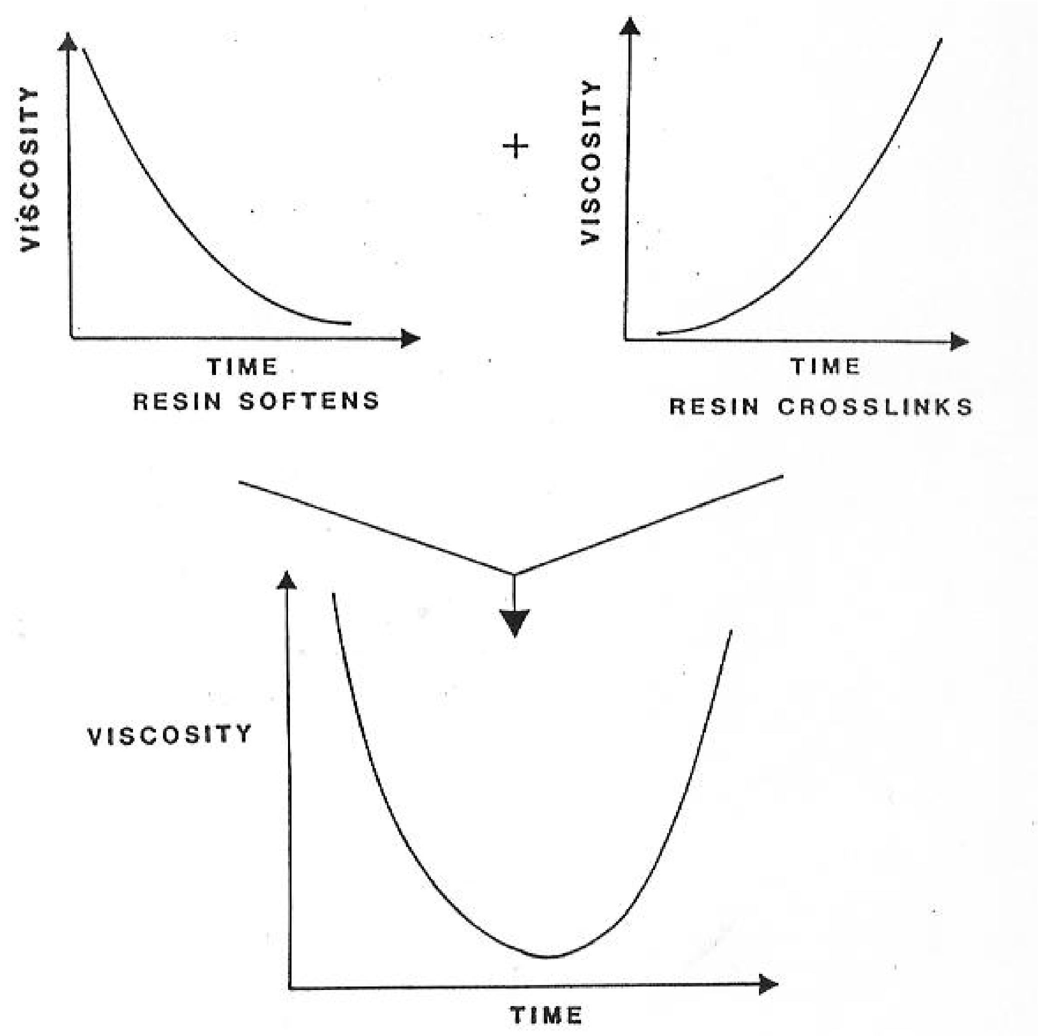
$\eta' = G'' / \omega$ (dynamic viscosity)

$\eta'' = G' / \omega$

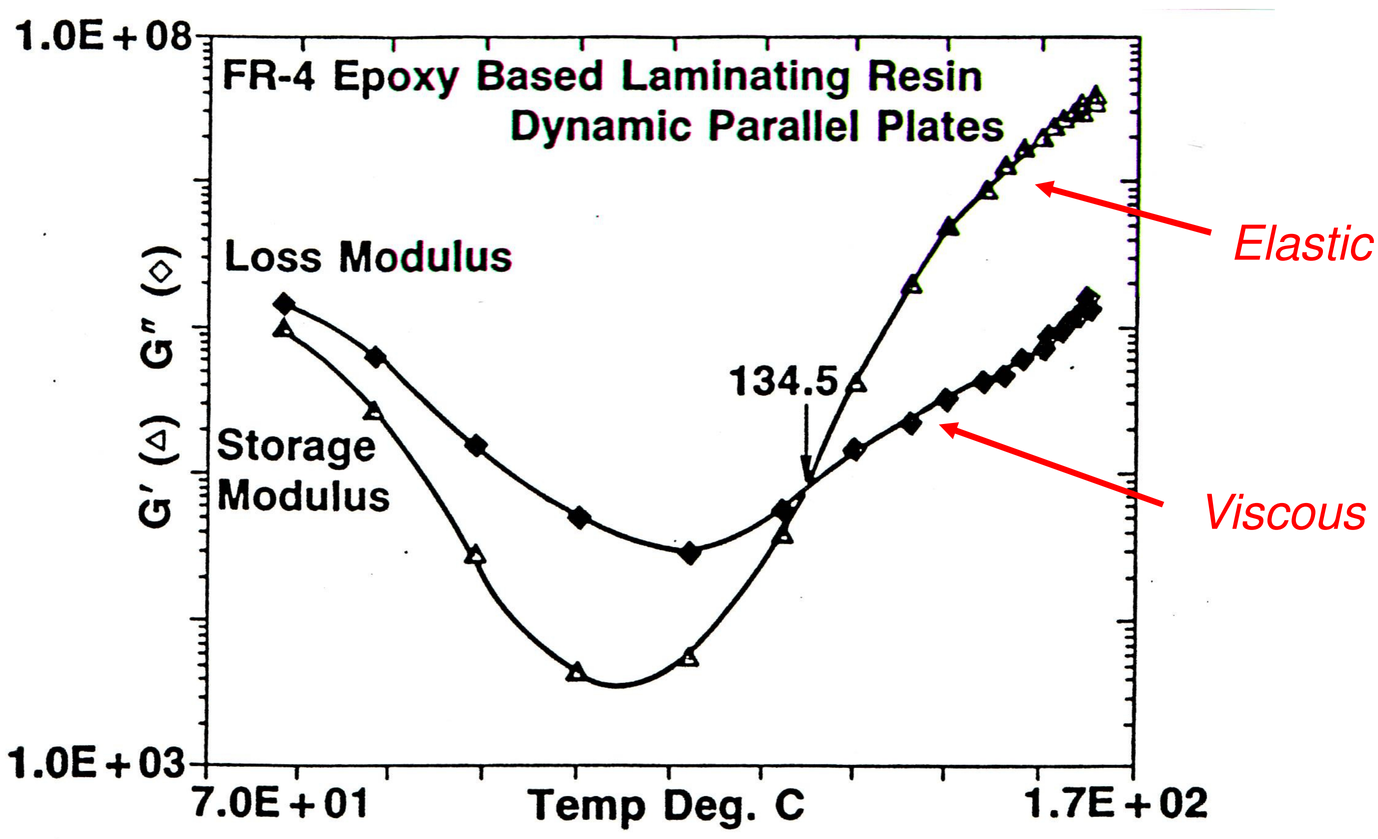
The complex viscosity is given by:

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2}$$

Evolution of Viscosity during Cure

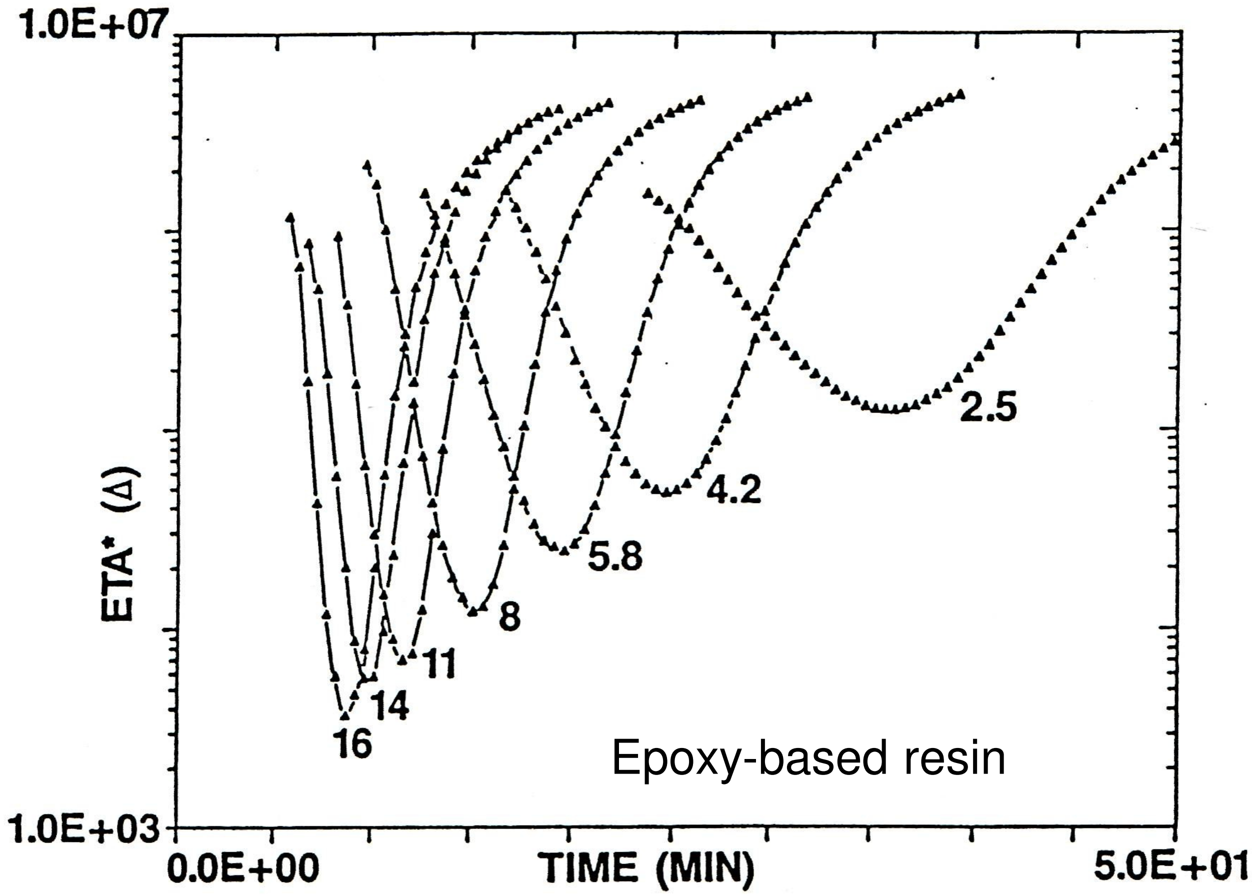


Dynamic Moduli During Curing



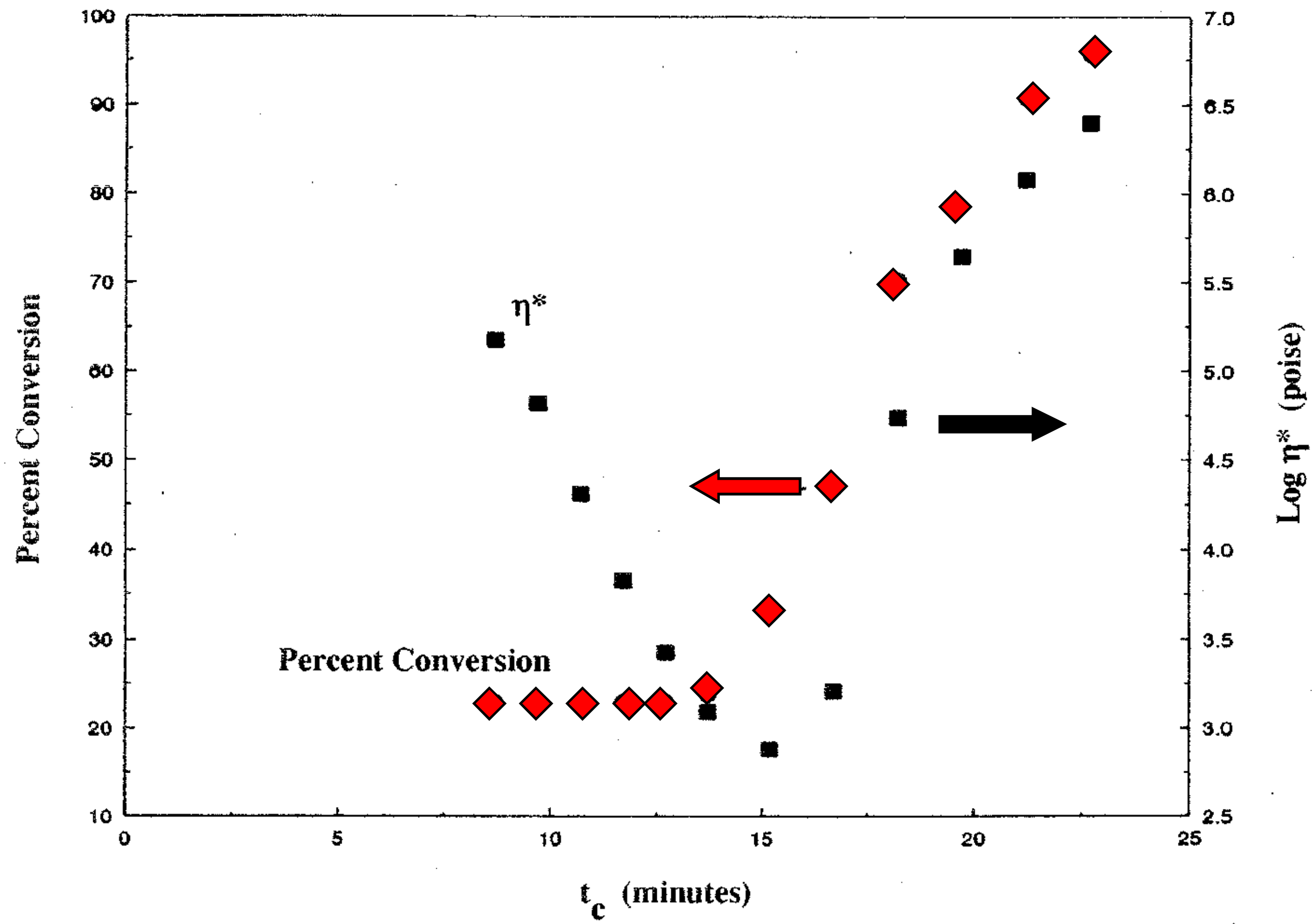
Loss is viscous component, Storage is elastic component of the complex modulus

Viscosity at Several Heating Rates



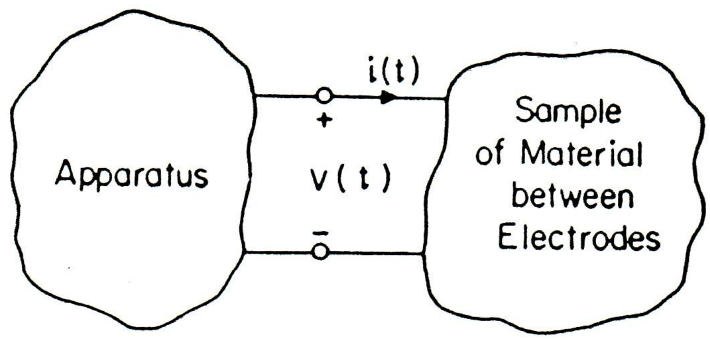
Minimum viscosity and width of the flow window depend on heating rate

Viscosity and Conversion



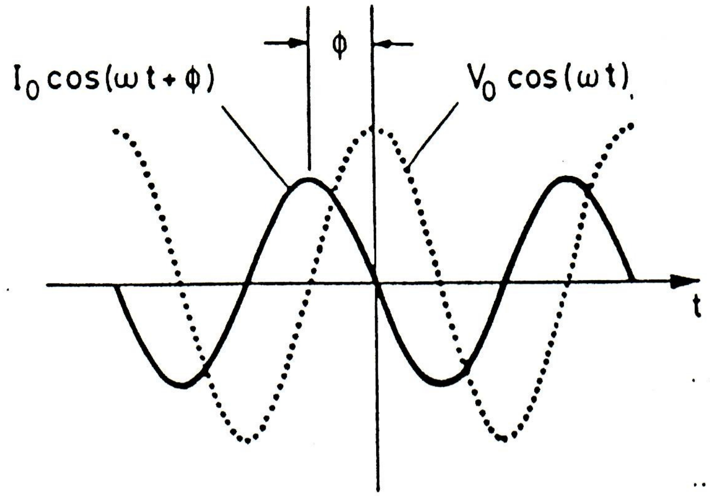
During initial softening, the conversion remains constant

Black Box View



- Apply a time-varying voltage v(t)
- Measure the time-varying current i(t) (or the time-varying charge Q(t))

Analogous to Dynamic Mechanical but Excite With Time-Dependent Voltage



$$v(t) = V_0 \cos(\omega t)$$

$$i(t) = I_0 \cos(\omega t + \phi)$$

Dynamic Dielectric Measurements

Where:

$$\varepsilon' = \left(\frac{I_o}{V_o}\right)\cos\phi$$ Permittivity

$$\varepsilon'' = \left(\frac{I_o}{V_o}\right)\sin\phi$$ Loss Factor

The complex dielectric constant:

$$\varepsilon^*(\omega) = \varepsilon' + j\varepsilon''$$

Definitions

- Dielectric Permittivity:
  - Represents the polarization of the medium
  - Typically called the "dielectric constant", but for curing systems, the dielectric "constant" changes as a function of temperature and cure state
- Dielectric Loss Factor:
  - Arises from two sources
    - Energy loss associated with time-dependent dipolar relaxations
    - Bulk (ionic) conduction

Dielectric Loss Factor

$$\varepsilon'' = \frac{\sigma}{2\pi f \varepsilon_o} + \varepsilon''_d$$

Where:

σ is the ionic conductivity

f is the frequency

ε_o is the permittivity of free space

ε''_d is the contributions from dipoles

$$\sigma = \sum_i q_i N_i \mu_i$$

q = charge magnitude

N = number of species per unit volume

μ is the ion mobility

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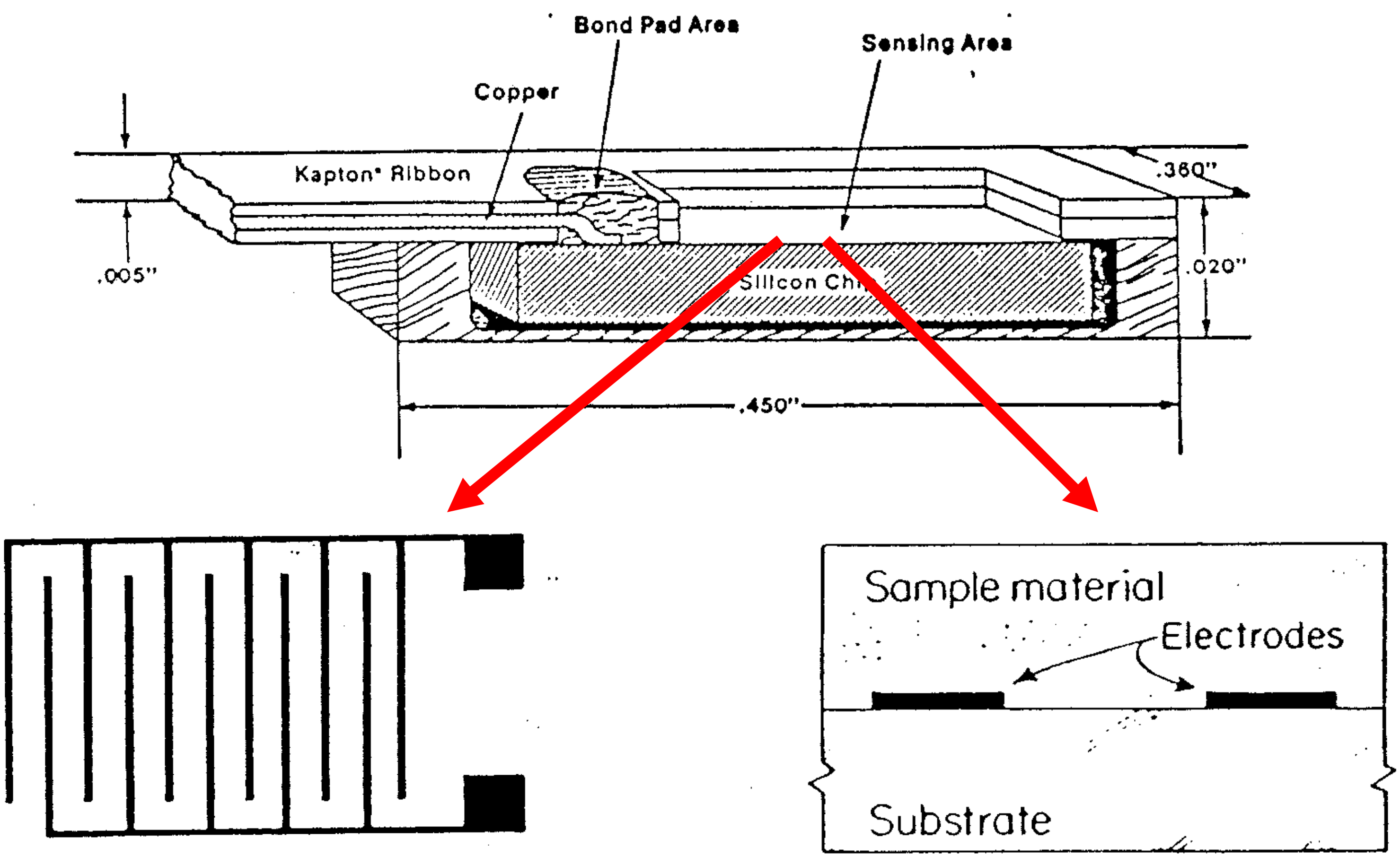
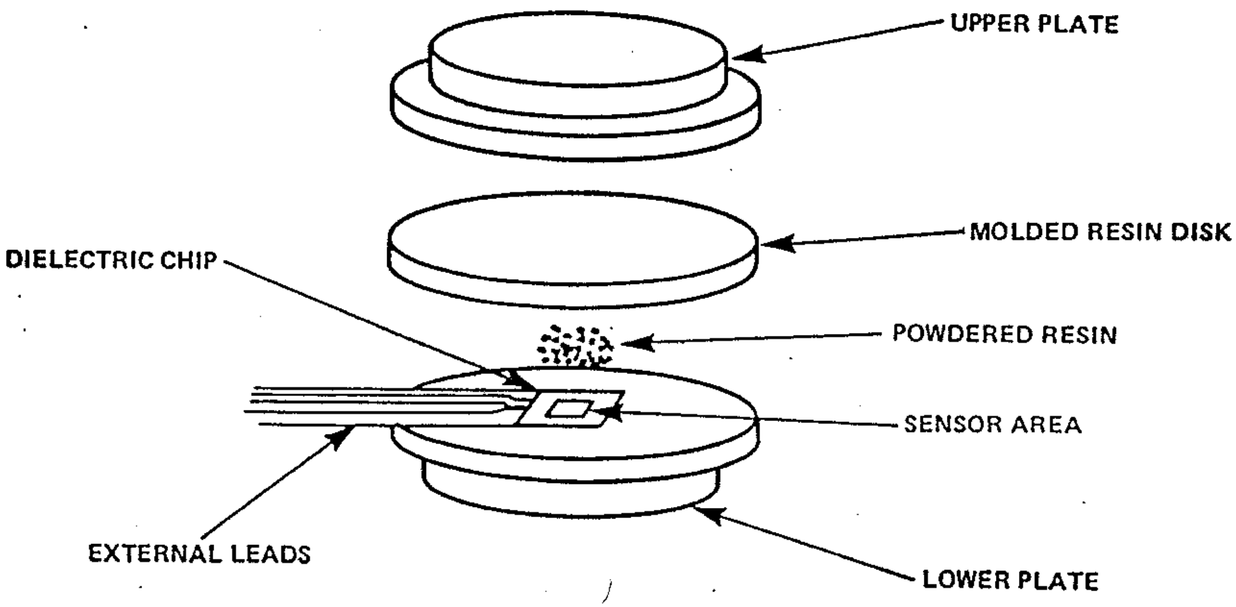
Dielectric Sensor Geometry

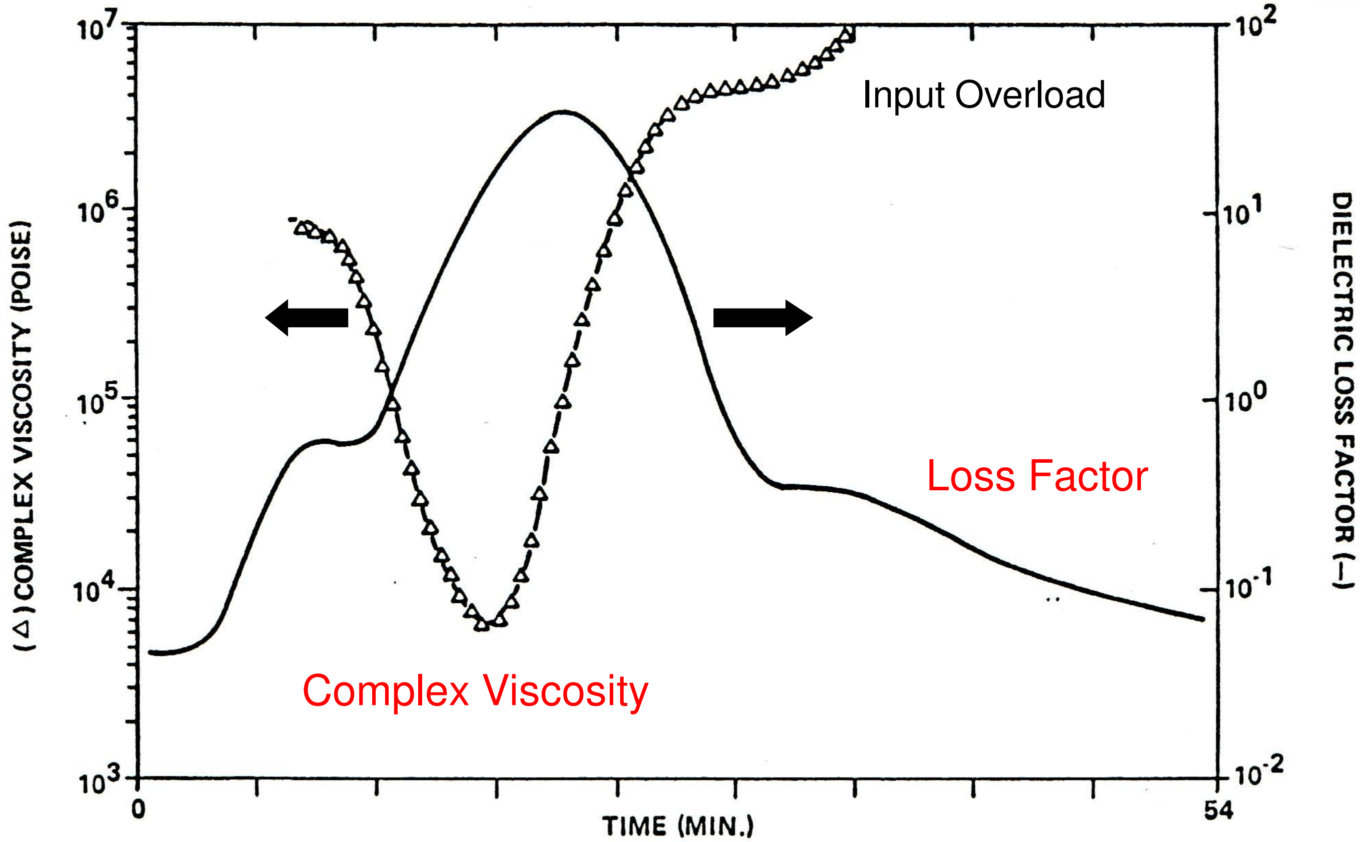


Dielectric Sensor Embedded in Plates

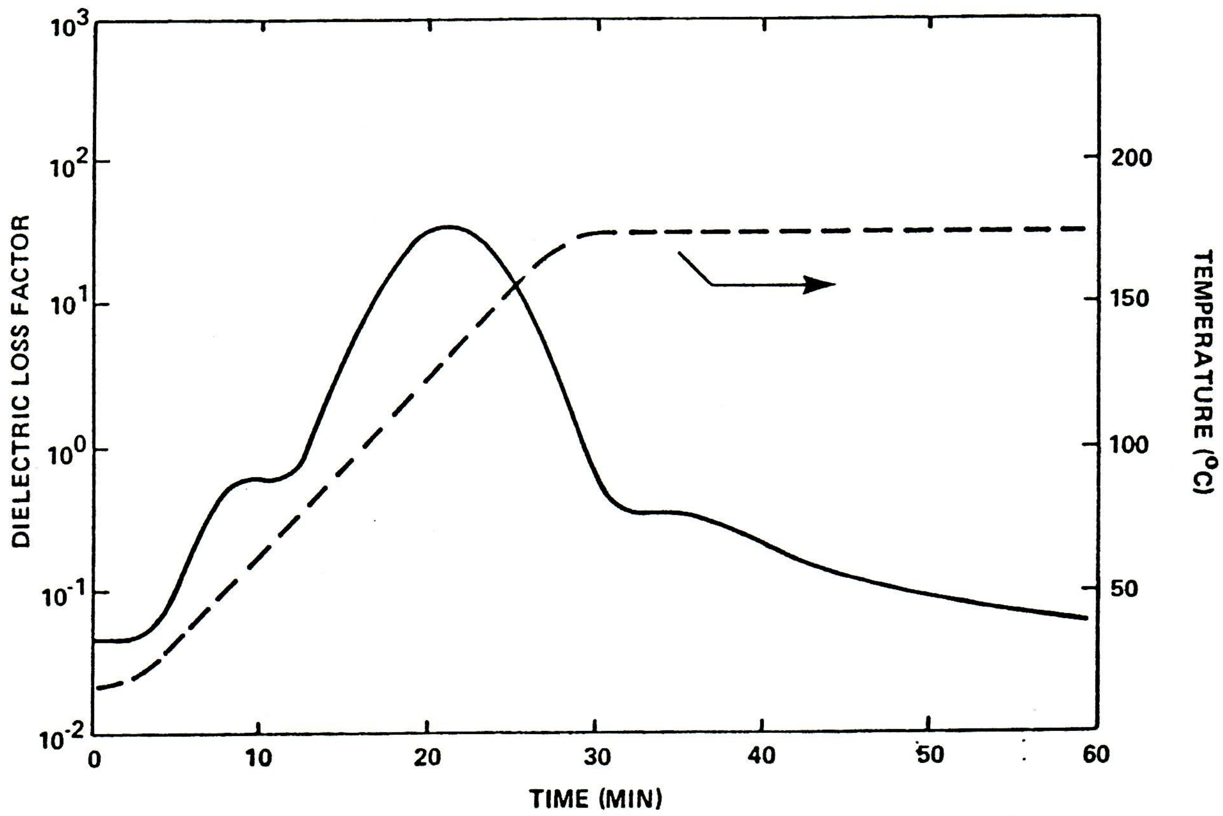


Simultaneous measurement of dielectric and dynamic mechanical response

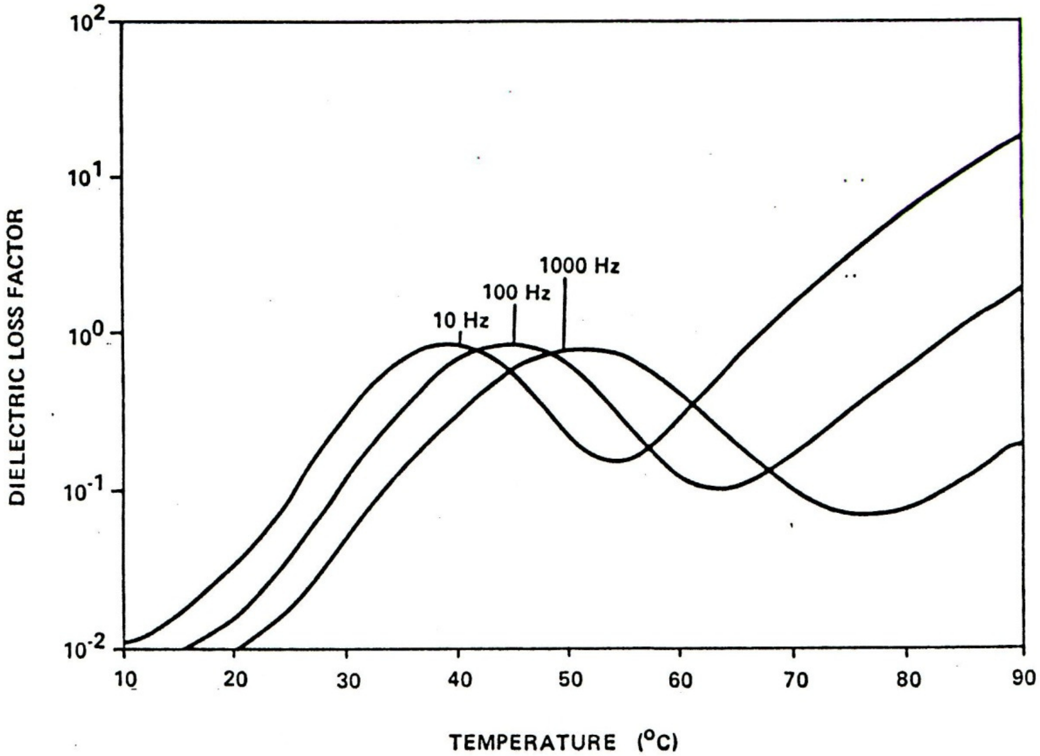
Simultaneous Measurements



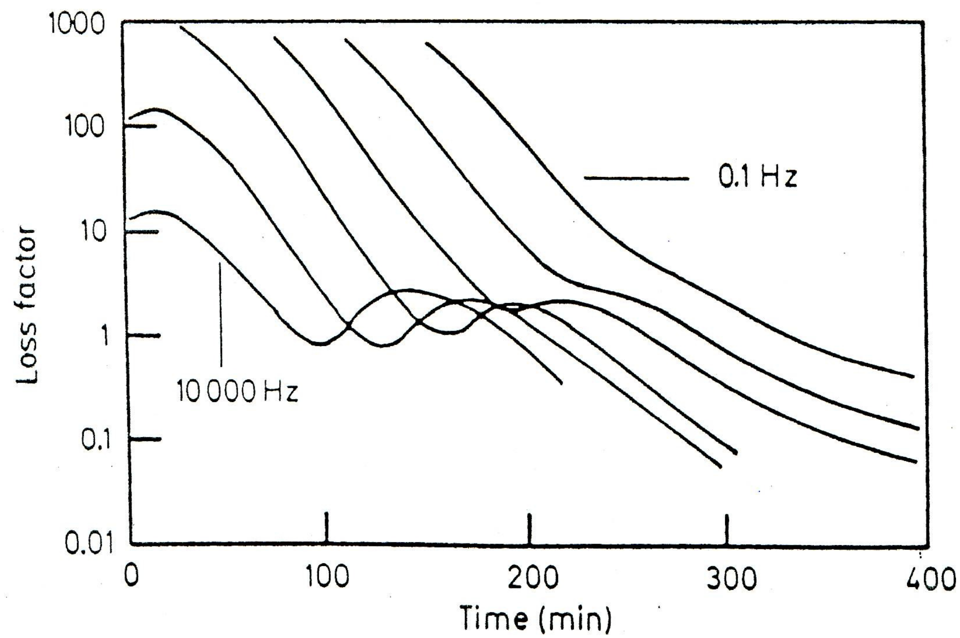
Dielectric Loss Factor



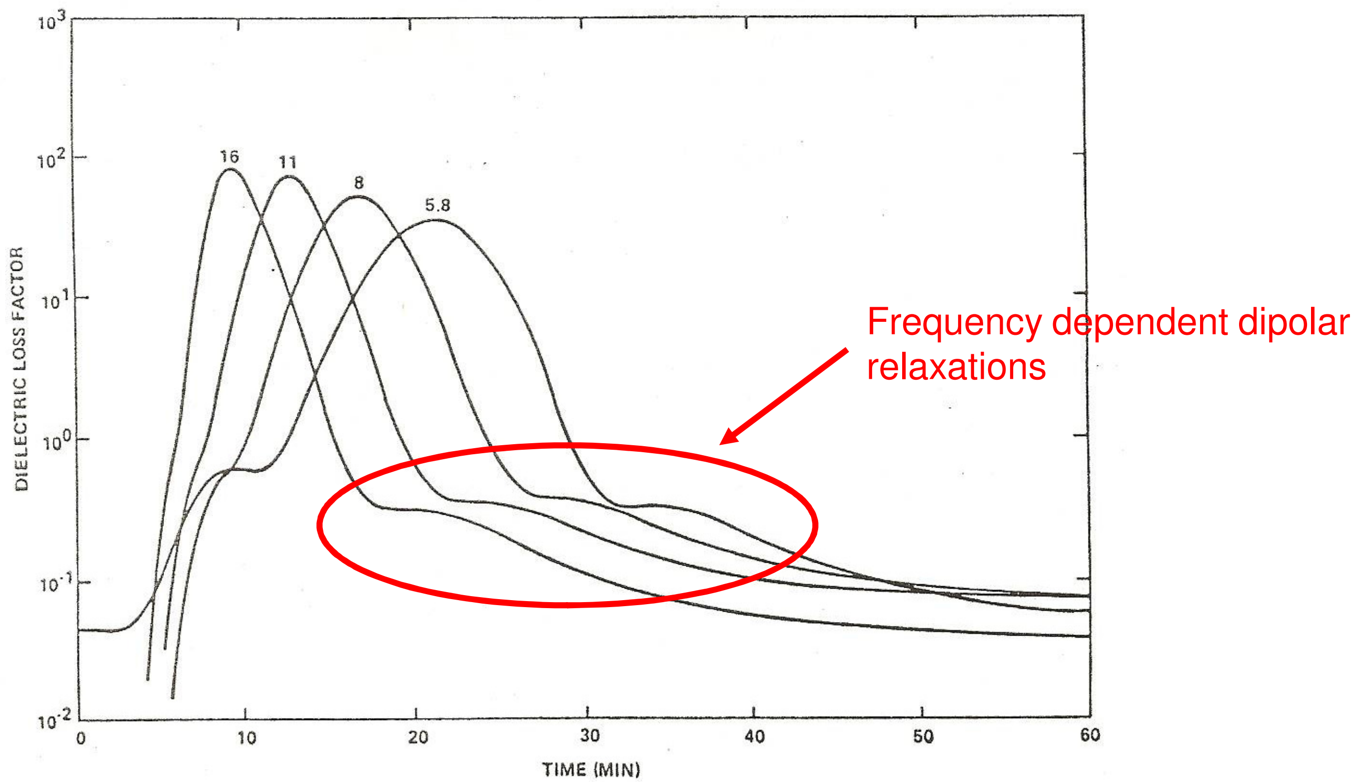
Dipolar Relaxations at Tg



Dipolar Relaxations During Vitrification

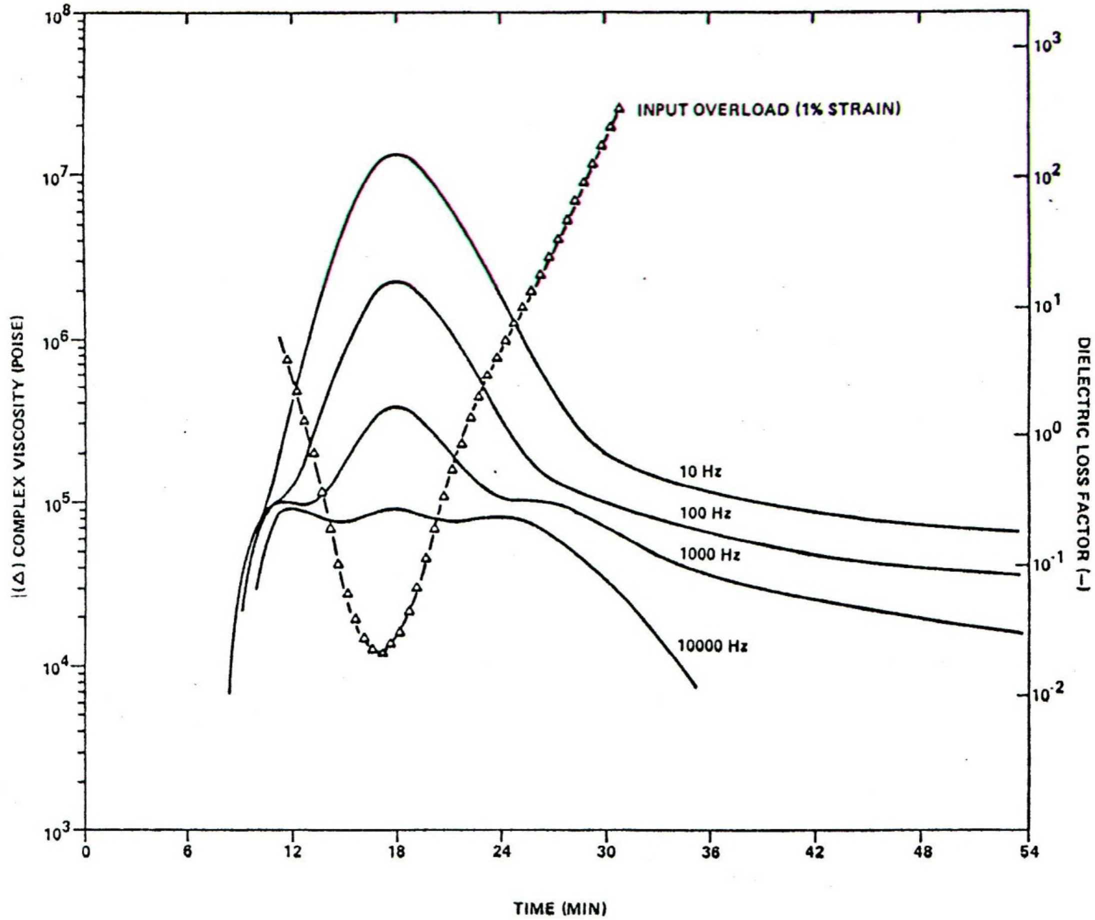


Full Loss Factor Spectrum During Curing



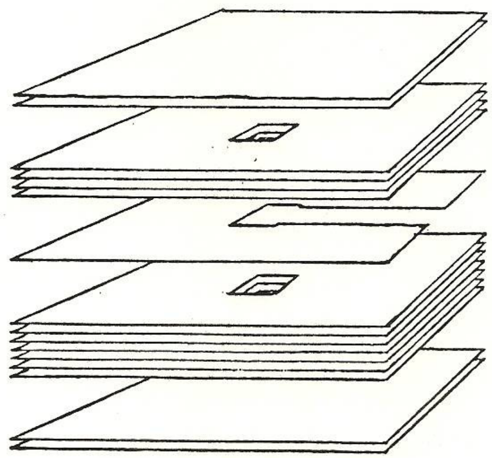
Tg is higher than the cure temperature, vitrification occurs during heating

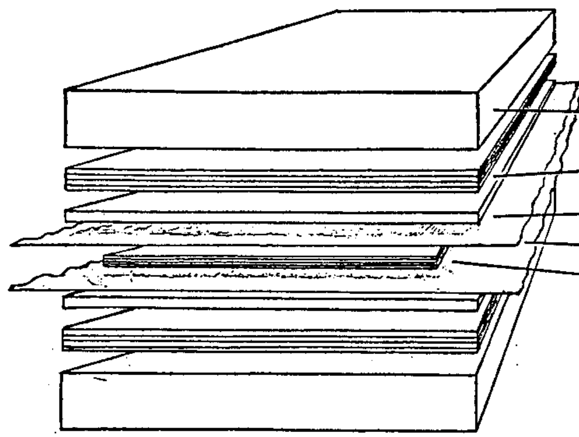
Similar Profile for Epoxy Resin



Magnitude of the ionic conductivity governed by the frequency

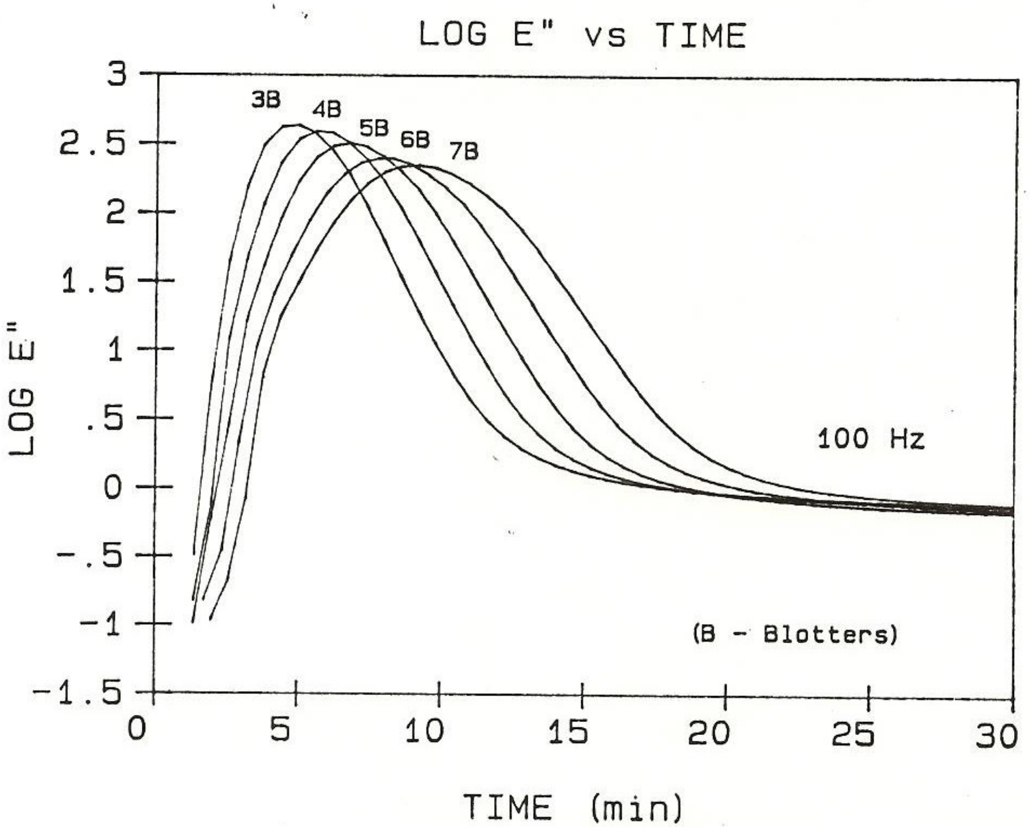
In-situ in Lamination Stack





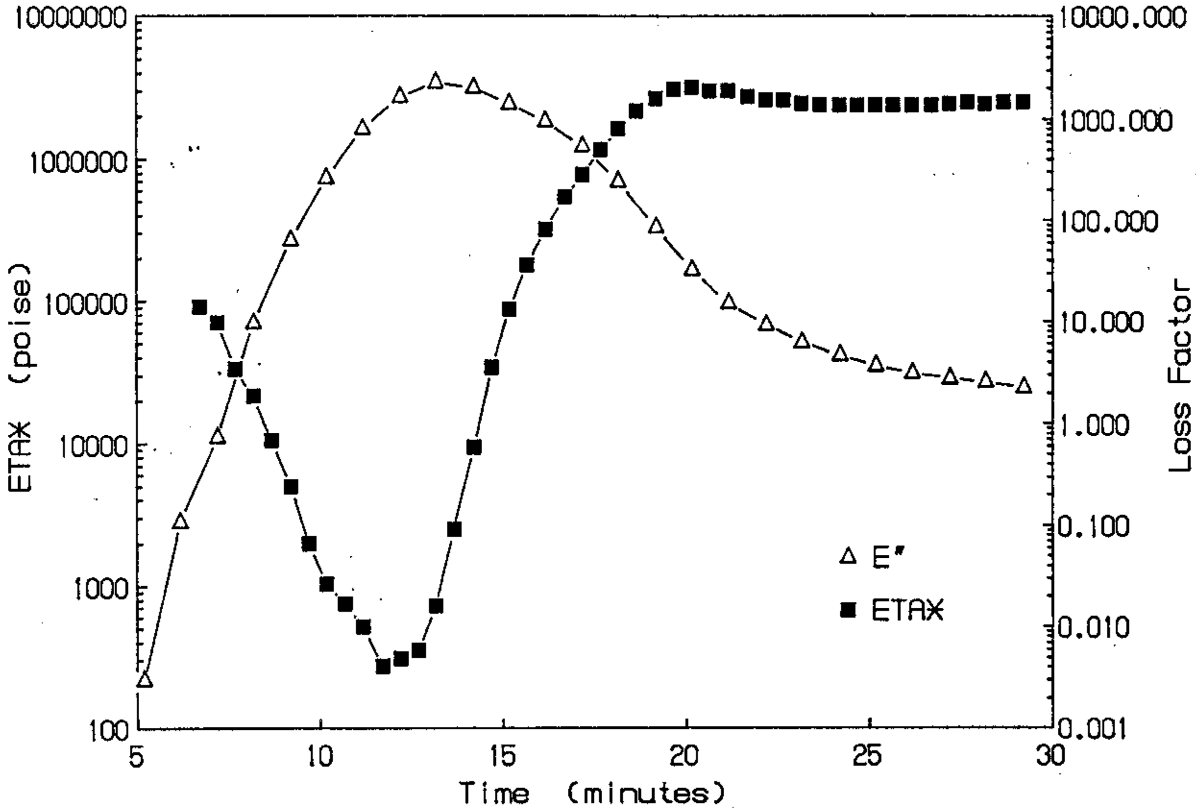
Embed dielectric sensor in lamination stack to measure cure profile

Dielectric Profile During Lamination



Heating rate influences rheology, cure-path independent

Loss Factor Correlated to Viscosity



Summary

- Chemorheology of thermosetting polymers can be investigated using:
  - Dynamic Oscillatory parallel plate rheometry
  - Dynamic Dielectric measurements
- Simultaneous dynamic dielectric and dynamic mechanical measurements provide detailed insight into the physical changes during curing
- In-situ dielectric measurements can be used as cure monitors during the processing of thermosetting polymers

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