Analyzing & Testing

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Leading Thermal Analysis

Cure Monitoring of Thermosetting Resins by Dielectric Analysis (DEA)

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Dielectric (Thermal) Analysis (DEA/DETA)

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- Traditional Thermal Analysis laboratory procedure
- Normally utilizes dielectric sensors located in (heated) testing cell
- Measure changes in permittivity (dielectric constant), loss factor and ionic conductivity as a function of time or temperature
- Used to determine transitions in materials or reactions in polymerization/curing reactions

Questions for Cure Monitoring

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Quality Control (QC) of Incoming Goods,

Quality Assurance (QA) and Failure Analysis of Your Products:

At which temperature does curing start?

What‘s the optimum curing process?

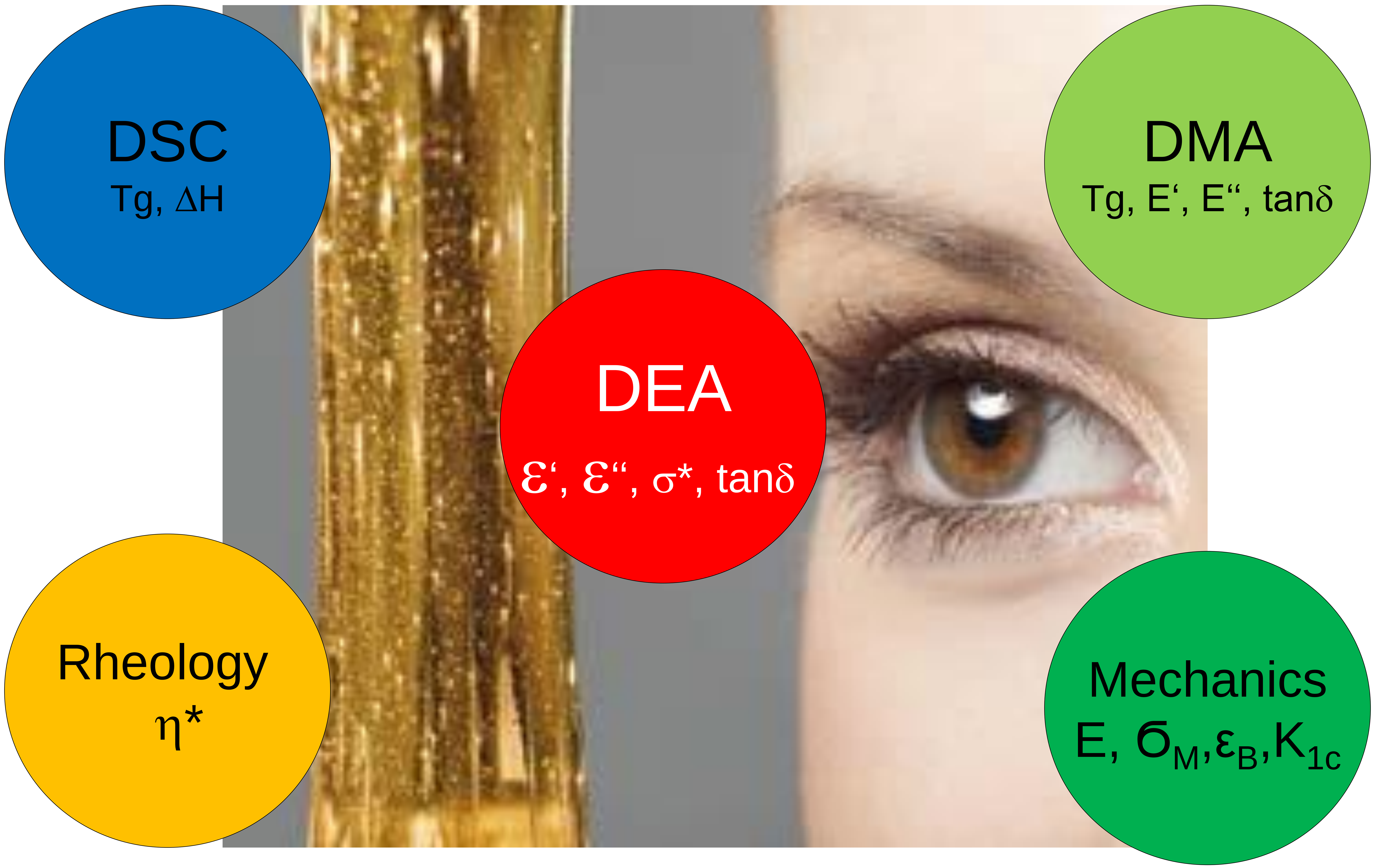
Is this the right resin for the process?

Is the reactivity of the new material higher?

Does the part show a potential for post curing?

Curing Insight

Dielectric Analysis for Cure Monitoring



Dielectric Cure Monitoring

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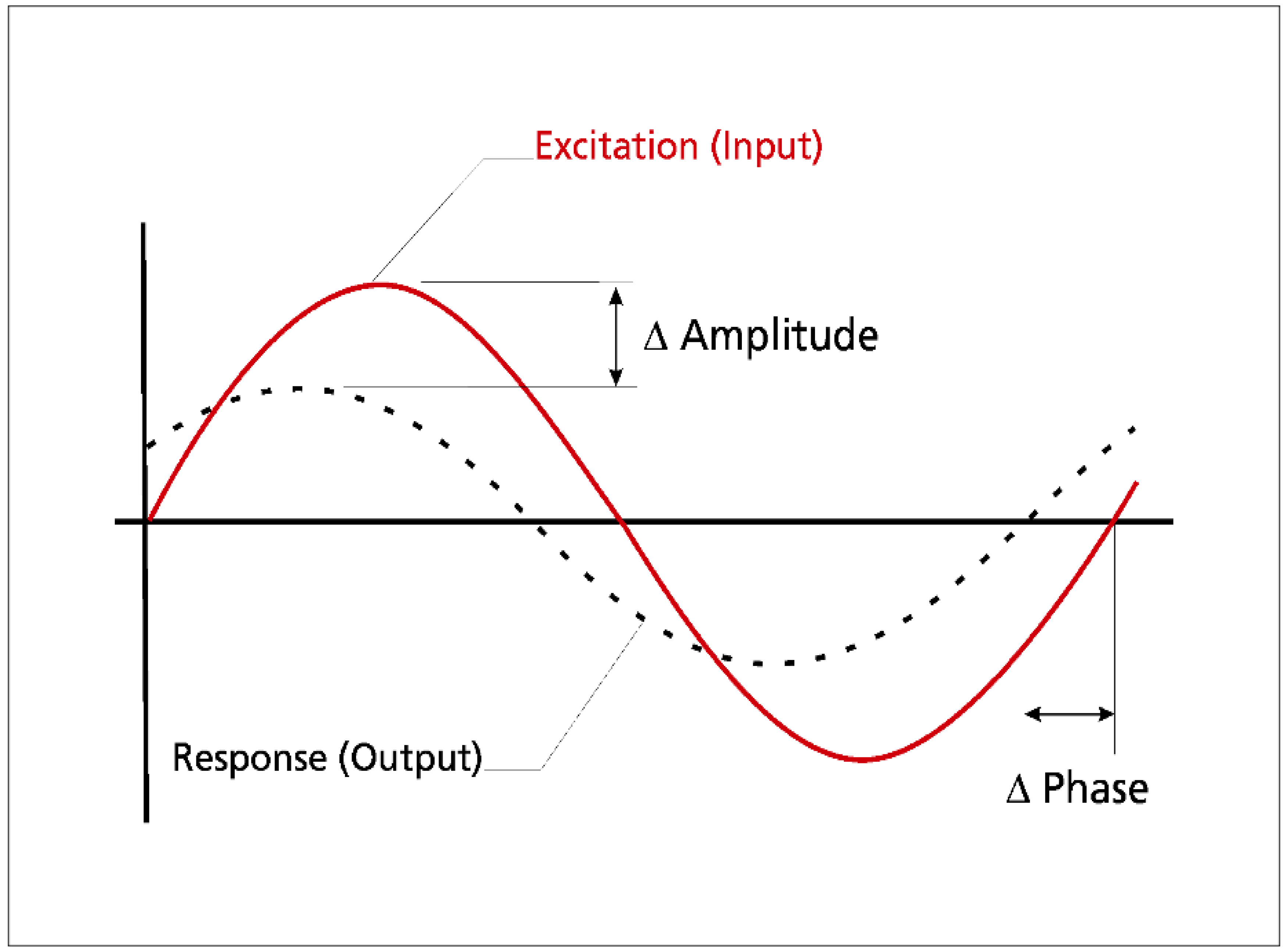
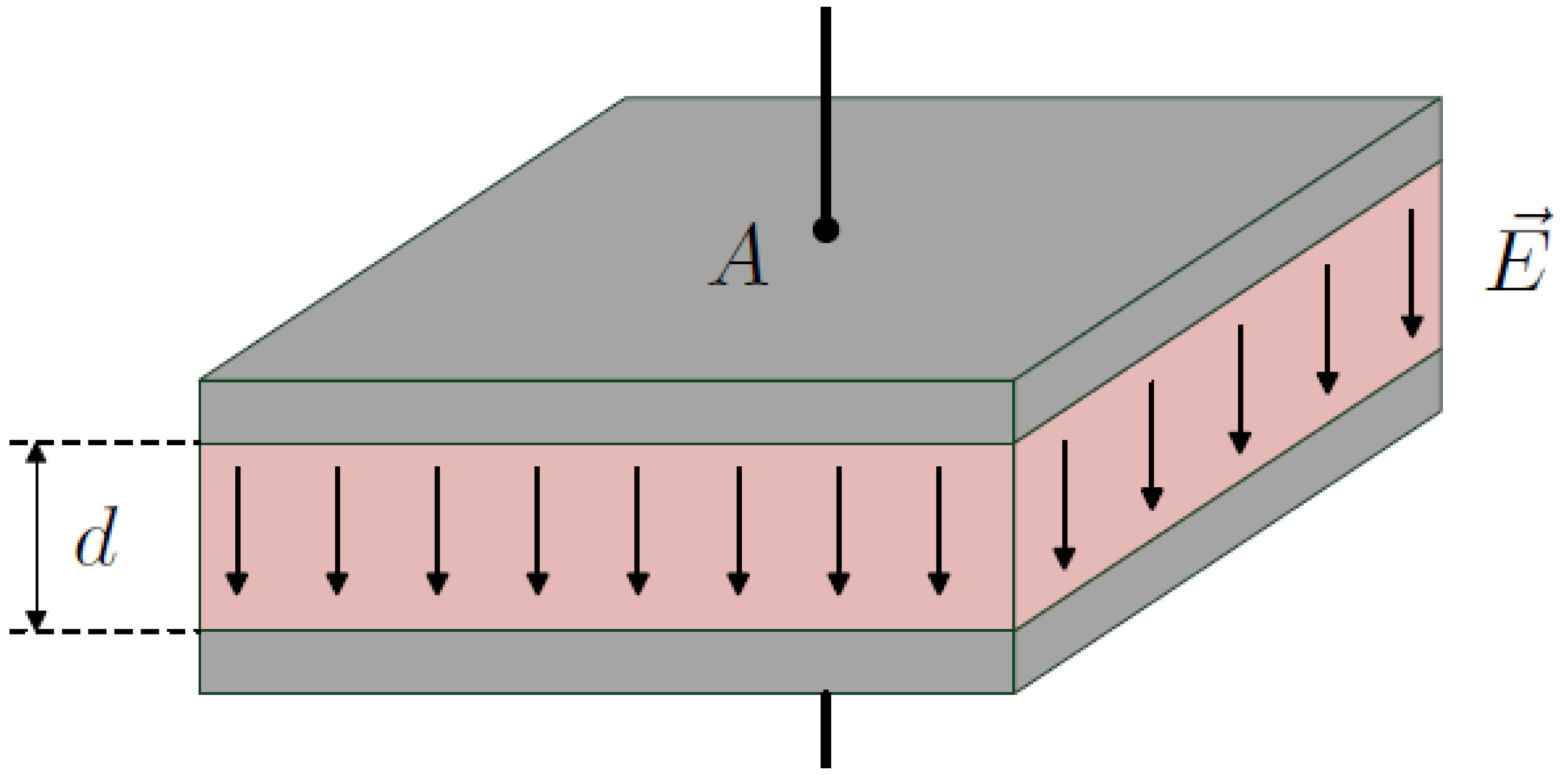
- For laboratory & in-process measurements
- Primarily used for studying curing reactions of thermosetting resins, composites, paints, coatings, etc.
- Measure changes in ionic mobility (electrical conductivity or resistivity) as a function of time to monitor changes in viscosity, cure rate and cure state
- Measurements made with robust dielectric sensors placed in contact with the material
- Measurements can be made in ovens, presses, autoclaves, etc.
- Applications in R&D, QA/QC, process monitoring and process control

DEA Theory – Fundamental Principle of DEA



A low voltage AC signal (input) is applied at one electrode

The response signal (output) detected at the other electrode is attenuated and phase has shifted

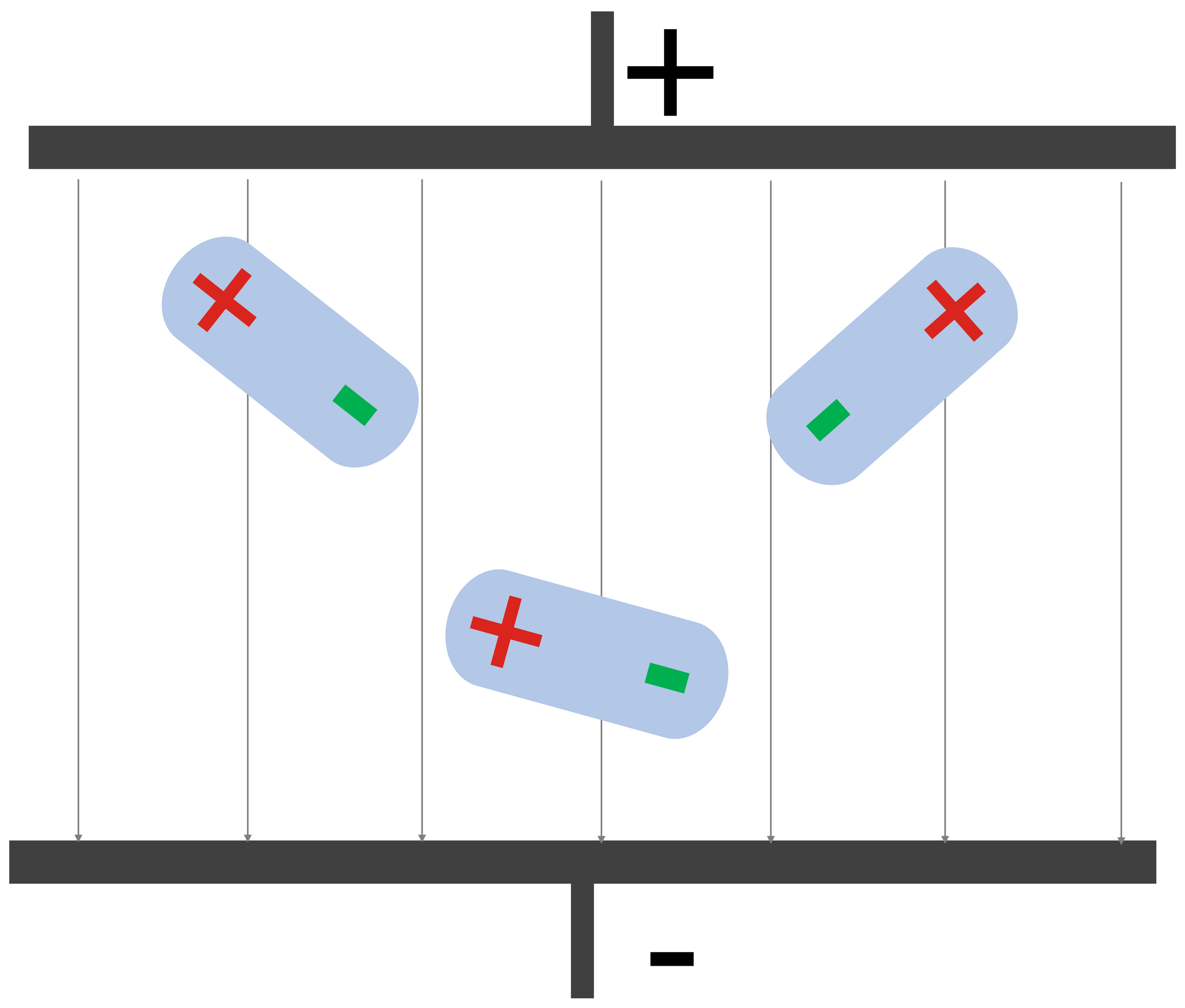


Measurement of:
- **Alignment of dipoles**
- **Mobility of ions**

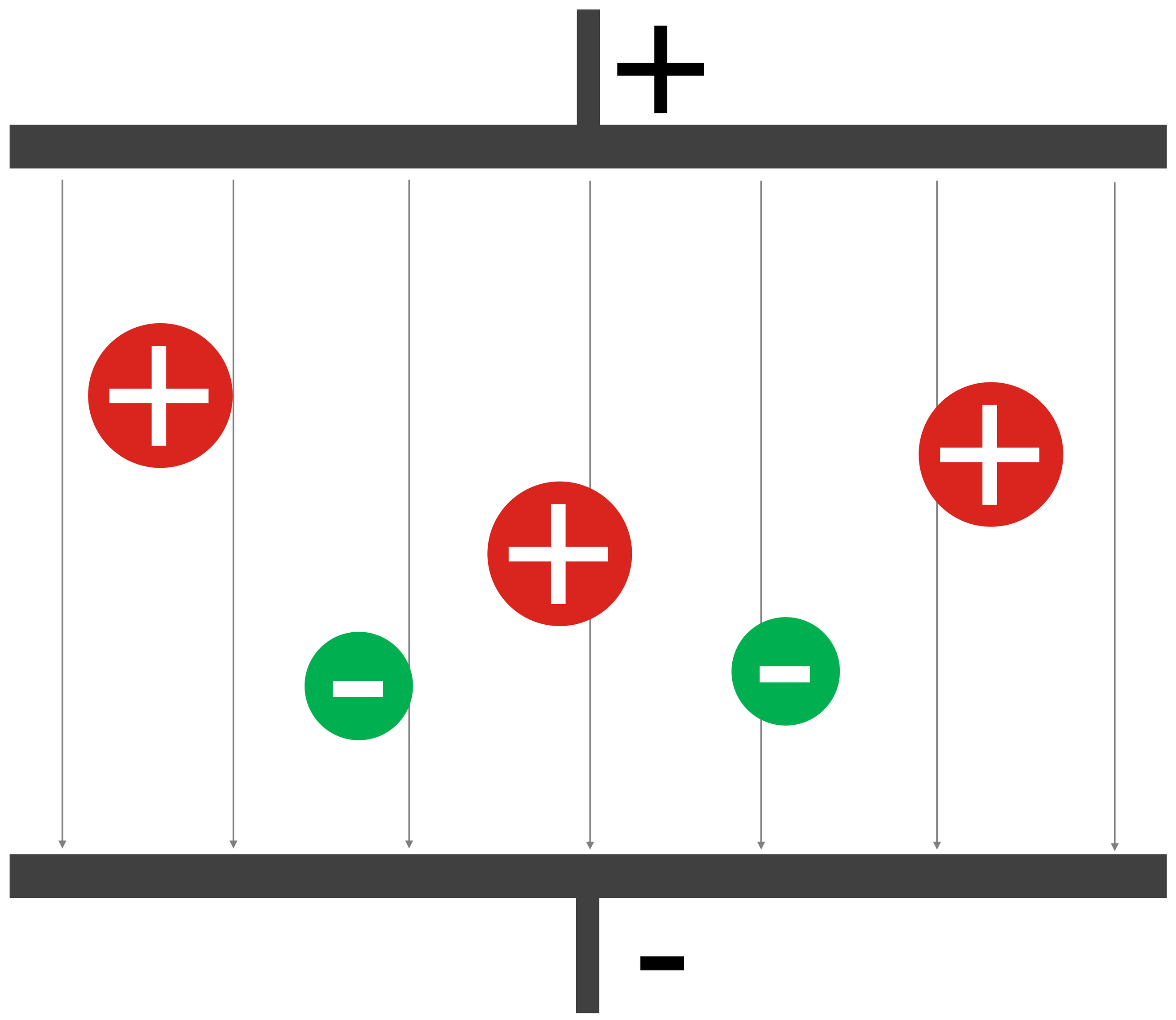
$$C^* = \varepsilon_0 \varepsilon^* \frac{A}{d}$$

ε^*: material parameter ε_0: physical constant

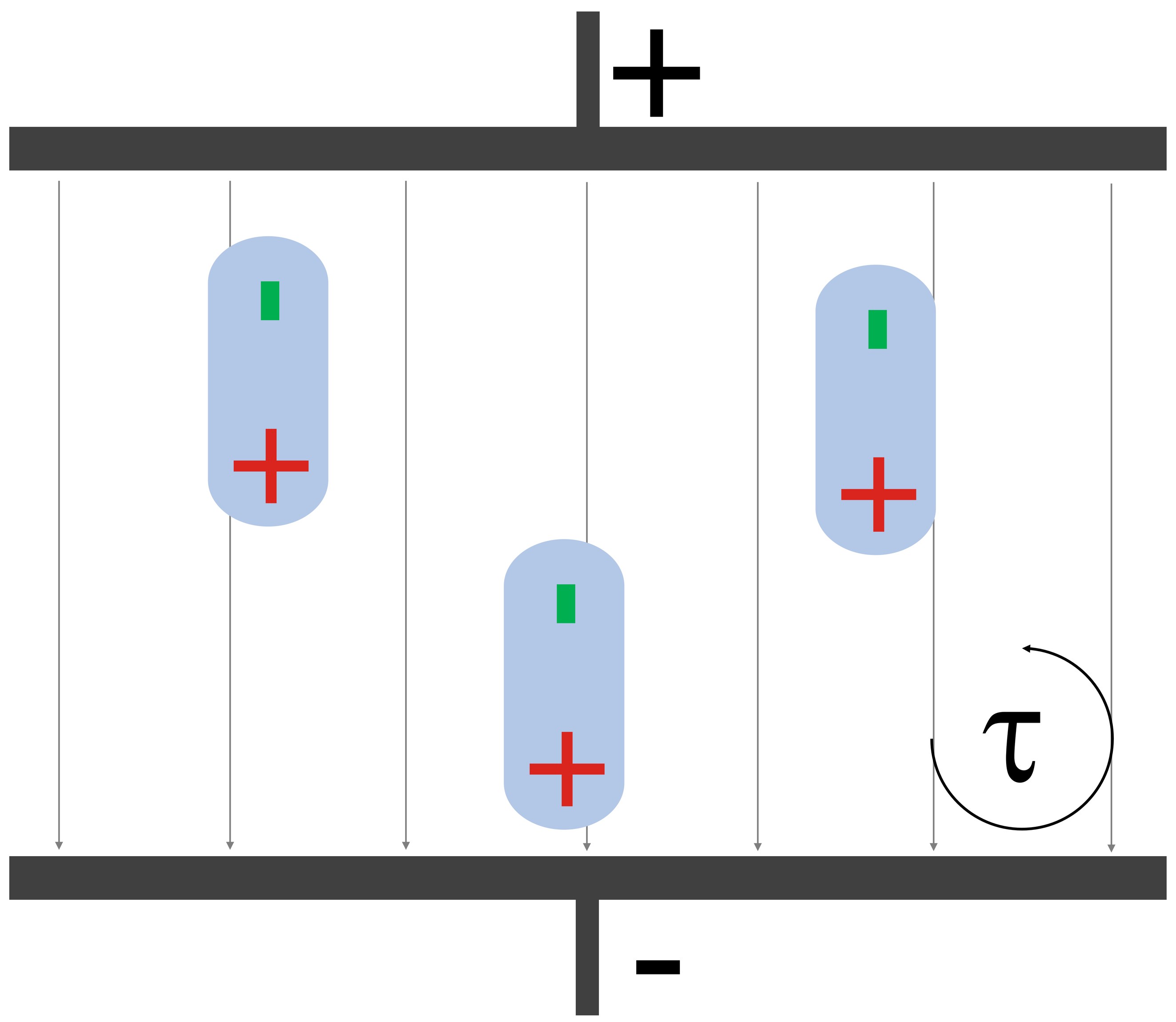
DEA Theory – Fundamental Principle of DEA



dipole relaxation due to the absence of the external electric field



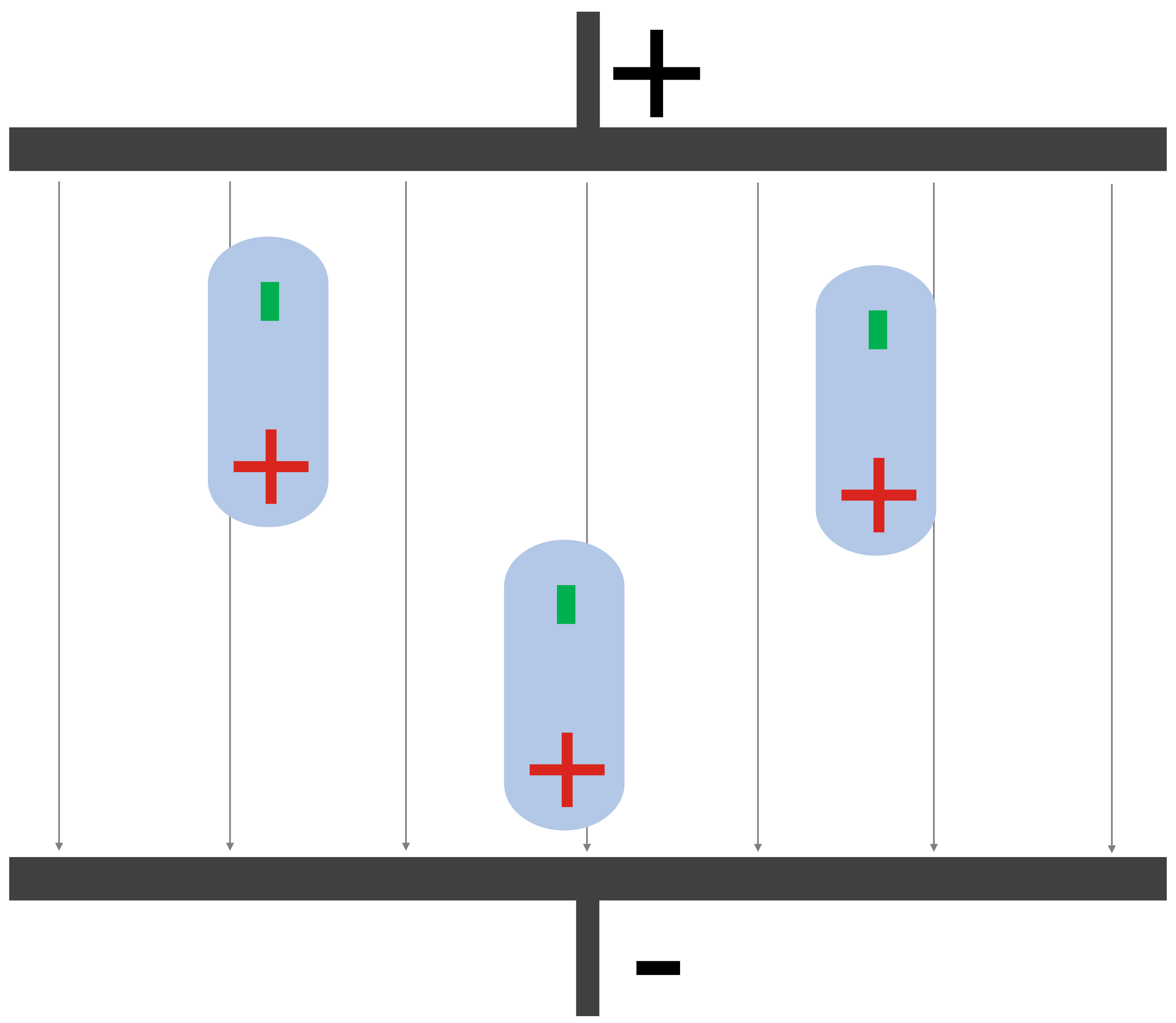
conductivity due to free charge carrier movement



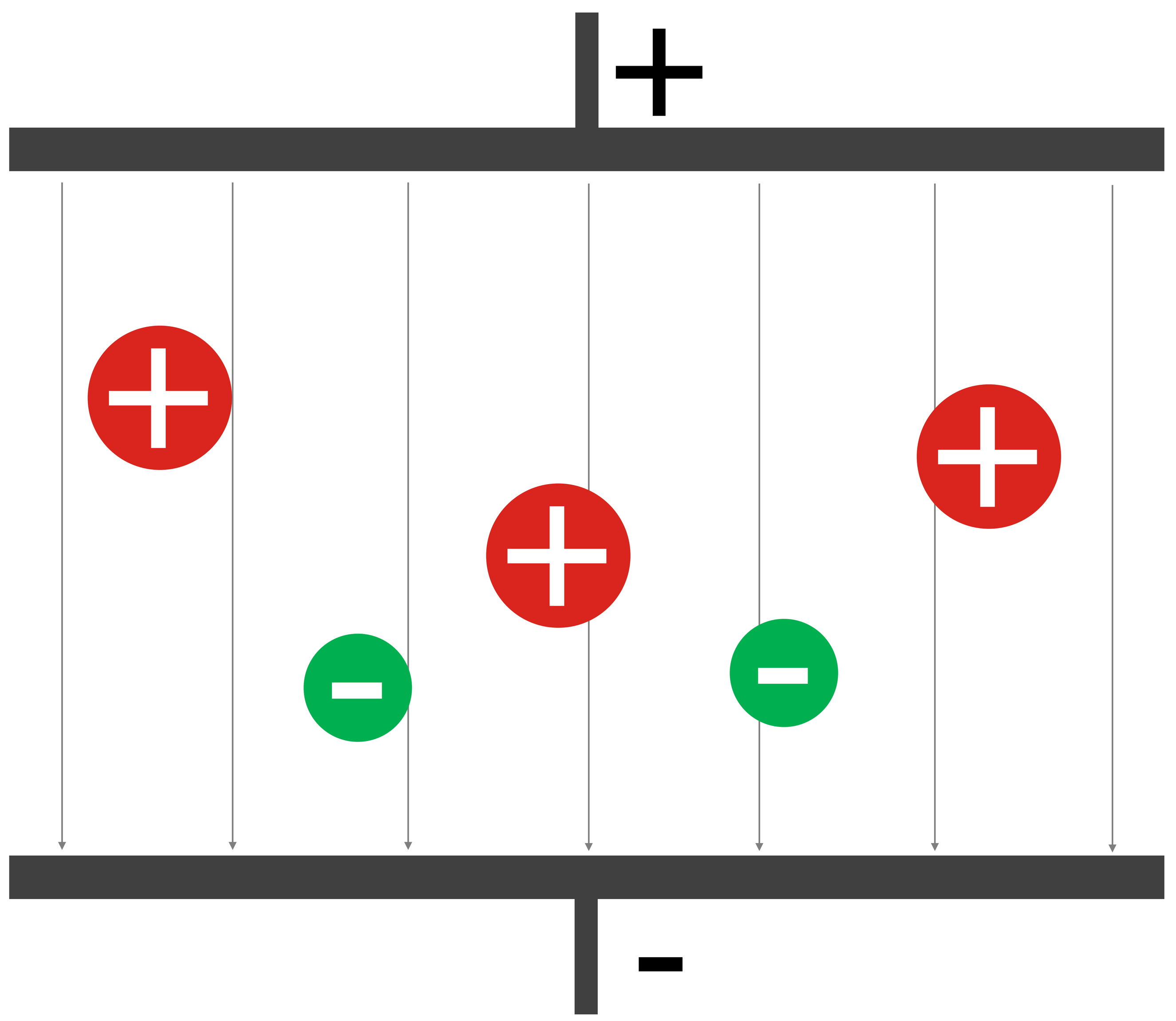
dipole orientation

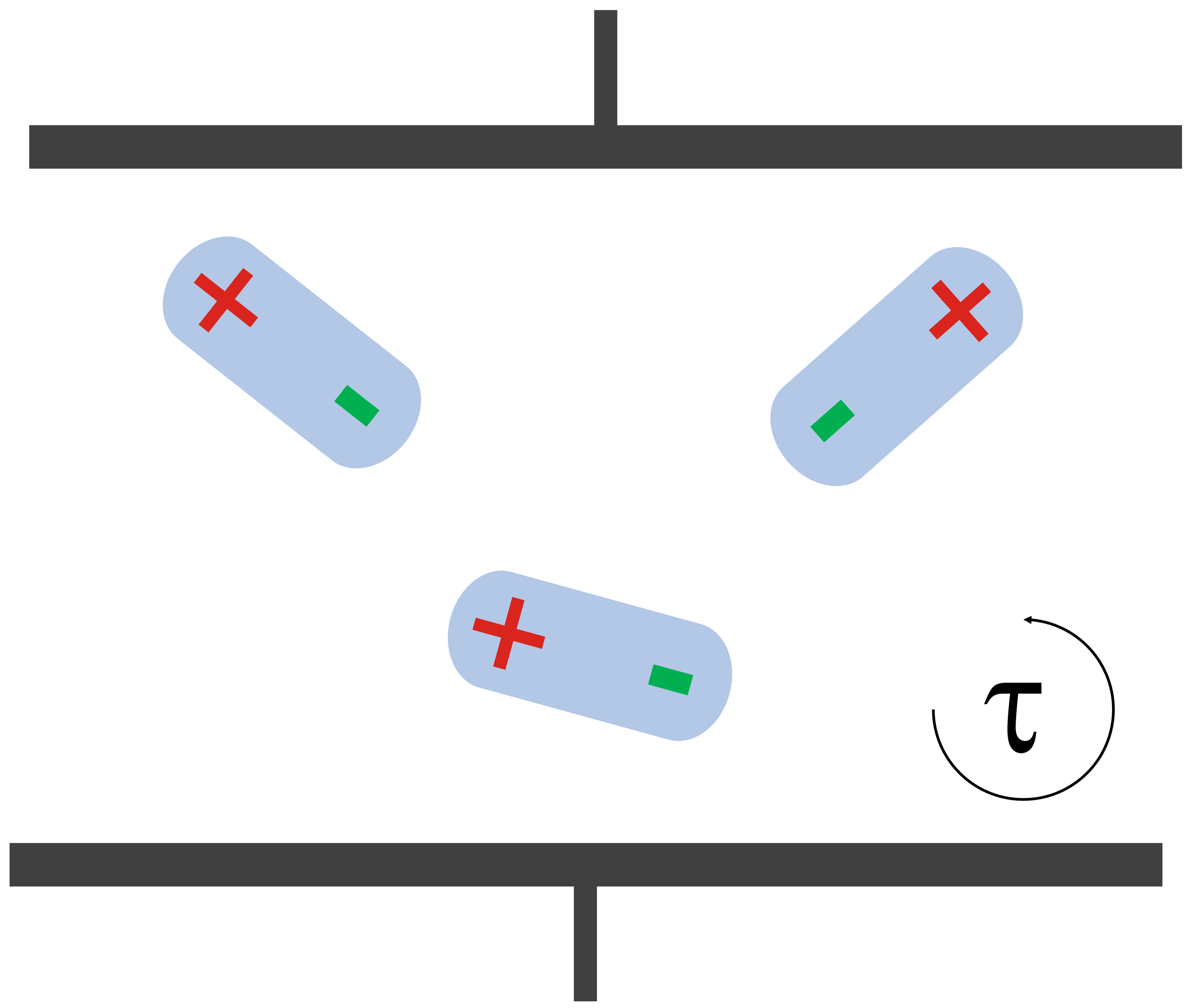
DEA Theory – Fundamental Principle of DEA

ε'



ε''





magnitude of conductivity due to free charge carrier movement

magnitude of energy loss due to relaxation of deflected dipoles

DEA Theory – Fundamental Principle of DEA

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Capacity $\mathbf{C} = \varepsilon_r * \mathbf{C_0}$

with $\varepsilon_r = \varepsilon_r' - i\ \varepsilon_r''$

ε'= Permittivity (Dielectric constant)

A measure of the alignment and number of dipolar groups in a material.

ε''= Loss factor = $\varepsilon''_{Ion} + \varepsilon''_{Dipole}$ = conductivity/frequency + ε''_{Dipole}

A measure of total energy lost due to the work performed aligning dipoles and moving ions in a material.

tan δ = Dissipation factor = $\varepsilon''/\varepsilon'$ = tan (90°- φ),
φ = phase shift

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Ionic Conductivity

$$\boldsymbol{\sigma} = \varepsilon'' * \omega * \varepsilon_0$$

[S / m] = [1 / Ωm]

Loss Factor

$$\varepsilon'' = \frac{\sigma}{\omega * \varepsilon_0}$$

[-]

Ion Viscosity

$$\boldsymbol{\rho} = \frac{1}{\sigma}$$

[Ω * cm]

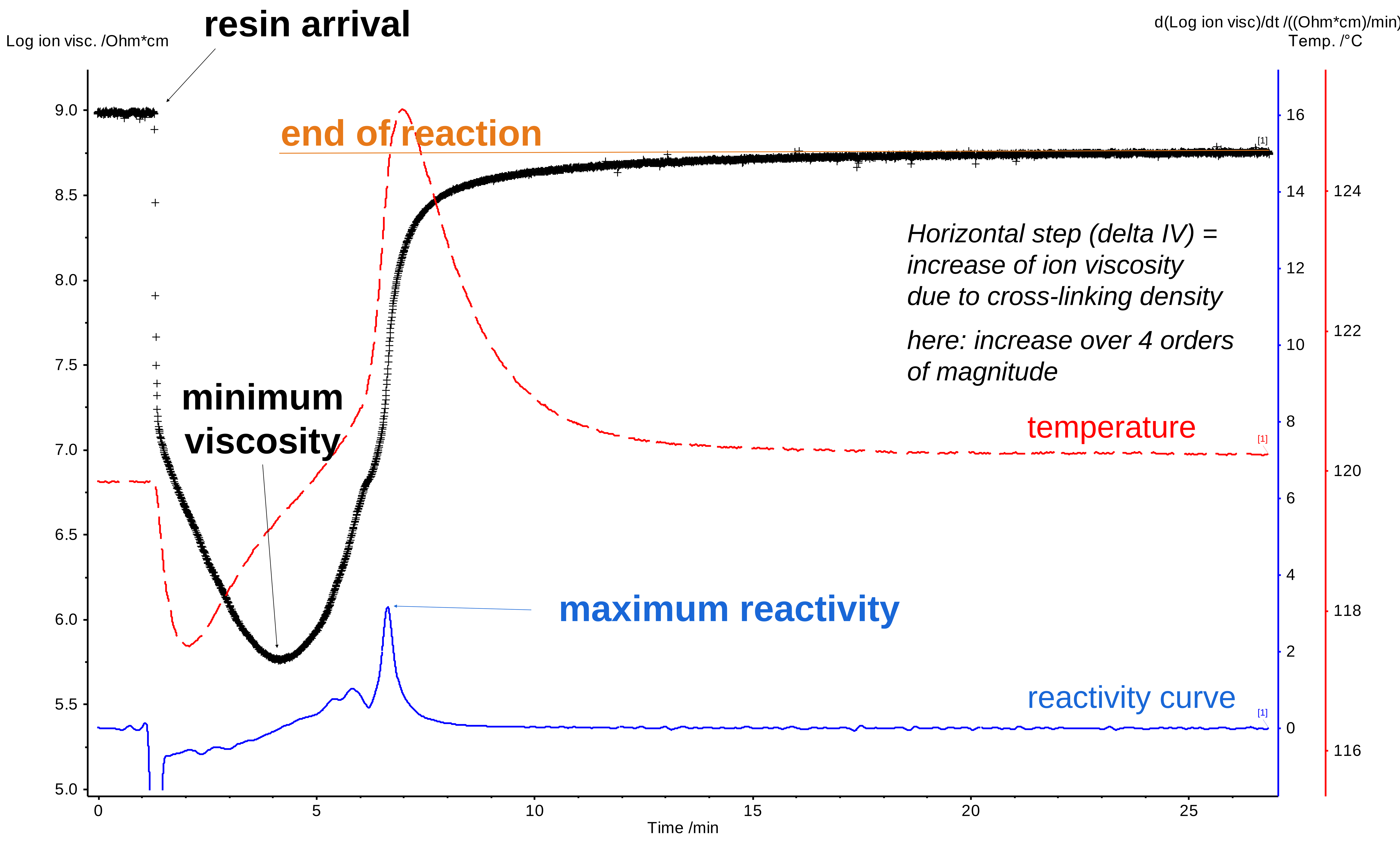
ω = Angular frequency = 2π f

f = Frequency [Hz] = [1 / s]

ε_o = Permittivity of free space = $8.854 * 10^{-12}$ F/m

[F / m] = [C / Vm] = [As / ΩAm] = [s / Ωm]

What a dielectric measurement looks like?



DEA correlation with glass transition (Tg) increase during isothermal epoxy cure

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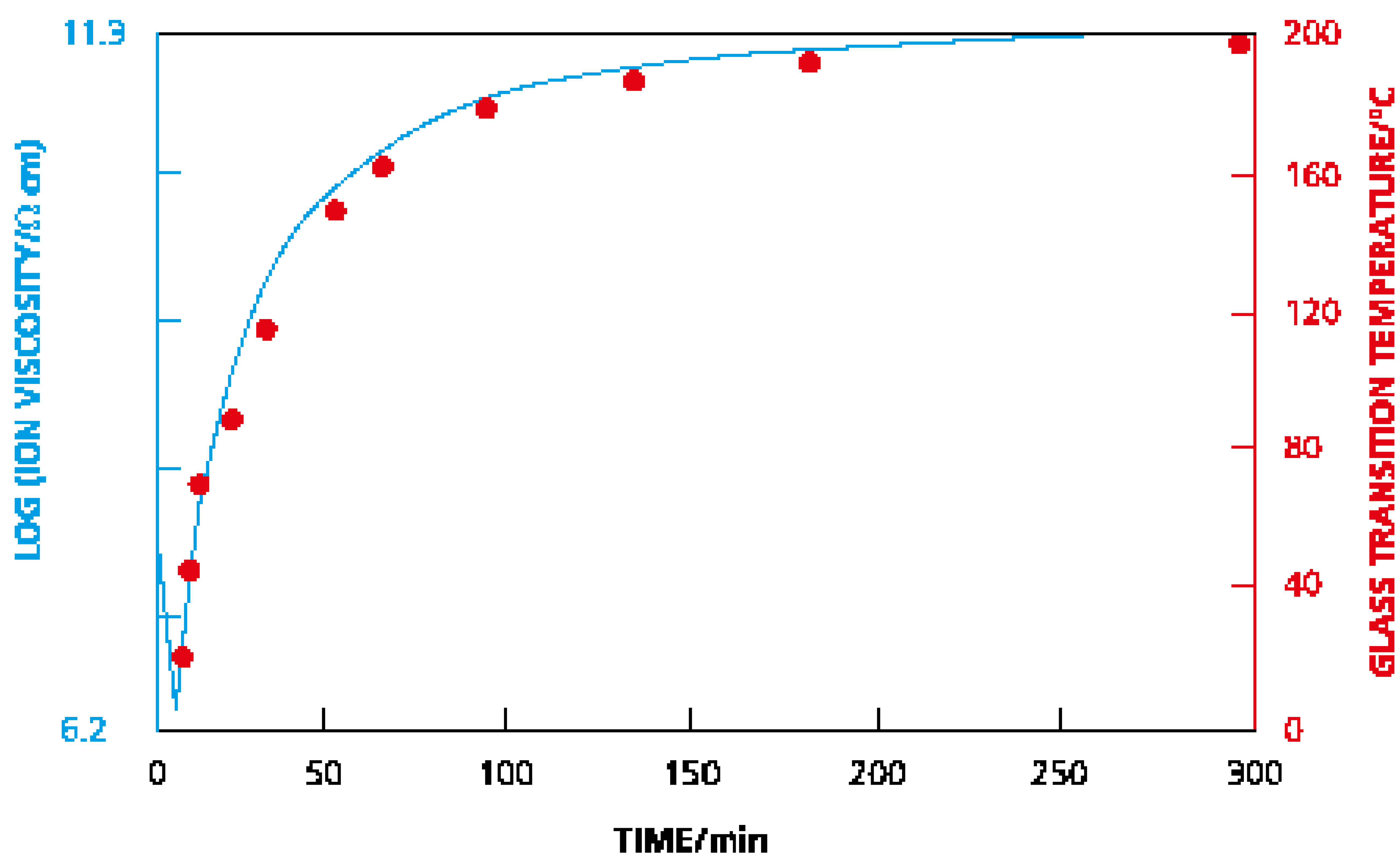

- During the isothermal cure of an epoxy resin, the increase in log ion viscosity correlates well with the increasing glass transition temperature of the resin.
- This demonstrates that the ion viscosity can be used to continually monitor the increase in the cure state of a resin during processing.

DEA and DSC: Comparison of Degree of Cure Sensitivity

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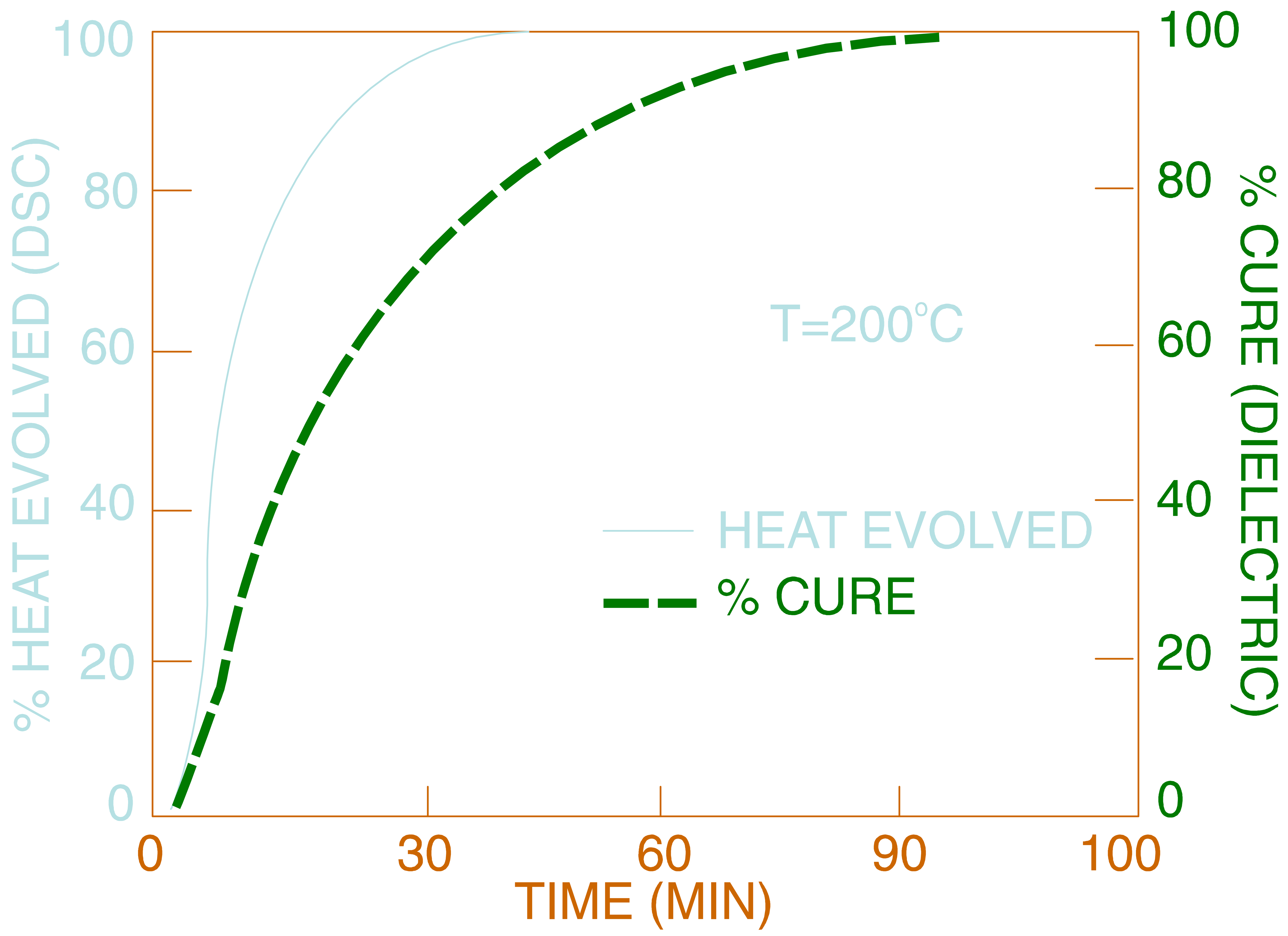
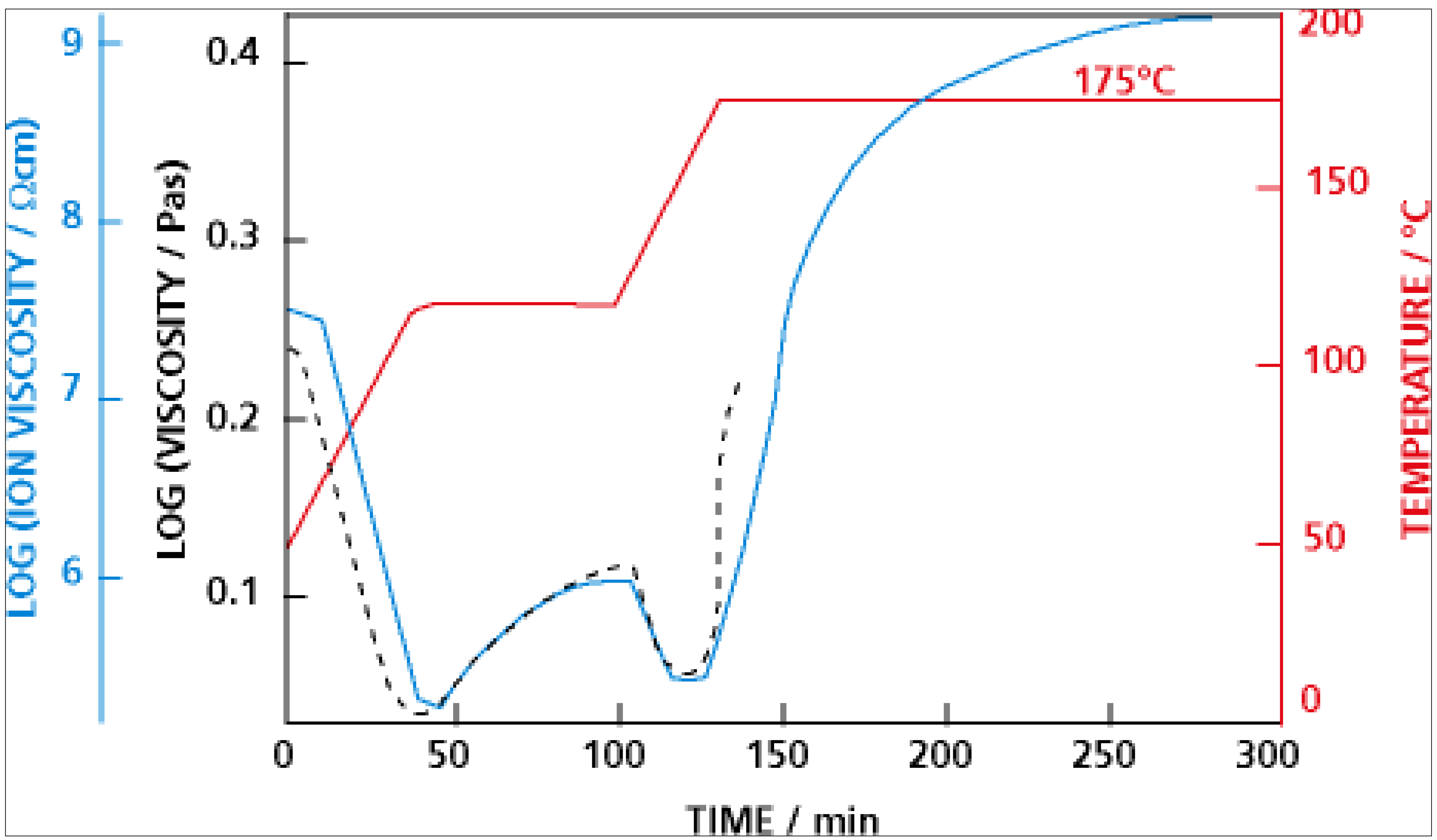
•**Dielectric Analysis is very sensitive to end of cure**



Comparison of Ion Viscosity (DEA) and Dynamic Viscosity (Rheology)

- Change in Ion Viscosity correlates with change in physical viscosity as measured by rheometer.
- After vitrification, rheometer can no longer make measurements.
- Ion Viscosity can monitor through the end of cure.



DEA Applications

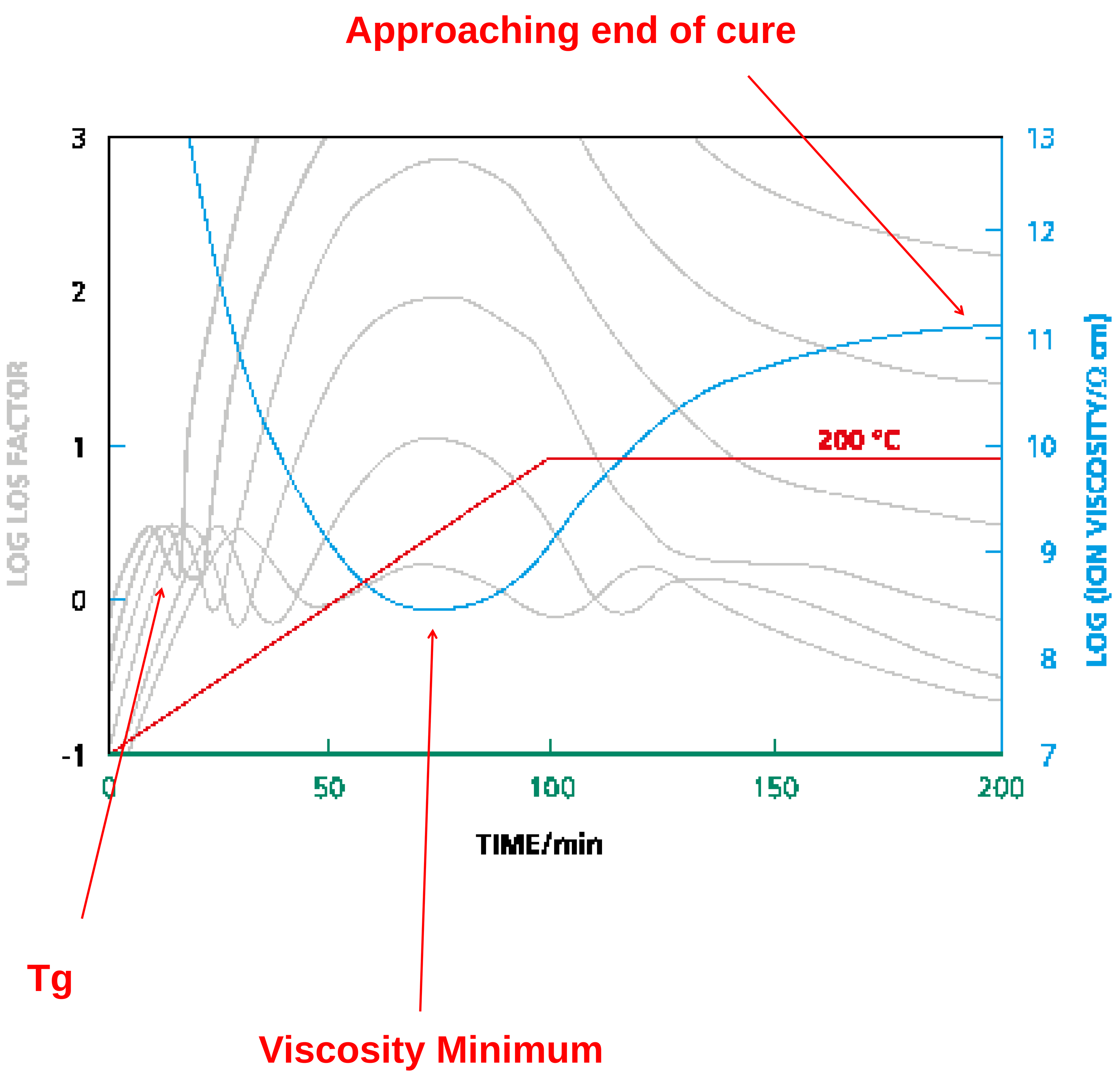
- Epoxy & polyester composites (graphite and fiberglass prepreg, RTM)
- Semiconductors (epoxy molding compounds & glob tops, silicone encapsulants, other potting compounds)
- Adhesives & bond lines (acrylic, epoxy, etc.)
- Coatings (powder coatings, e-coats)
- Polyurethane foam
- Batch reaction monitoring of resin polymerization
- Elastomers and rubbers
- Diffusion studies

Epoxy Resin during Melting and Curing: multiple frequencies

- Temperature is ramped, the loss factor shows a series of dipole relaxation peaks as the epoxy resin passes through the Tg temperature.

- The loss factor then rises rapidly as the epoxy melts, due to the increase in ionic mobility in the resin.

- The ion viscosity (the viscosity of the polymer before gelation and rigidity after gelation) initially decreases with increasing temperature. The initiation of reaction, competes with the temperature effect by restricting mobility and results in viscosity minimum. After the minimum the ion viscosity increases due to the curing. When the Ion Viscosity no longer increases, no additional cure is occurring.



DiBenedetto delivers the relationship between conversion and T_g

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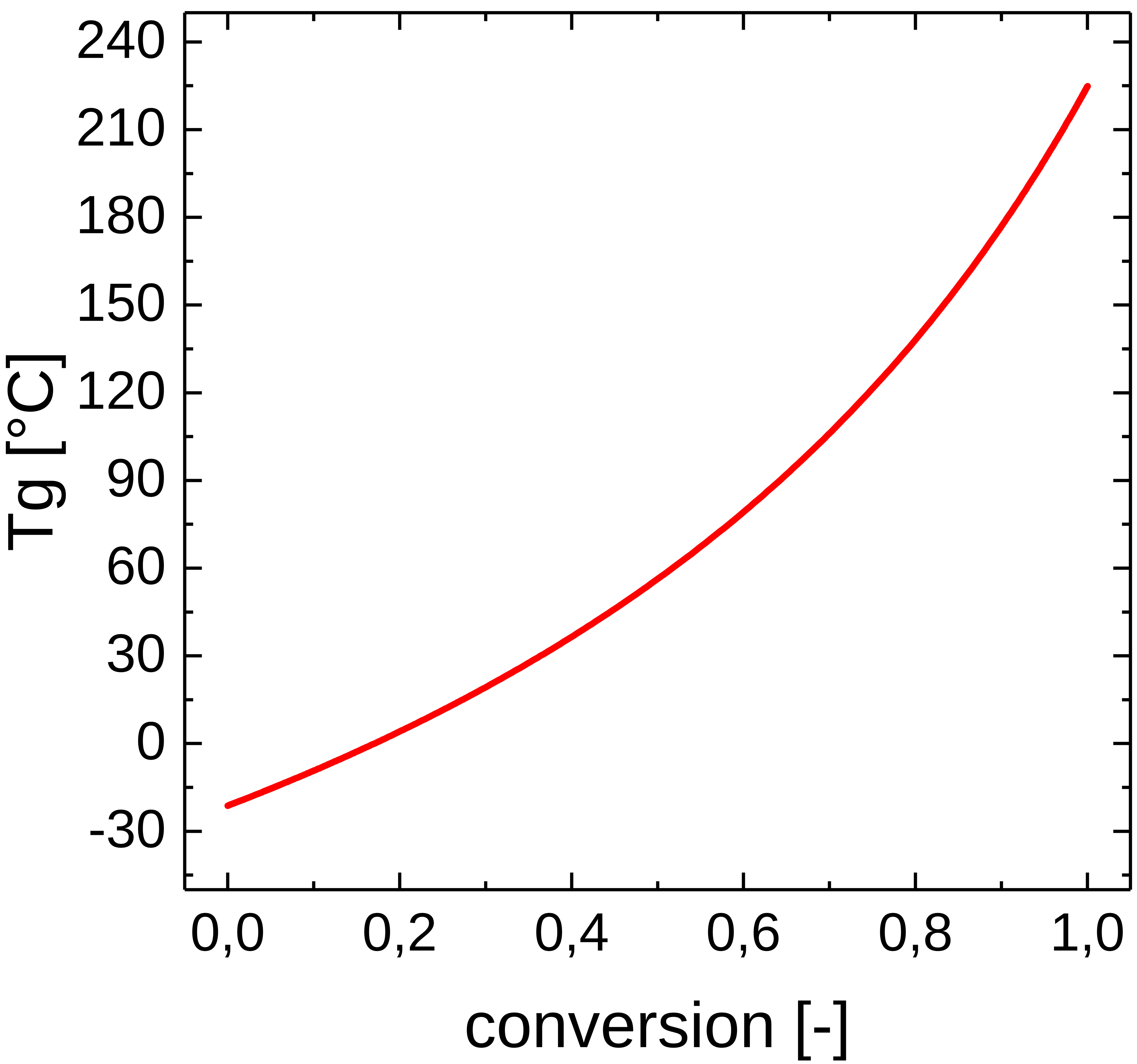

$$T_g(\alpha) = \frac{\lambda\alpha(T_{g1} - T_{g0})}{1 - (1 - \lambda)\alpha} + T_{g0}$$

α: conversion

λ: fit parameter

T_{g0}: glass-transition temperature of the uncured resin

T_{g1}: glass-transition temperature of the cured resin

Conversion and glass-transition temperature evolution

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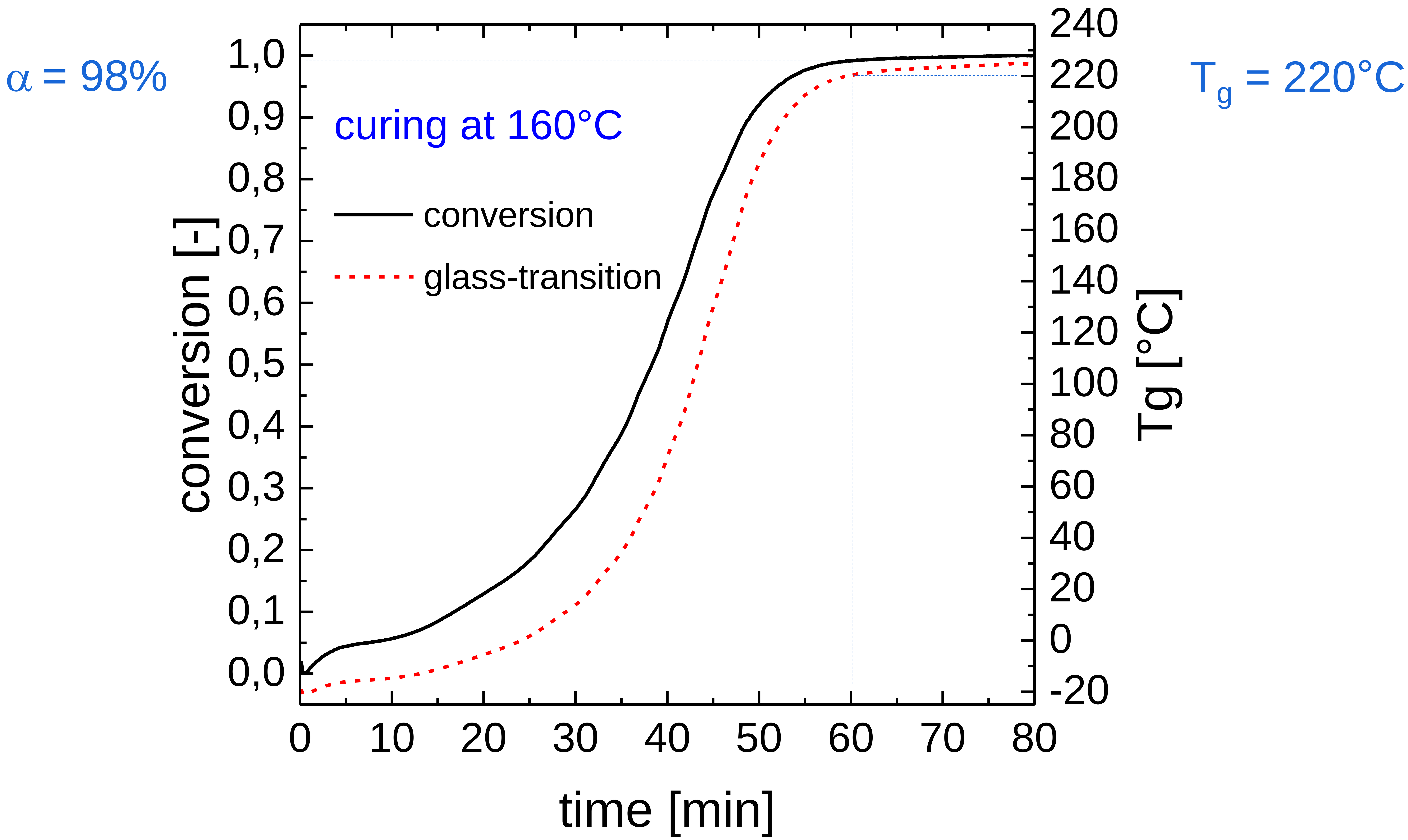

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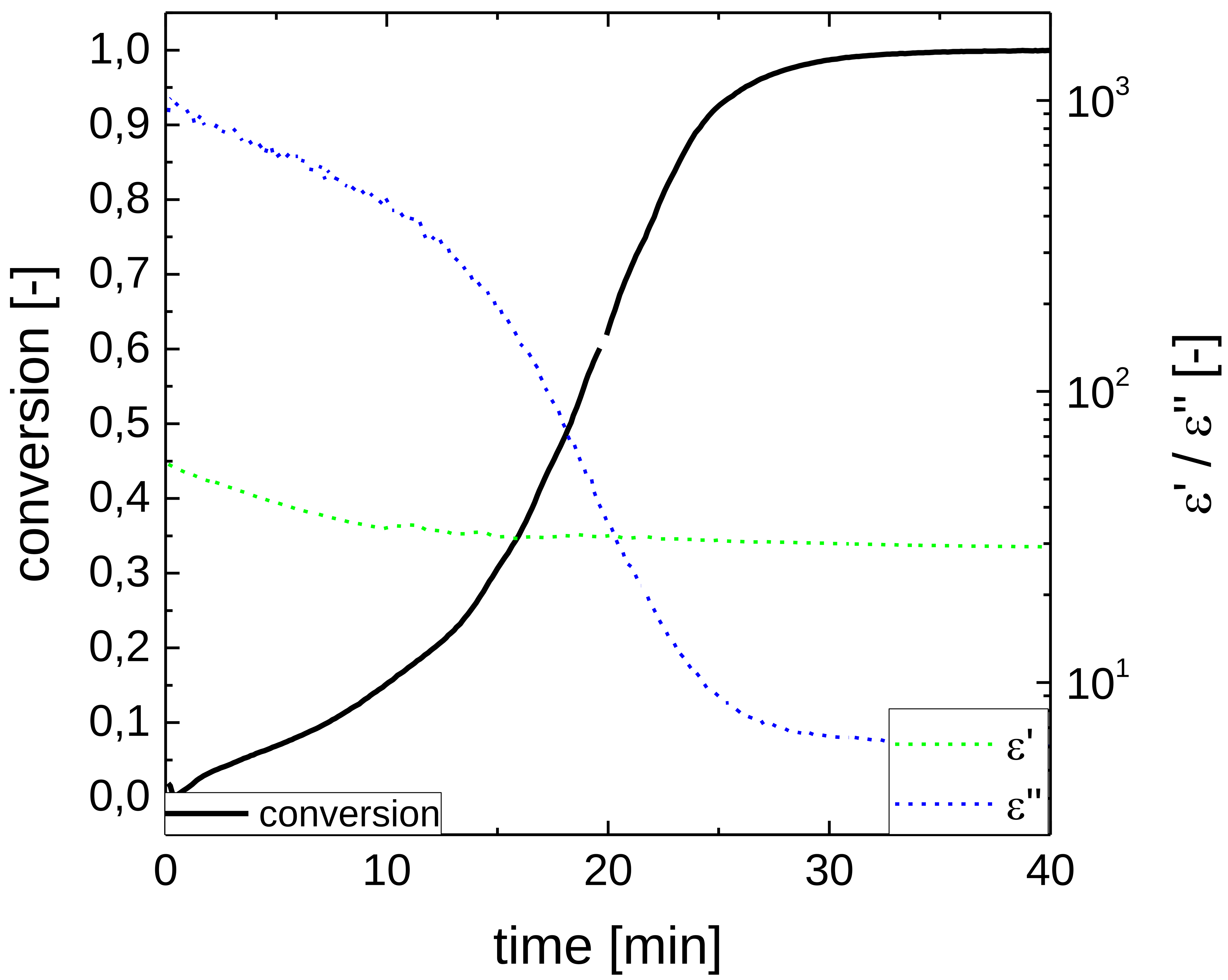
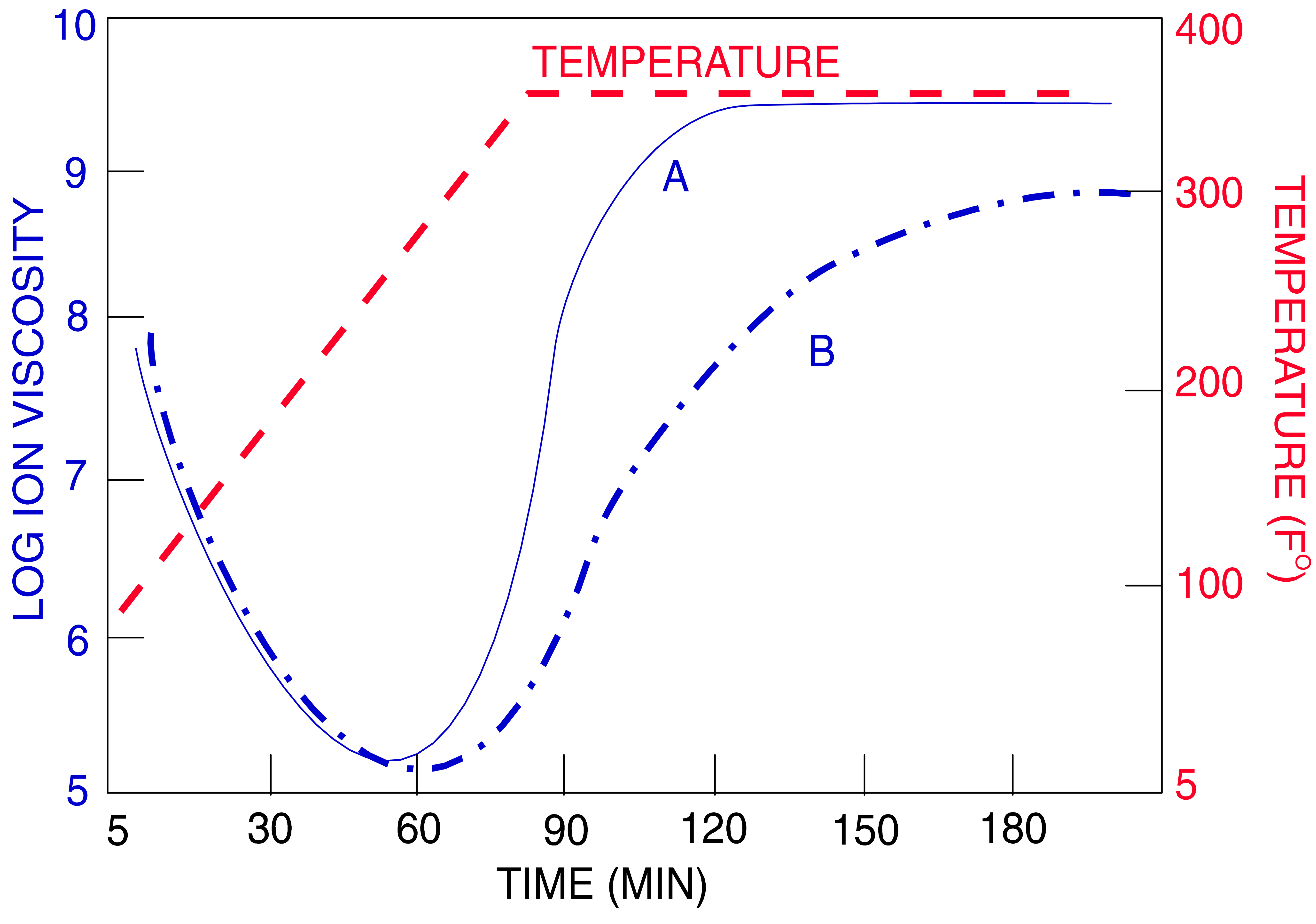
Gel-point as the point where resion stops flowing



Comparison of Epoxy Prepreg Cure

Two different suppliers of prepreg

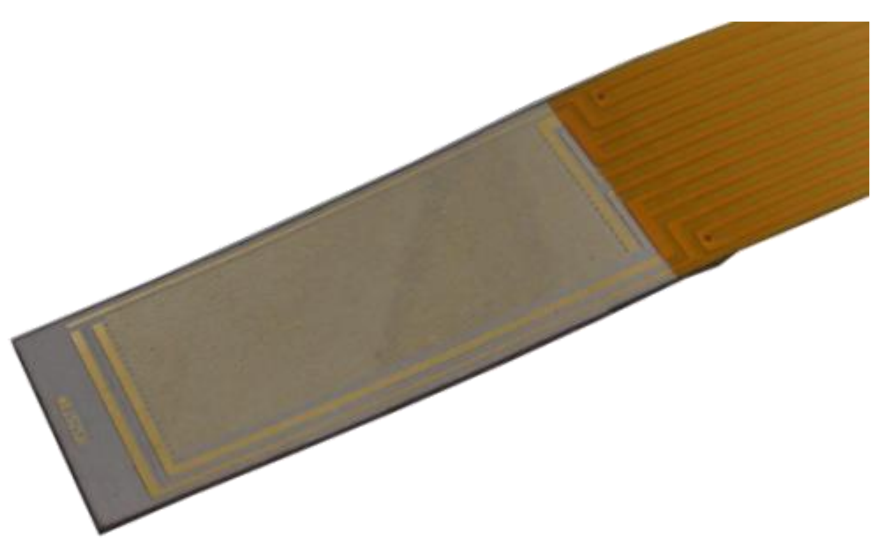


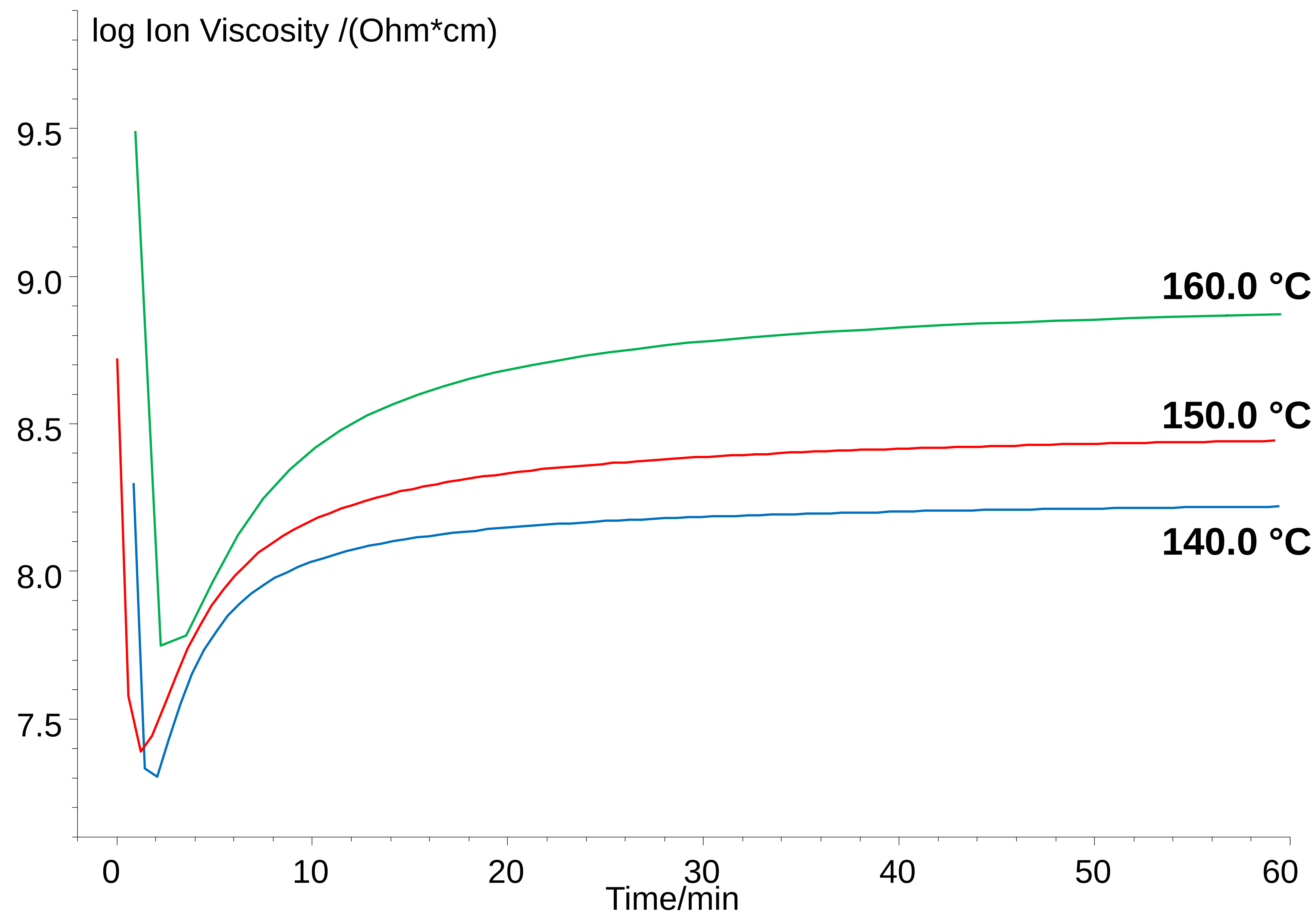
Cure Monitoring of Epoxy Powder Coating

3 Samples in DEA Furnace with IDEX-Sensor

Temperature of furnace: 140, 150 or 160°C

Cold powder coating was applied to preheated IDEX-Sensor



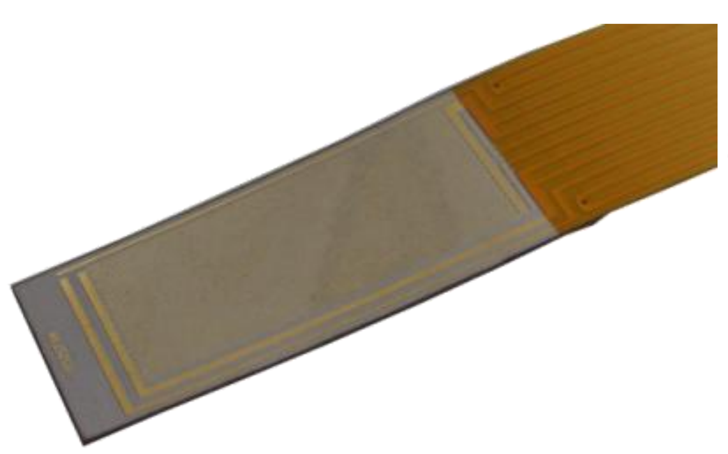


Ion viscosity @ 10 Hz and 3 Temperatures

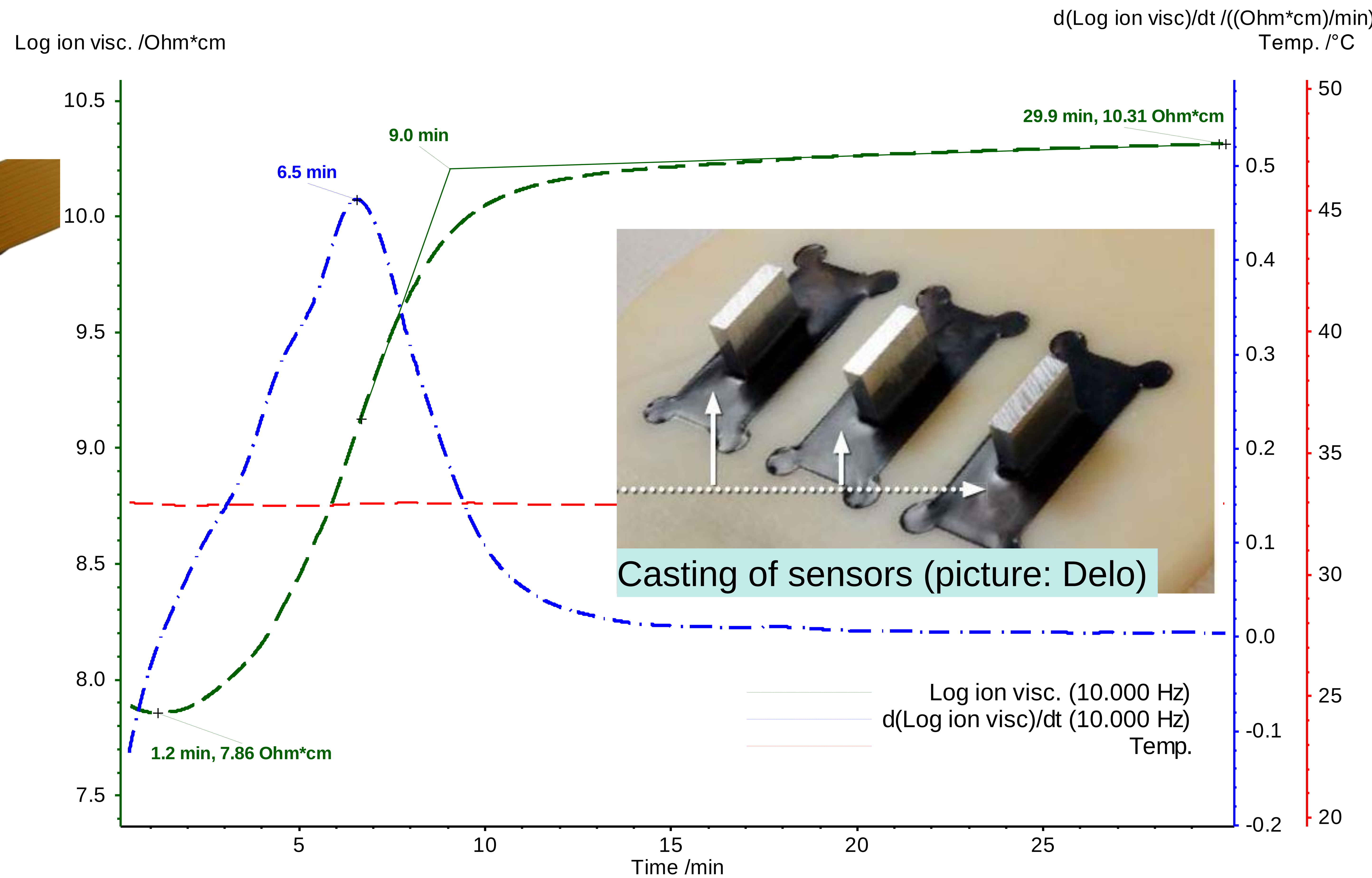
Cure Monitoring of Adhesive

DEA Furnace with IDEX-Sensor

Frequency: 10 Hz/ Temperature of furnace: 23 °C



IDEX

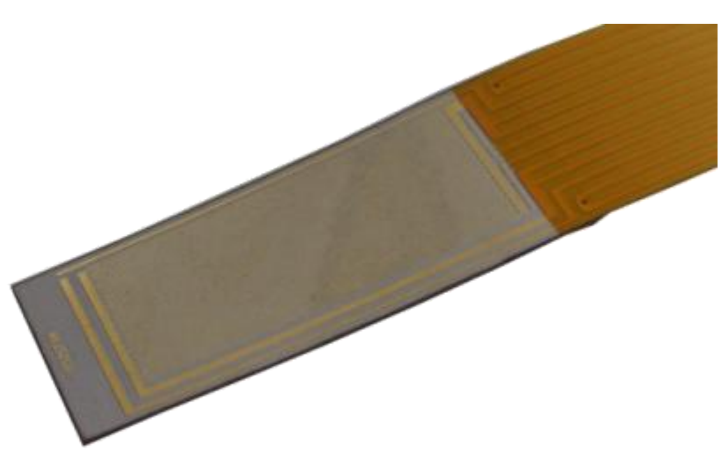


Curing of a 2-Component Epoxy Adhesive at Room Temperature

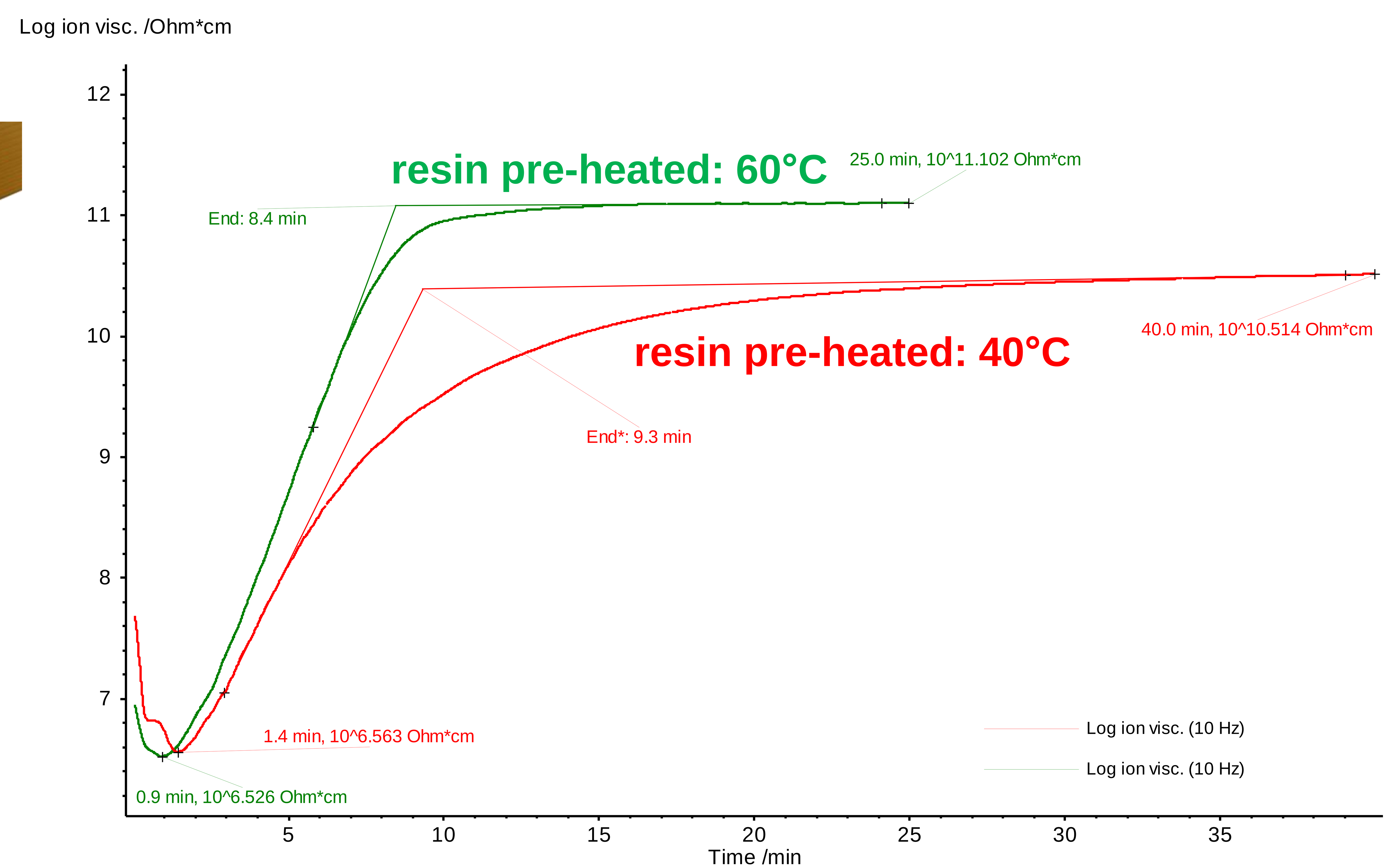
Cure Monitoring of Adhesive

DEA 288 *Epsilon,* Lab Furnace, IDEX 115/40

Material: 2C-Epoxy resin, Two resin samples were preheated to 40°C (red) or 60°C (red), respectively, Curing in DEA Furnace at 80 °C

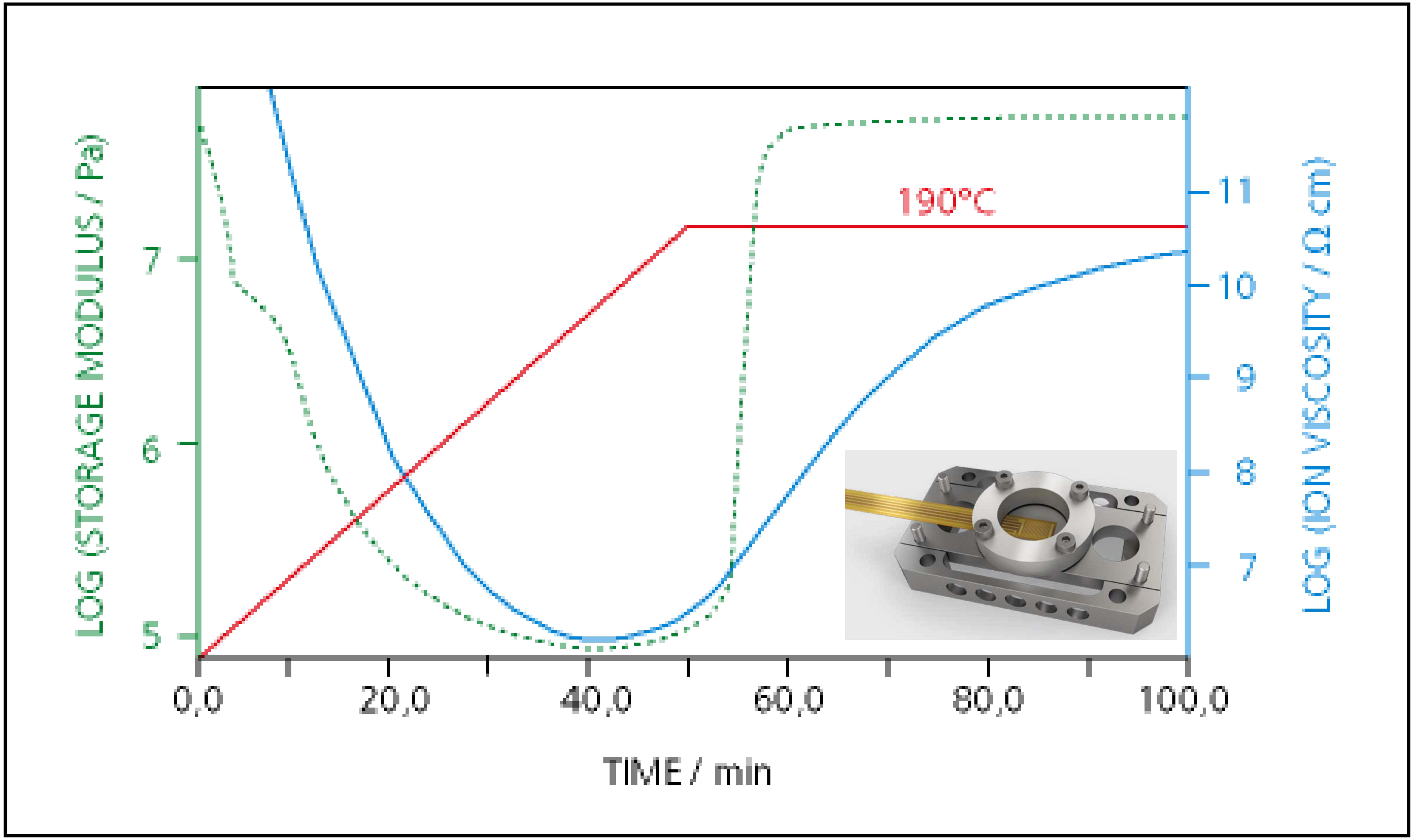


IDEX



Influence of Curing Temperature

Simultaneous DEA-DMA Measurement During Epoxy Resin Cure



Complementary techniques:
DEA with ion viscosity and DMA with storage modulus

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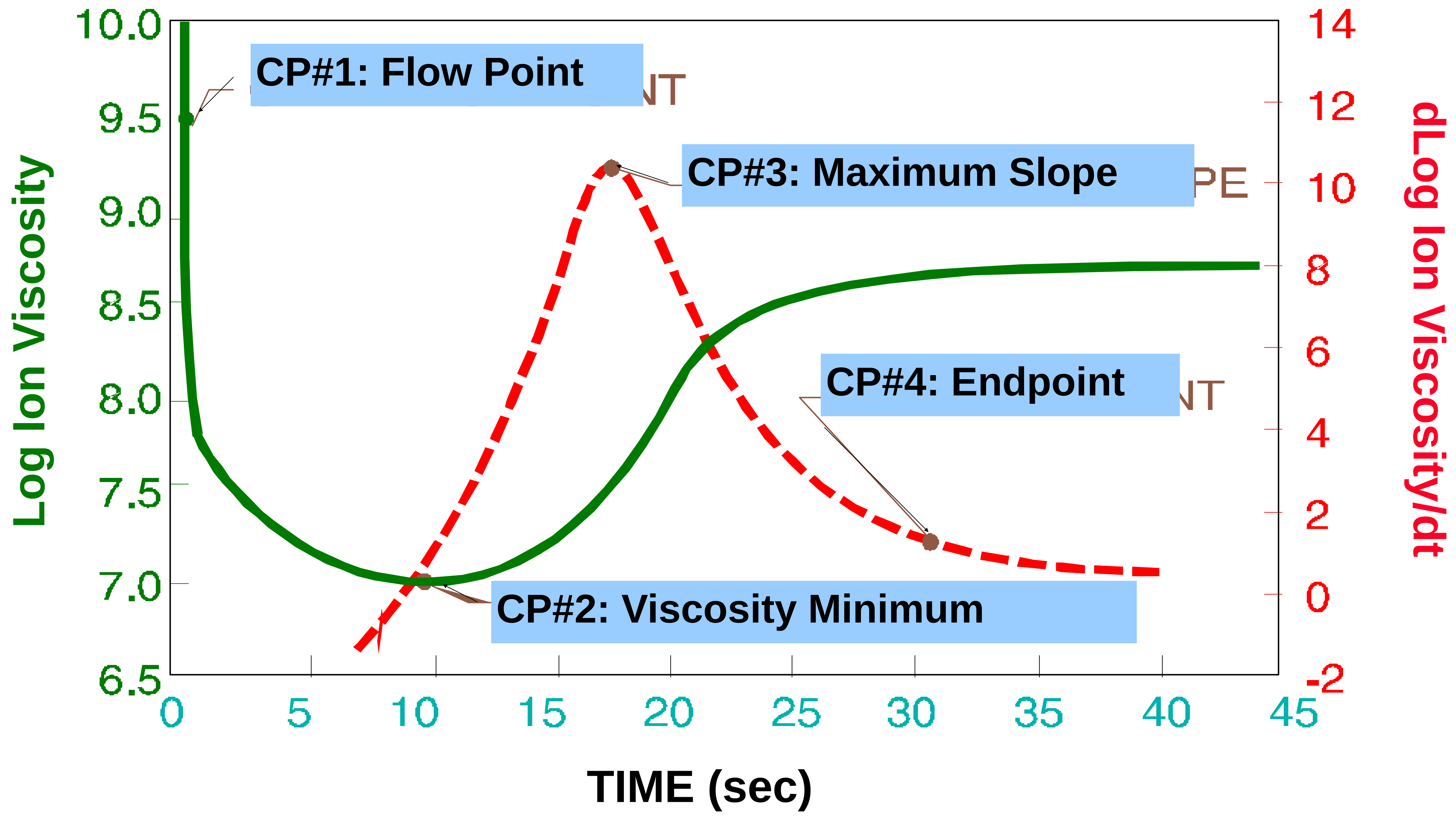
Dielectric cure monitoring is a common test in the polyester molding compound industry for:

- Quality evaluation (molding compounds producers and users)
- R&D of cure behavior (catalyst suppliers, molding compound producers)
- Process development of cure cycles (molders)
- Process monitoring & control (molders)

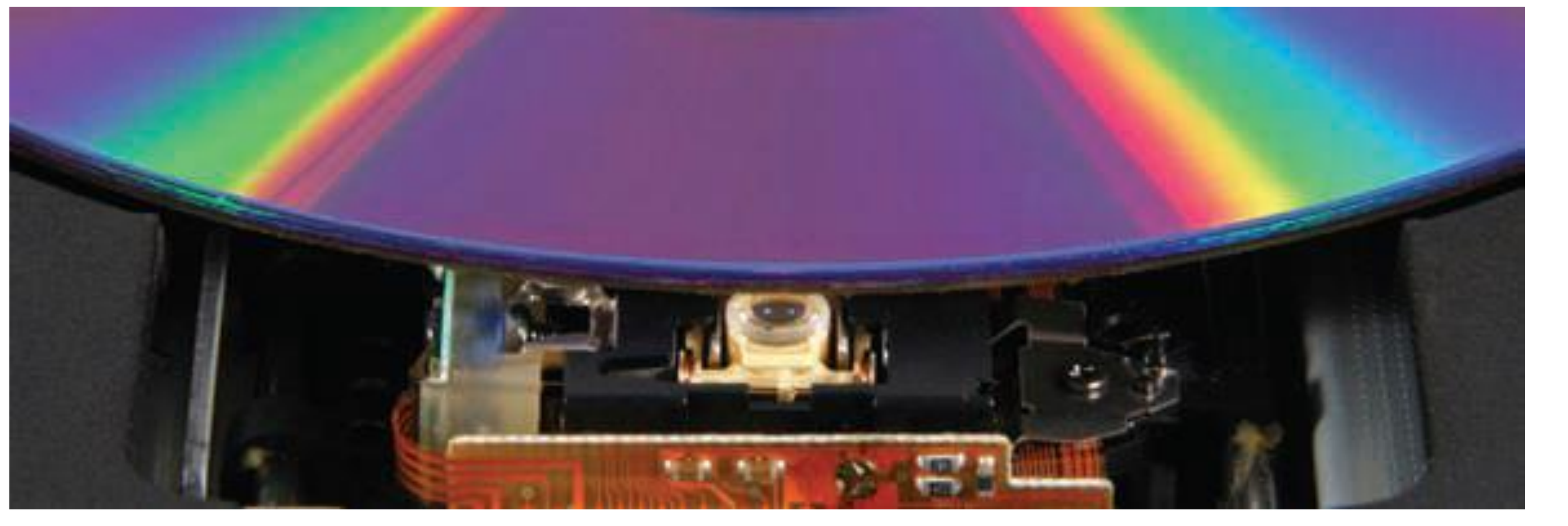
Polyester Bulk Molding Compound (BMC) Cure



UV Curing of Adhesives

Advantages of UV Curing

- High speed (high throughput)
- Low energy (no heating)
- No solvents (ecological aspect)



Different Types of UV Curing

Free radical UV systems (very fast)

Cationic UV systems (fast)

Dual cure systems (UV + heat)

Different Types of UV Adhesives

UV pressure sensitive adhesives (PSA)

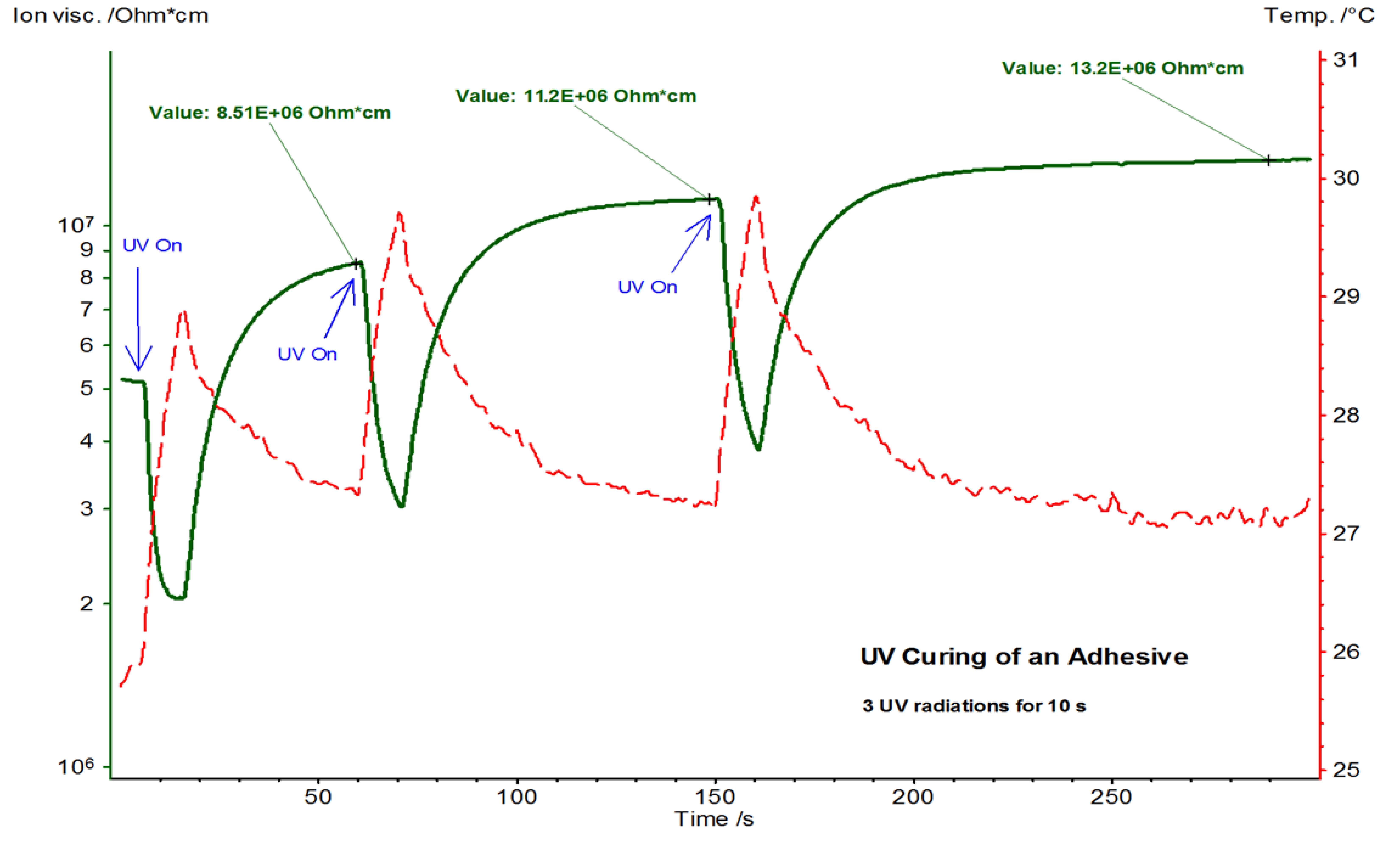
Constructive UV adhesives

UV laminating adhesives

UV Curing of an Vinylester-based Adhesive

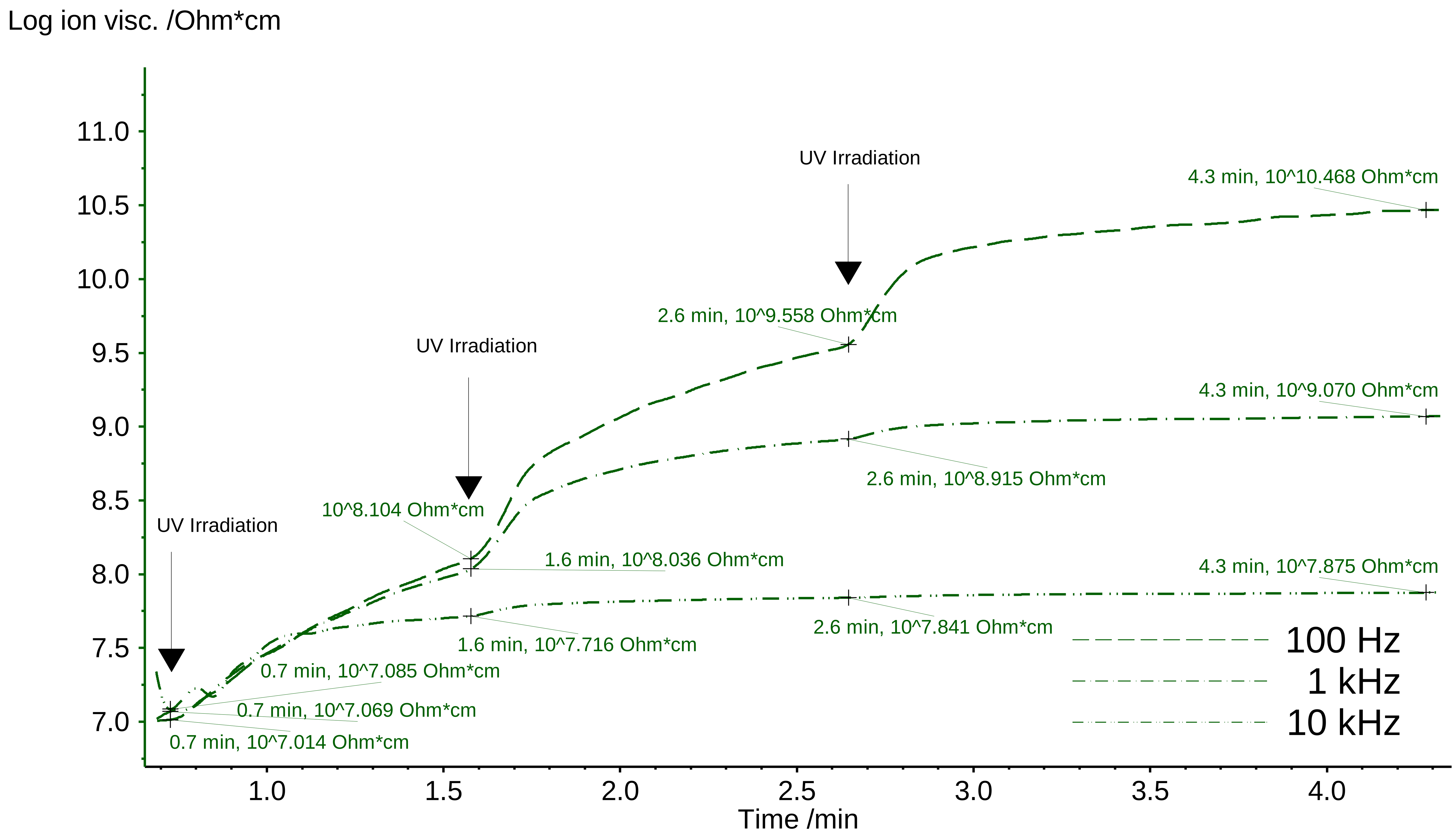
IDEX, 1000 Hz, 3 irradiations for 10 s each

Higher Ion Viscosity level after each exposure shows higher degree of cure achieved



Multifrequency-DEA-Measurement on Acrylate-Coating

100, 1000 und 10000 Hz, RT, Irradiation time 3 x 2s



Summary

- DEA (Dielectric Analysis) for cure monitoring is versatile and complementary to other thermoanalytical methods such as DSC or DMA.
- DEA with the high data acquisition rate is ideal for the fast UV cure monitoring - even in-situ.
- Along with the DEA electronics and comprehensive software, various sensors are available – tailored to your application.
- DEA is not restricted to the lab scale. It can be used in-situ in several industrial processes such as Resin Transfer Molding (RTM) and Sheet Molding Compounds (SMC) or for UV curing of paints and adhesives.
- With DEA the curing process can be not only monitored but also optimized in order to achieve high quality products.

Thank you for your attention!

Optimizing Your Curing Process of Thermosetting Resins by DEA

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