DEA Combined with Rheometry: More than the Sum of Two Methods

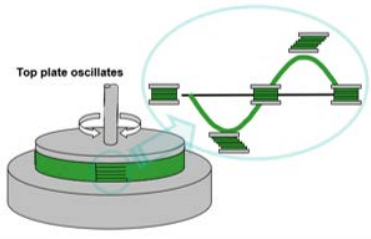
Applications Laboratory Rheology, Selb

Introduction

Accurate analysis of material properties is essential for optimizing performance and quality in industrial and research settings. The integration of Kinexus rheometry along with Dielectric Analysis (DEA) enables simultaneous assessment of the mechanical and electrical behavior within a single experimental framework. Combining these complementary techniques leads to deeper insight into complex materials, including polymers, composites, and curing systems. This approach allows for comprehensive understanding of the viscoelastic characteristics and dielectric responses, providing valuable data for process development, quality control, and advanced materials research.

Measurement Principle Rotational Rheometry

Rotational rheometry characterizes the viscoelastic properties of a material by measuring its response to an applied deformation under controlled conditions. In a typical oscillation test, the sample is placed between two geometries – commonly parallel plates or a cone-and-plate setup. One plate oscillates while the other remains stationary (see Figure 1), imposing a shear force on the sample.



1 Schematic of a rotational rheometer measurement: the sample is loaded between two plates, and an oscillational motion is applied to induce shear.

Controlled angular displacement or torque is applied, generating a shear strain, $\gamma(t)$:

$$\gamma(t) = \gamma_0 \cdot sin(\omega t)$$

The material responses with a measurable shear stress:

$$\tau(t) = \tau_0 \cdot sin(\omega t + \delta)$$

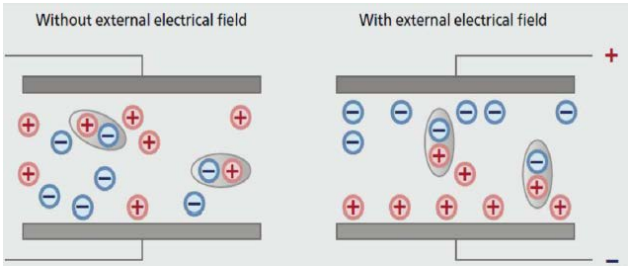
Here, γ_0 is the strain amplitude, ω is angular frequency, τ_0 is the stress amplitude, and δ is the phase lag between the applied strain and the measured stress. This phase lag reflects the material's viscoelastic properties.

Key rheological parameters include the elastic shear modulus (G´), viscous shear modulus (G´´), and complex viscosity (η^*). These are derived from the measured stress and strain responses and indicate the material's structure.

As the material undergoes changes (such as curing), its ability to resist deformation evolves. The formation of a polymer network increases stiffness and modifies the ratio of the viscous shear modulus, G´´ to the elastic shear modulus, G´ behavior.

Measurement Principle Dielectric Analysis

Dielectric analysis (DEA) is used to monitor changes in a material's dielectric properties during a controlled time/temperature program. In a typical DEA experiment, the sample is positioned between two electrodes – either parallel plates or interdigitated comb sensors (see Figure 2).



2 Principle of dielectric testing

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A sinusoidal voltage is applied:

$$U(t) = U_0 \cdot \sin(\omega t)$$

The material responds with an electrical current:

$$I(t) = I_0 \cdot sin(\omega t) + \phi)$$

Impurities within the material provide charge carriers that migrate toward the electrodes, while dipolar species (such as monomers or oligomers) orient themselves in the electric field. This behavior results in the measured current.

As curing progresses, a three-dimensional polymer network forms, reducing ion mobility and limiting the ability of dipoles to reorient. This restricts charge-carrier movement and dipole displacement. A key parameter derived from the measurement is the ion conductivity, σ. This ion conductivity depends on the mobility of free charge carriers and on the energy dissipated through dipole reorientation. The ion viscosity, ρ, is defined as:

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

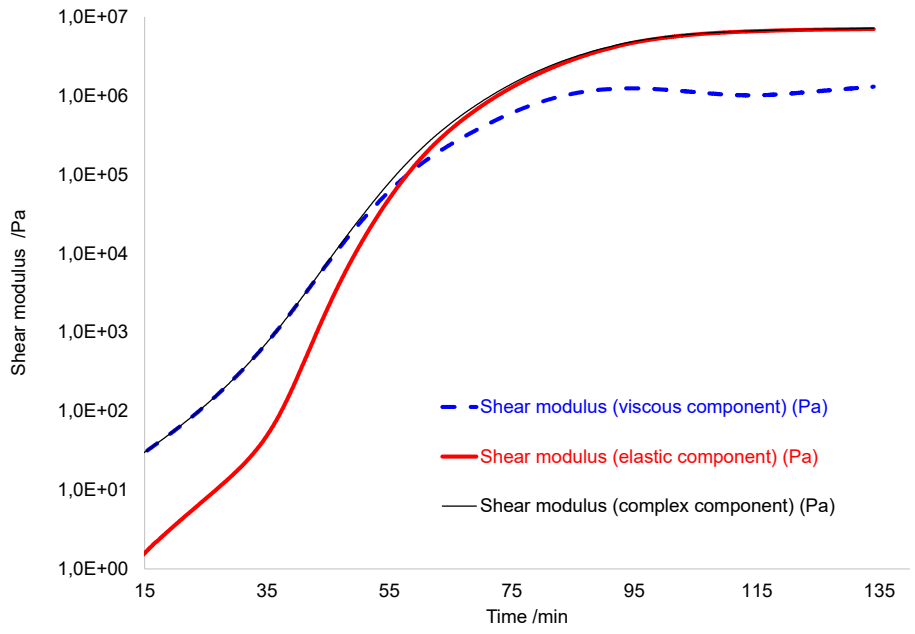
As curing advances, the expanding polymer network lowers the ion conductivity. This corresponds to an increase in ion viscosity.

Measurement Conditions

The combined measurement was performed using parallel plate rheometry (diameter: 8 mm) and dielectric analysis (DEA) on UHU Plus Endfest 300 (epoxy glue) at a constant temperature of 60°C. The rheometer operated with a 1% elastic shear strain and a frequency of 1 Hz. The normal force, shear modulus (G´), viscous shear-modulus (G´´), and complex shear viscosity (η*) were recorded as a function of time. The DEA measurement was performed simultaneously, using 100 mHz, 10 Hz, 100 Hz, and 1 kHz excitation frequencies, tracking the log(viscosity) in Ohm·cm over time.

Measurement Results

The rheological measurement shows a typical time-dependent curing profile of the epoxy adhesive at 60°C (Figure 3). Initially, the viscous shear modulus, G´´ is higher than the elastic shear modulus, G´, indicating a liquid-like state for the applied test conditions. As curing progresses, both signals increase, with G´ surpassing G´´ at 57°C, reflecting the transition from a liquid to a gel-like and finally to a solid network. This crossover G´/G´´ corresponds to the gel point for the timescale of the applied frequency (1 Hz).



3 Rheological curves resulting from the combined Kinexus/DEA test

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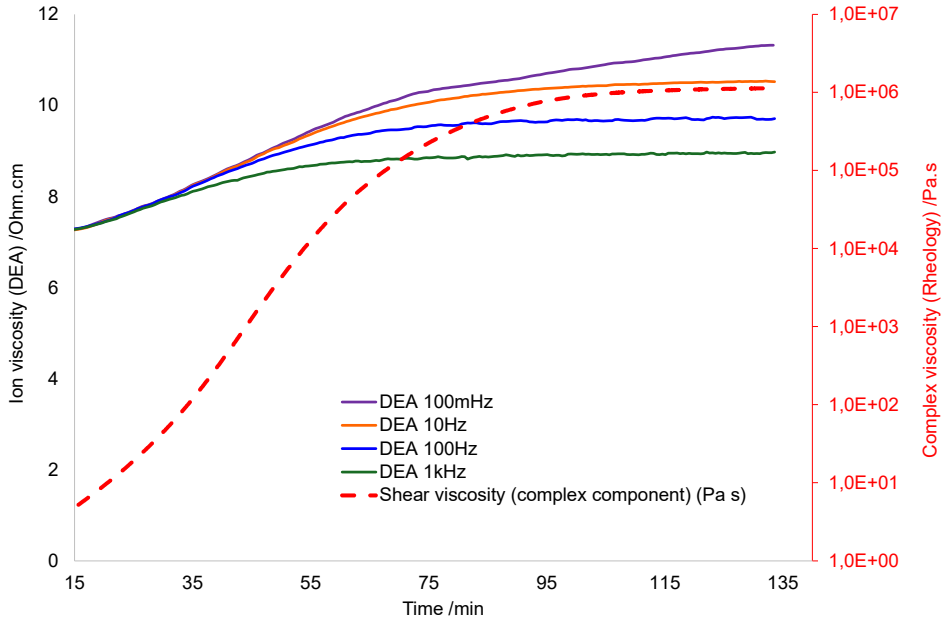

4 Curves of the complex shear viscosity (rheology) and ion viscosity (dielectrical analysis) during isothermal curing

Figure 4 presents the evolution of the complex shear viscosity (rheometer) along with the ion viscosity (DEA). The increase in ion viscosity measured for all frequencies indicates a decrease in dipolar and ion mobility as crosslinking increases. The plateau indicates the completion of the curing process. The higher the frequency, the more rapid is the plateau reached. At lower frequencies, such as 100 mHz, the signal does not reach a plateau by the end of the measurement, suggesting that the reaction is not yet complete. The frequency dependence of the signals reflects their differing sensitivity to fast and slow segmental motions.

An important aspect of combined analysis is the complementary sensitivity of the two methods. While rheological data provide robust information on network formation and mechanical transitions, rheometry becomes less informative once the sample has become very stiff: the mechanical data tend to plateau, as further network development cannot be resolved through macroscopic deformation. In contrast, dielectric analysis (DEA) remains highly sensitive to ongoing molecular dynamics and changes in ion mobility, even after the sample has become too stiff for mechanical deformation. This is illustrated by the 100-mHz DEA curve, which continues to evolve and indicate ongoing reaction, even when the rheological curve has reached its plateau. Thus, DEA provides valuable additional insight into the later stages of the cure and ensures a more complete picture of the reaction progress.

Conclusion

This application demonstrates the advantage of combining rheometry and DEA for monitoring epoxy curing. The NETZSCH system provides simultaneous mechanical and dielectric data, allowing users to track both macroscopic and molecular-level changes throughout the entire process. While rheometry excels at identifying mechanical transitions and the gel point, DEA continues to deliver detailed information on the reaction's progress, even after the sample has become too stiff for further mechanical probing. As a result, DEA offers unique value by ensuring full visibility of the ongoing curing, supporting process optimization and ensuring high-quality, fully cured products.

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