NETZSCH

Analyzing & Testing

Dielectric Cure Monitoring

Method, Technique, Applications

Leading Thermal Analysis

DEA 288 *Epsilon* – Opening a New World of Cure Monitoring

Clear-cut Determination of the Curing Behavior

Dielectric Analysis (DEA) or Dielectric Thermal Analysis (DETA) is a technique for monitoring changes in the viscosity and cure state of thermosetting resins, adhesives, paints, composites and other kinds of polymers or organic substances by measuring variations in their dielectric properties.

Advantages of DEA

Customized Test Conditions

The multi-functional design of the DEA 288 *Epsilon* (including furnace or laboratory press) allows for a great variety of different test conditions such as heat, cold, humidity or UV light. This makes it easy and convenient for the user to determine the best parameters for processing the material.

Practicality of Design for Sample Handling

One great advantage of DEA is the fact that it does not require a different amount or geometry of sample than is used in the real process. By applying the wide range of available sensors, almost any practical application can be reproduced:

- Spray coating of thin films
- Application by a drawbar
- Spreading of low- or medium-viscosity materials
- Positioning of the sensor between the layers of a prepreg
- Dipping of the sensor in a liquid

Selection of implantable sensors

Additional information

www.netzsch.com/DEA288

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Your Benefit

Development of Optimized Resin Formulations

Often, polymers achieve their full performance potential only upon being combined with active additives. Such additives serve to adjust the morphology or the polymer architecture in a targeted manner. Whit the DEA 288 *Epsilon*, the effectiveness of accelerators, inhibitors, and antioxidants, can be measured quickly and reliably, as can the impact of substances such as fillers. Such insight can have tremendous impact on efforts toward shortening the development process.

Determination of Ideal Process Parameters

Both the lab and the slim versions of the DEA 288 *Epsilon* (see page 6) were originally designed specifically for use in laboratories - whether industrial or academic. However, the same instruments and sensors can also be used in manufacturing environments. The DEA 288 *Epsilon* thus allows for the transfer of parameters developed in the lab directly to production.

Laboratory version of the DEA 288 *Epsilon* with up to 8 DEA modules

Dielectric (Thermal) Analysis – The Method

DEA (or DETA) Technique

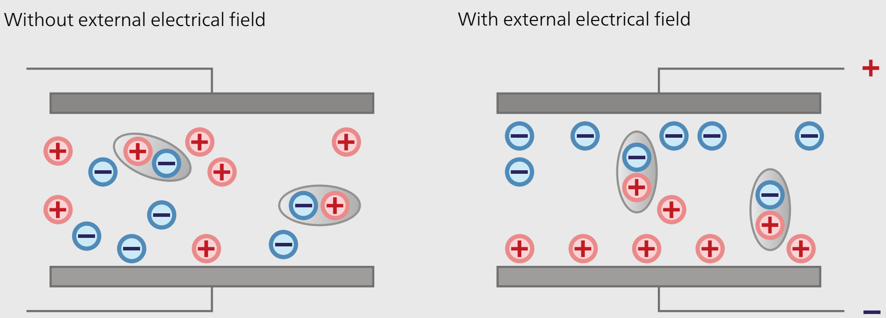
Fundamental Principle

The functional principle is consistent with that of an impedance measurement.

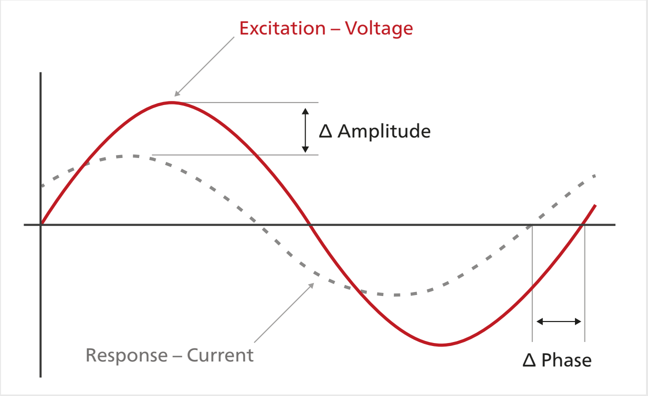
In a typical test, the sample is placed in contact with two electrodes (the dielectric sensor). When a sinusoidal voltage (the excitation) is applied, the charge carriers inside the sample are forced to move: positively charged particles migrate to the negative pole and vice versa. This movement results in a sinusoidal current (the response) with a phase shift.

In the frequency range of the DEA 288 *Epsilon* (up to 1 MHz), the charge carriers are mainly ions (often present as catalysts or impurities), but dipole alignment also takes place within the electrical field.

The amplitude and phase shift of the current signal are a function of the ion and dipole mobility. This relationship makes dielectric (thermal) analysis an ideal method for cure monitoring. As the curing reaction progresses, the sample material becomes increasingly viscous. As a consequence, the mobility of the charge carriers decreases, followed by a corre-sponding attenuation of the amplitude and an increased phase shift in the resulting signal.



Behavior of ions and dipoles inside an external electrical field



DEA – Measurement principle

Measurement Information and Results

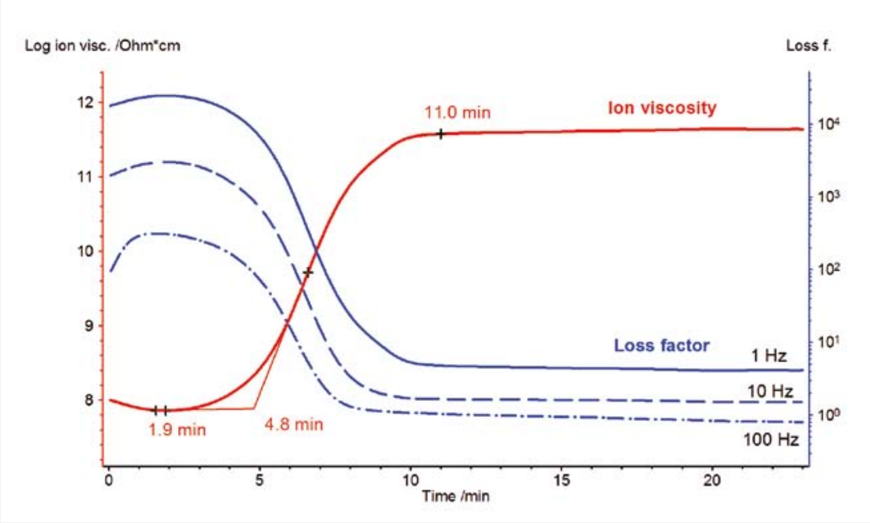
The measured amplitude is correlated with the dielectric permittivity ε' and reflects the number of dipolar groups in the resin.

The dielectric loss factor ε'' can be calculated from the phase shift. It is a measure of the total energy lost due to the work performed while aligning dipoles and moving ions in a material. In addition, ε'' is proportional to the ion conductivity, σ, which is the reciprocal value of the ion viscosity, ν. This ion viscosity is the most relevant parameter for curing studies. It describes curing processes very well and correlates with the dynamic viscosity.

DEA laboratory version with 8 DEA modules (backside view) plus adaptor box for connection to implantable sensors

Application Areas

- Research
- Process Development
- Quality Control
- Quality Assurance



Graphical presentation of the loss factor (in logarithmic scaling - for 1,10 and 100 Hz) and the corresponding ion viscosity of a 2-C epoxy adhesive as a function of time at room temperature. Following the decrease in ion viscosity (blue, logarithmic presentation) – as a result of the spreading of the sample on the sensor – the curve starts to increase when curing begins. Taking the extrapolated onset temperature of the ion viscosity (4.8 min) into account, the maximum working time can be derived to be approx. 4 minutes. On the whole, the ion viscosity increases during curing for about 4 orders of magnitude and is finished after approx. 11 minutes.

DEA Measurement Information

- Ion viscosity
- Flow behavior
- Reactivity
- Cure monitoring
- Degree of cure
- Glass transition temperature
- Process control and optimization
- Diffusion properties
- Aging
- Decomposition effects

Elaborate DEA 288 *Epsilon* Instrumentation

Cutting Edge Technology – Benchmark for Dielectric Analyzers

A complete dielectric analyzer consists of the DEA electronics and a sensor. Disposable sensors are connected via an adaptor box. For laboratory use, two models of DEA 288 *Epsilon* are available: the regular laboratory version and the slim version.
Both instruments are equipped with the same state-of-the-art electronics and have the ability to control additional accessories such as the lab furnace or lab press. The technical differences between the devices are in the design of the casing, the footprint and the maximum number of channels.

Slim version of the DEA 288 *Epsilon* with 2 DEA modules (channels)

DEA 288 Laboratory Version

The laboratory version is a perfect fit into the NETZSCH instrument line for thermal analysis and thermophysical properties detection (see picture below) which is also reflected by its physical design.

The footprint of the laboratory version is identical to that of a DSC or a TGA system. Additionally, the multi-channel option allows up to 8 samples to be measured in one run, making this instrument ideal for process development.

DEA 288 Slim Version

This instrument is specially designed for lab environments in which there is a very limited amount of space. The cabinet of this "slim version" only occupies approximately as much bench-top space as a sheet of paper (DIN A 3 or Tabloid B size). The device is also portable.

This instrument is ideally suited for research on thermosetting resins, composites, paints, adhesives and coatings.

Sensible testing configuration for analyzing curing reactions: DEA 288 *Epsilon* (laboratory version, left), adaptor box, DSC 204 ***F1*** *Phoenix*® with ASC (right)

Both DEA 288 versions cover a wide range of measurement frequencies (from 0.001 Hz to 1 000 000 Hz) in order to accurately determine the changes in dielectric properties during reaction. With their minimum data acquisition time of less than 5 ms, the instruments can even handle quickly curing systems such as UV curing. All devices come ready-equipped to be connected to thermocouples (separate or integrated into the DEA sensor) or to resistive temperature detectors (RTDs), so that the temperature data can be collected along with the dielectric information. Each channel has its own input.

Technical Specifications of the DEA 288 *Epsilon*

General	
Frequency range	1 mHz to 1 MHz, freely selectable values
Data acquisition multiple DEA modules	True simultaneous operation of all channels
Minimum data acquisition time	< 5 ms
Sensor connection	Guarded, 4-wire technique (compensation of resistivity and capacity of the wire as a prerequisite for precise measurements)

Model specific		
	Slim Version	Lab Version
Footprint (without cabling)	(W x D) 25 cm x 45 cm	(W x D) 57 cm x 53 cm
Number of DEA modules	Up to 2	Up to 8

Calibration plug for automatic adjustment of the electronics

Adaptor box - fast, easy and reliable connection of all implantable sensors, thermocouples or RTD sensors

Characteristics of the NETZSCH DEA 288 *Epsilon*

- Modular concept
- Simultaneous multi-channel measurements
- High data acquisition rate
- State-of-the-art technology

High Flexibility by Means of Various Sensor Types

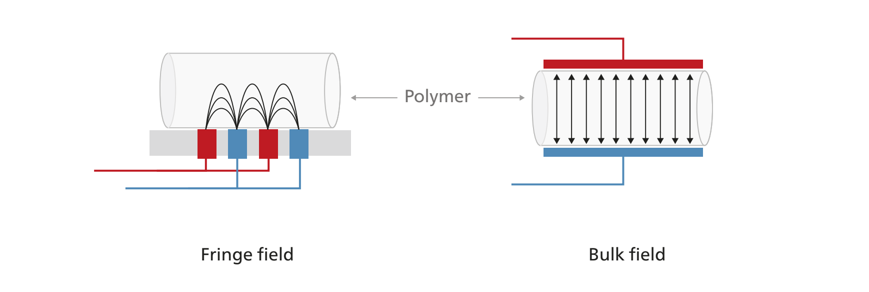
Sensitive and Versatile Sensors for Any Application

In order to meet the requirements of a multitude of polymer processing applications, NETZSCH offers a great variety of dielectric sensors. These sensors can be classified as implantable or reusable. The latter type can be permanently mounted, for example, into a press, a mold or even into a sample holder for both DMA and rheometer.

Implantable sensors are designed for one-time use and can be positioned at the desired location within a part or simply coated with material. A typical implantable sensor subtype is the standard IDEX (interdigitated electrode) sensor.

Most sensors are comprised of two interdigitated comb electrodes on an inert substrate. The resulting field of measurement is a fringing pattern; a localized measurement of the dielectric properties is carried out near the sensor/sample interface. The penetration depth of the electrical field lines into the sample is of approximately the same magnitude as the electrode spacing.

With comb electrodes, care should be taken that the sample particles are able to penetrate into the space between the electrodes. For inhomogeneous samples or sample materials containing larger particles, wider electrode spacing is recommended.

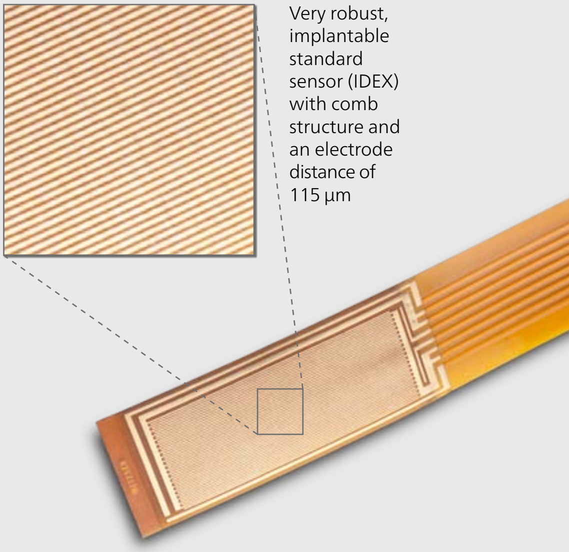


Course of the field lines in comb sensors (left) and sensors with parallel plate electrodes (right)

Reuseable TMS™ Sensor

A brand-new technology for implantable sensors is our integrated RTD (resistive temperature detection). The need for separate thermocouples to determine temperature is now a thing of the past.

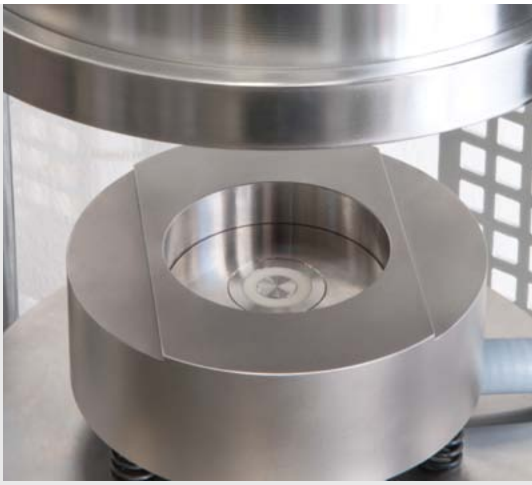
Additionally, reusable sensors are available which use a parallel plate electrode configuration and determine the bulk properties of a sample material. The Monotrode sensor can act as one of these plate electrodes. The opposing piece can be, for example, the corresponding grounded metal cover of a mold. If there is no mold or if the sample is very thick, the sensor housing acts as a second electrode.



Very robust, implantable standard sensor (IDEX) with comb structure and an electrode distance of 115 µm

For optimal matching to different mold geometries, NETZSCH offers both Monotrode and Tool Mount Sensors in various diameters. The sensors contain an integrated thermocouple. Moreover, they are pressure-resistant and able to withstand temperatures of up to 220°C.

By using a rugged cabling (> 20 m; theoretically unlimited in length), it is also possible to measure samples which are located at a considerable distance from the DEA device – for example, for in-process tests.



Monotrode sensor flush-mounted in a mold

Specification of Available Sensor Types

Sensor Type	Sensing Area	Max. Temperature	Electrode Spacing	Main Application	
Micron Sensor (MS)	2.5, 26 or 70 mm²	200°C or 350°C (depending on the wiring of the sensor head)	1, 5 or 25 µm	Paints, inks, adhesives	
Mini-IDEX (Interdigitated Electrode)	33 mm²	375°C	100 µm	All resins (small cavities)	
IDEX (Interdigitated Electrode)	20, 233 or 40 mm²	200°C or 375°C (depending on the wiring of the sensor head)	17.5, 115 or 1600 µm	All resins (epoxy, polyester PES, polyurethane PUR, etc.)	
IDEX, filtered	233 mm²	200°C or 375°C (depending on the wiring of the sensor head)	115 µm	Carbon fiber reinforced polymers (CFRP)	
Monotrode	Ø 4, 10 or 30 mm	220°C	-	Especially for SMC/ BMC, PUR foams	
Tool Mount Sensor (TMS™)	Ø 18 or 38 mm	220°C	500 µm	All resins (EP, PES, PUR, etc.)	

Smart Accessories for Process-Oriented Application

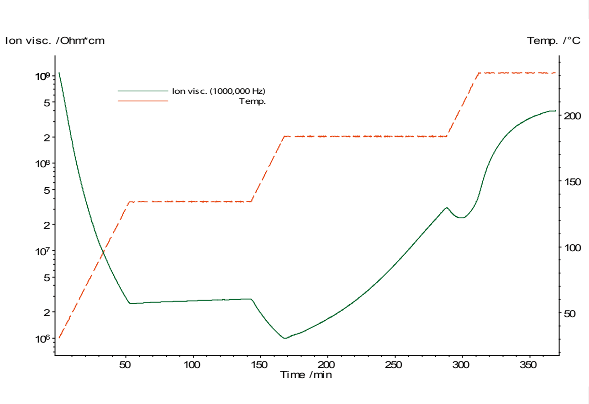
Accessories for Customized Test Conditions

For proper simulation of industrial-scale processes, NETZSCH provides a series of pertinent add-ons to the DEA instrumentation, such as the laboratory furnace, laboratory press, UV lamp for fast curing reactions, and humidity generator. These supplements can help bridge the gap between research, process development and production.

Multi-functional Lab Furnace

With the easy-to-operate, collapsible lab furnace, it is possible to carry out heating, isothermal or cooling steps in the temperature range from -150°C to 400°C by using either two IDEX (or MS) sensors or a single TMS™ (or Monotrode) sensor. Cooling can be realized via air compressor, Vortex tube (also air cooling), intracooler or liquid nitrogen (LN_2).

To establish a defined gas atmosphere inside, two purge gases (switchable by magnetic valves) can be attached. The furnace is designed to be connected to the fiber light guide of a UV lamp and/or a humidity generator.



With the DEA furnace, multiple temperature steps can be realized

DEA 288 *Epsilon* with accessories

Pneumatic Bench-Top Lab Press

Laboratory tests on Sheet Molding Compounds (SMCs), Bulk Molding Compounds (BMCs) and prepregs can be performed in an environment mimicking processing conditions by using a lab press, which is able to apply heat and pressure to the sample at the same time. The sample itself is either situated directly between the platens (including DEA sensor) or – optionally – in a separate spring mold, equipped with a Monotrode or a TMS™ sensor. The temperature program of the press can be controlled via the NETZSCH *Proteus*® software.

Technical data of the lab press:

- Temperature range: RT to 300°C
- Maximum force: 20 kN (at 10 bar)
- Platen diameter: 165 mm
- Force sensor

UV Lamp

The DEA 288 *Epsilon* system supports the OmniCure S2000 UV lamp for studying light-induced reactions such as the UV curing of adhesives, inks or paints. The duration and intensity of the UV exposure are software-controlled (via NETZSCH *Proteus*®). Multiple shots can be triggered during each segment.

The fiber light guide of the UV lamp is connected to the lab furnace.

Humidity Generator

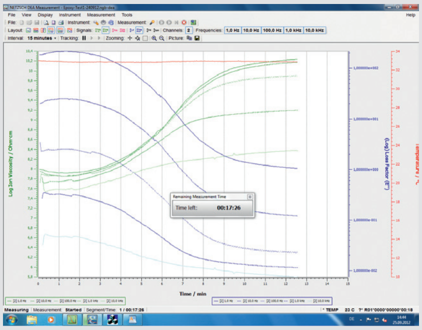
The humidity generator add-on serves to investigate the water uptake of cured samples or other organics. With the humidity generator displayed here, it is possible to create relative humidity values of between 5% and 90% in the temperature range from RT to 70°C.

Proteus® Software – Powerful and Easy to Use

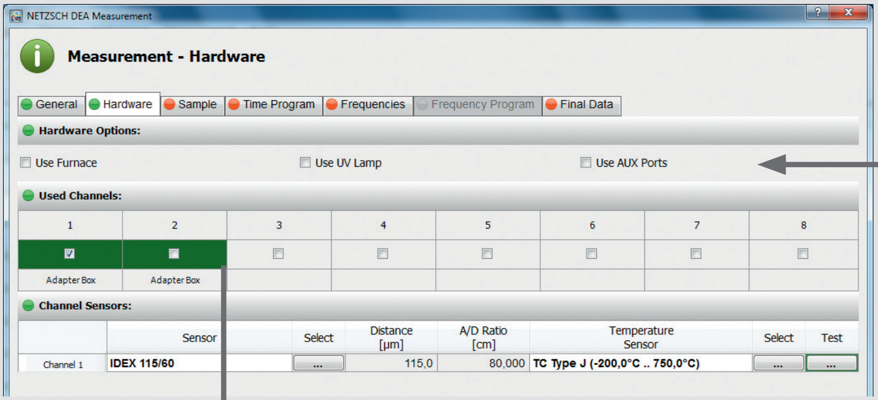
Comprehensive and Reliable

The measuring part of the software provides the user with a modern, user-friendly operating interface. *Proteus*® now offers a quick and convenient input assistant for programming all relevant measurement parameters. Color-coded tabs facilitate data entry and guarantee that no important parameter is forgotten – whether it relates to information about the sample, the temperature/time program or the desired frequencies.

Very helpful is the ability to post-program (for frequencies or duration) during a running measurement, as well as the option of online evaluation (SNAPSHOT).



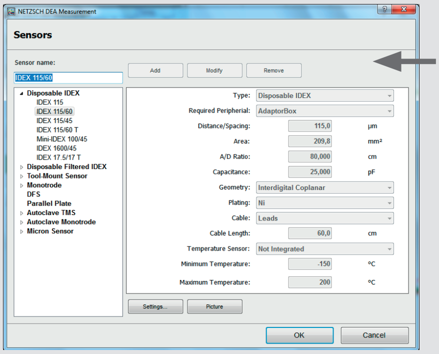
Screenshot of the user interface during a running measurement



Communication with certain accessories can be activated with a simple click. The NETZSCH *Proteus*® software controls the temperature profile of the lab furnace and triggers the UV lamp.

User Interface for Programming a Test Run

The desired channels can be easily enabled by selecting the appropriate check box. Active channels are colored green.

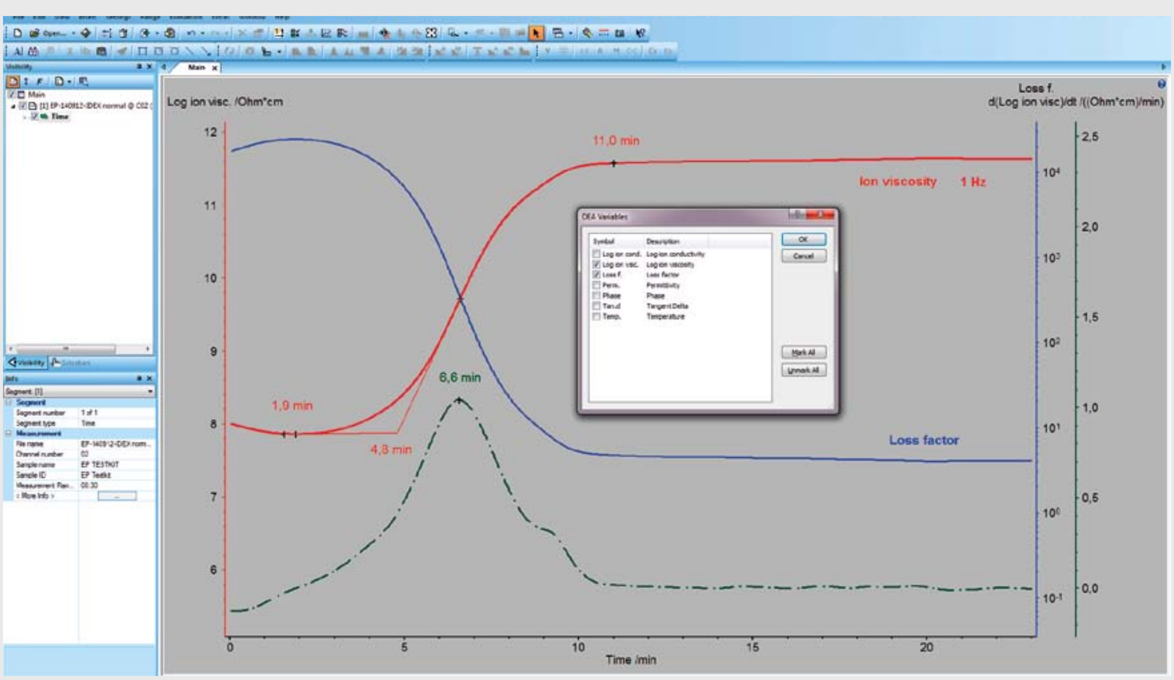


Selection of a suitable sensor is very easy. The software contains a complete list of all available sensors, including their particular technical specification. Important parameters such as electrode spacing (distance) or A/D ratio (ratio between area and distance) are automatically set together with the sensor type. Additionally, user-defined sensors are possible.

The well-proven *Proteus®* software will ensure a comprehensive analysis.

The software offers these features, among others:

- DEA variables: ion viscosity, ion conductivity, loss factor, permittivity phase, tanδ as a function of time/temperature
- Multiple-window technique – clear presentation and evaluation of measurement data or graphical excerpts in multiple windows
- Multi-method plot – conjoint evaluation and presentation of, for example, DEA, DSC and DMA curves in a single graph for detailed material characterization
- Determination of characteristic values such as peak or extrapolated onset or endset, on a single curve or on a curve family
- Comparative analysis of up to 64 curves or segments from the same or different measurements
- Storage of the analysis results and status for later restoration and continuation with analysis
- Raw data preservation – original measurement data is always available
- Smoothing of the measuring curves with adjustable filter factors
- Data (ANSI, ASCII, csv) and graphic export (JPEG, BMP, EMF, PNG, TIFF)



Screenshot of the analytical software

Various Applications – Sheet Molding Compound

Sheet Molding Compound (SMC)

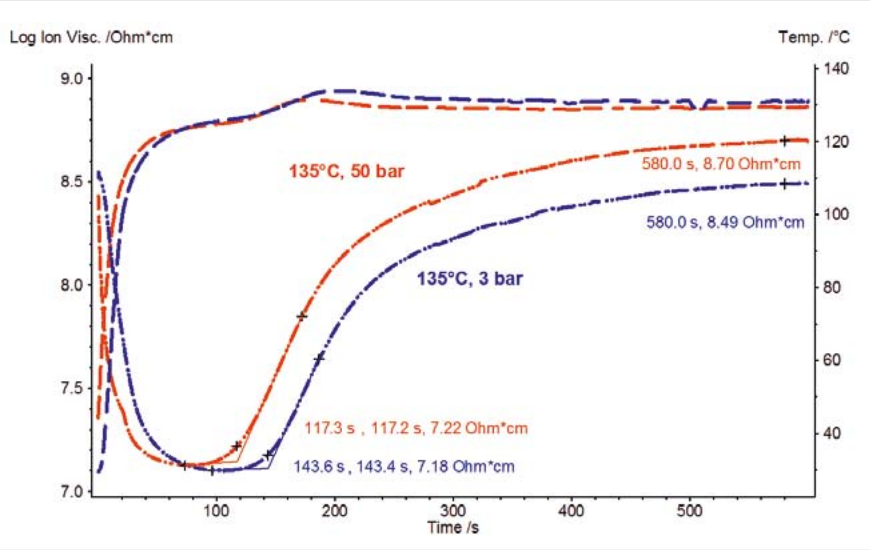
The term SMC (Sheet Molding Compound) describes both a process and a reinforced composite material. A fiber-matrix semi-finished material, consisting of a resin (mostly polyester or vinyl ester resins), chopped glass fibers, mineral fillers and additives, undergoes a compression molding process and cures under elevated temperature and pressure. The properties of SMCs are defined in the European standard EN 14598.

SMC parts are used in high quantities in the automotive industry, for example, as spoilers or trunk lids. But they can also be found in the aeronautics field, in the electro/electronics sector, in the building industry and in hobby and leisure (e.g., pieces of sports equipment).

The advantages of sheet molding compounds are:

- Electrically non-conducting
- Engineering of complex designs possible (whereby the thermal expansion is similar to steel)
- Corrosion-resistant
- Paintable
- Economical
- Low in weight

Especially the last item is very important to car manufacturers, because SMC parts are 20% - 30% lower in weight than their steel panel counterparts, which is essential for a lightweight solution.



Comparison of the DEA results of two SMC samples; presentation of the log ion viscosity as a dashed-and-dotted line and of the temperature as a dashed line. The temperature increase around 200 s is caused by the heat generated during curing. The significant ion viscosities in linear scaling are 0.15E+08 and 3.1E+08 Ohm*cm for the 3-bar measurement, and 0.17E+08 and 5.0E+08 Ohm*cm for the 50-bar one.

In the present example, two SMC parts were analyzed in a press by using a test mold with a Monotrode sensor at 135°C at two different pressures: 3 bar (blue curves) and 50 bar (red curves). The sample thicknesses were approx. 5 mm and the measurement frequency for each test was 1000 Hz.

It can clearly be seen that curing is accelerated at higher pressures. The extrapolated onset temperature, indicating the working time before the curing process begins, takes place 27 seconds (about 20%) earlier in the 50-bar measurement (red curve). Compared to the test run at 3 bar, its curve ends up at a higher ion viscosity level (about 60%) at 580 s. Results such as these are important in process optimization.

Various Applications – UV Curing

UV Curing

The light-induced curing of paints, inks, varnishes, adhesives, casting compounds and composites is a quite young, but quickly growing technology. It is frequently applied in the automotive industry, in electronics, in medical engineering, in metal processing, and in machine and plant manufacturing.

One characteristic of UV curing is that the reaction occurs within a very short window of time – usually just a few seconds. Further processing and quality control of the coated parts, can for example then be carried out immediately.

Additionally, UV paints, printing inks and adhesives are usually solvent-free and therefore environmentally friendly.

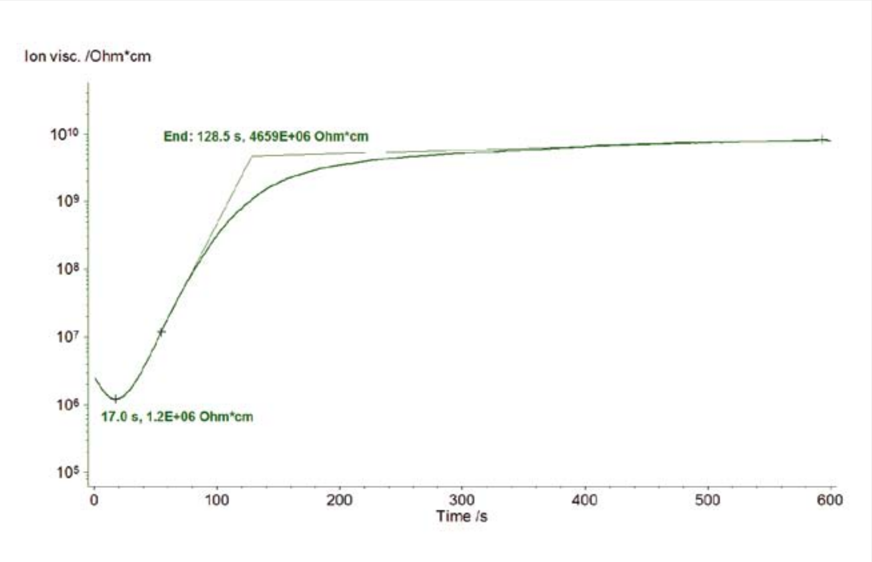
In total, there are three different types of curing systems:

- Radical curing systems
- Cationic curing systems
- Dual-cure systems (thermal and UV curing in one system)

The graph shows the UV curing of a flexible sealant used for protecting organic LEDs (OLEDs) and photovoltaics. It is a single-component EP resin which was applied onto an IDEX sensor as a thin film with a thickness of 200 µm. The sensor was placed in the lab furnace, which in turn was connected to the light guide of a UV lamp.

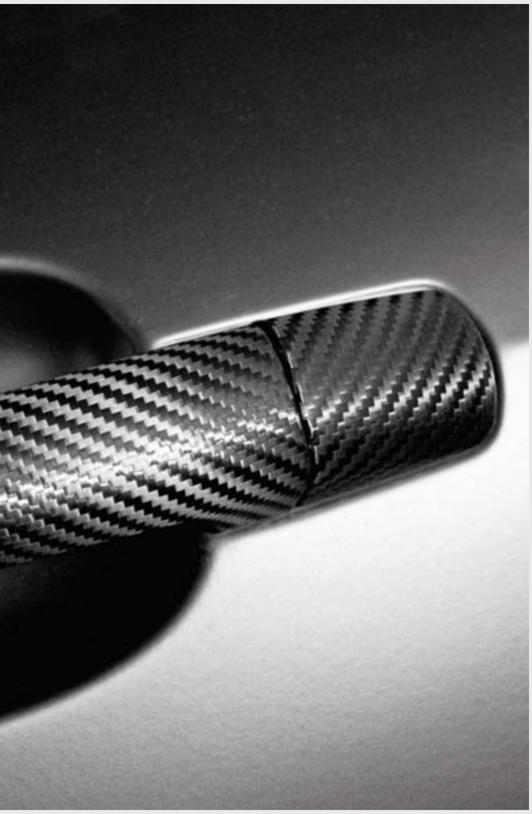
The light exposure was carried out with an irradiation time of 60 s and an intensity of 55 - 60 mW/cm² UVA at room temperature. The employed frequency was 1000 Hz.
During UV treatment, only 17 s pass until the curve of the ion viscosity rises, ending in a total increase of about 4 orders of magnitude after approx. 400 seconds (= ca. 6.7 min).

This result clearly demonstrates how DEA is also capable of detecting fast reactions.



DEA measurement on a UV curing adhesive based on a modified epoxy resin

Various Applications – Simultaneous DEA-DMA and DEA-Rheology



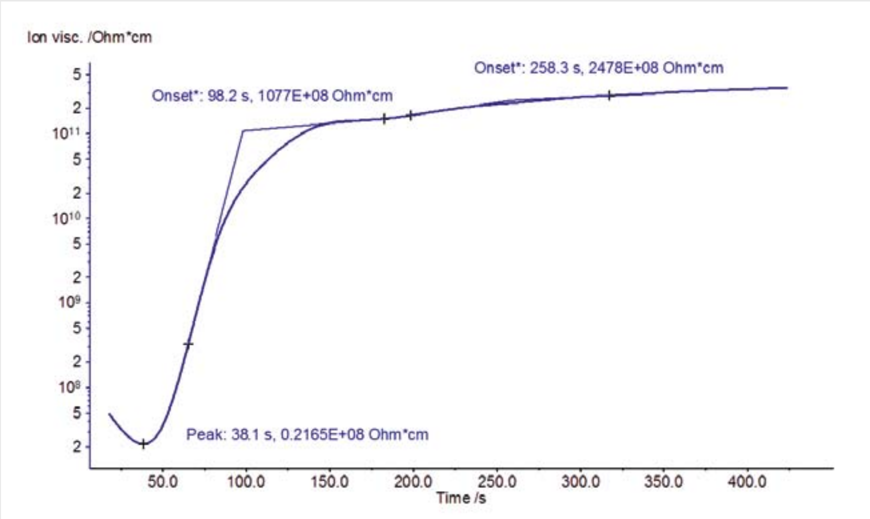
Resin Transfer Molding (RTM)

Resin Transfer Molding (RTM) is another closed molding technique for producing three-dimensional complex shapes or sandwich structures (with, for example, foams as the core material).

In the RTM process, a mixture of liquid resin and catalyst is injected into a closed mold already containing the dry reinforcing fibers such as mats or preforms. After curing (at elevated temperature and moderate pressure), the mold can be reopened and the finished component removed.

Depending on the application, the reinforcement may consist of natural fibers or fibers made of glass, carbon or aramid. Typical resins are of polyester, vinyl ester, epoxy or phenolic type. The selection of polymer and reinforcement dictates the mechanical and the surface finish performance of the molded part.

RTM as a method is widely used in the automotive industry, for wind energy converters, in the construction business, in shipbuilding, in aviation, and in motor sports, among other areas. The primary objective here is weight reduction.



DEA result of a measurement on a CFRP material based on an epoxy resin

A carbon fiber-reinforced epoxy resin was measured in a mold using a Tool Mount Sensor (TMS™) at 80°C and at a frequency of 10 Hz.

To prevent a short-circuit due to the bridging of the electrodes by the carbon fibers, the sensor was coated with a thin glass layer.

As depicted in the plot on the left, curing took place in two steps. The first one sweeps through more than 3 orders of magnitude in ion viscosity and reaches its plateau at around 170 s; the second, much smaller step, follows immediately.

Comprehensive Material Characterization via Coupling with DMA or Rheology

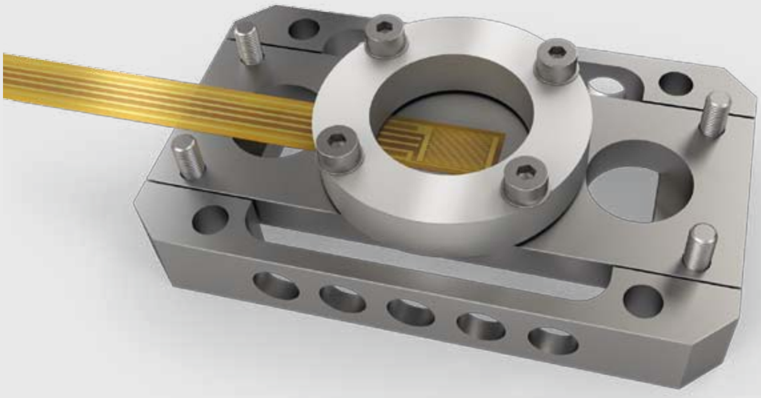
Since the consistency of most thermosetting materials changes completely during curing (e.g., from a liquid to a rigid solid), it is often difficult to study all points of interest with only a single analytical technique.

The DEA 288 *Epsilon* can therefore either be linked to the NETZSCH DMA 242 E *Artemis* dynamic-mechanical analyzer, or to a rheometer such as Mars III by Thermo Fisher Scientific, to perform simultaneous DEA-DMA or DEA-Rheology measurements. This allows for results to be obtained from two complementary instruments in a single run, for advanced analysis.

For DMA-DEA measurements a special compression sample holder is equipped with either a Monotrode or an IDEX sensor. Whereas the DMA is able to identify gelation and glass transition in a resin, the DEA is more sensitive in the area of its minimum viscosity and at the end of the curing reaction.
Combinations of the Mini-IDEX sensor in a suited DMA container can also be carried out.

Combining dielectric (thermal) analysis with rheology expands the accessible frequency range from 10^{-6} Hz to 10^{6} Hz. This helps to gain understanding about the flow properties of resins – for example, during injection (resin transfer molding).

DEA 288 *Epsilon* with reusable TMS™ sensor (comb sensor with 0.5-mm electrode spacing), integrated in a MARS III Rheometer (plate-plate, gap >0.6 mm)



Sample holder for simultaneous DMA-DEA

Conjoint DEA-DMA and DEA-Rheology analysis provides information about

- Resin flow (Rheology)
- Minimum viscosity (DEA/Rheology)
- Gelation (DMA/Rheology)
- Vitrification (T_g) (DMA)
- Reactivity (slope of the DEA curve)
- Completion of cure (DEA)

NETZSCH

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 2,700 employees at 140 sales and production centers in 27 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Adiabatic Reaction Calorimetry and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

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