NETZSCH

Proven Excellence.



DEA 288 *Ionic* – Dielectric Cure Monitoring

Method, Technique, Applications

Analyzing & Testing

DEA 288 *Ionic*

Opening a New World of Cure Monitoring

Clear-Cut Determination of the Curing Behavior

Dielectric Analysis (DEA), also known as 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.

DEA is the most powerful measurement technique for the critical, invisible in-mold curing that dictates the quality of a component.





DEA 288 *Ionic*: Portable version (left) and Rack version (right)

Advantages of DEA

Customized Test Conditions

The DEA 288 *Ionic* comes as either a process-implementable "Rack" version or an all-purpose "Portable" version. For laboratory investigations, several accessories are available:

- Laboratory furnace combinable with a UV-light source
- Humidity chamber and lab press for re-creating conditions similar to those occurring in-process

Designed for Comfortable Sample Handling

No special sample preparation – as is often the case for other measurement techniques – is necessary. 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
- In-mold cure monitoring

The Benefits to You

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. With the DEA 288 *Ionic*, 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 to shorten the development process.

Determination of Ideal Process Parameters

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

The following process parameters can be determined:

- Viscosity
- Gel point
- Cure behavior

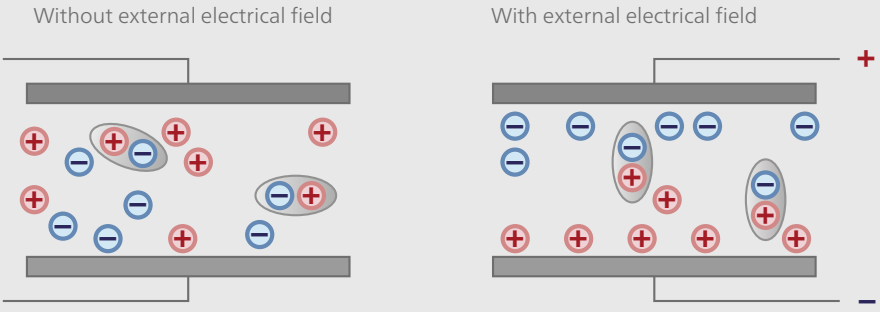
What You Can Investigate with DEA

- Degree of Cure
- Gel-Point
- Flow Behavior
- Reactivity
- Cure Monitoring
- Diffusion Properties
- Glass Transition Temperature
- Process Monitoring and Optimization
- Aging
- Decomposition Effects

THE METHOD

Dielectric (Thermal) Analysis

DEA (or DETA) Technique



Behavior of ions and dipoles inside an external electrical field

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 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 with a phase shift.

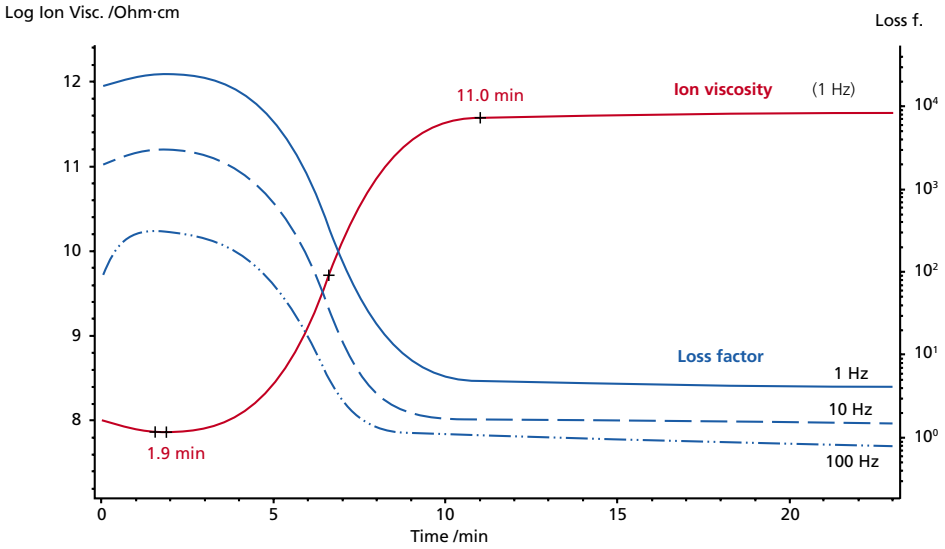
In the frequency range of the DEA 288 *Ionic* (up to 1 MHz), the charge

Results

An outer electric field generated by an excitation voltage is applied to the sample and the response, occurring as a current through the material, is measured. Dipoles will be aligned and the ions will move towards the oppositely charged electrode, which can be seen in ε' and ε'', respectively. Based on the sample's characteristics, a time shift between excitation and response signal is detected that, together with voltage and current, allows for the calculation of dielectric magnitudes.

In detail, this yields information about:

- Flow behavior
- Reactivity
- Cure progress



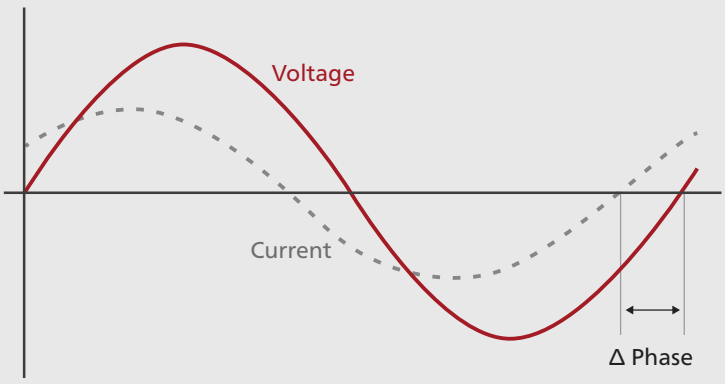
Loss factor and ion viscosity depict the cure progress of a two-component epoxy adhesive at room temperature. The best flow behavior is reached at the lowest viscosity value at 1.9 min, the cure progress ends at 11 min. The slope of the ion viscosity increase is the reactivity during the cure progress.

Application Areas

- Research
- Process development
- Process control
- Quality control/assurance

carriers are mainly ions (often present as catalysts or impurities), but dipole alignment also takes place within the electrical field.

The response signals – current and phase shift – are a function of the ion and dipole mobility. This relationship makes dielectric (thermal) analysis an ideal method for cure monitoring, the sample's viscosty is increasing dramatically. As a consequence, the mobility of the charge carriers decreases, followed by a corresponding attenuation of the amplitude and an increased phase shift in the resulting signal.



DEA – Measurement principle

CHARACTERISTICS

- *Modular design*
- *Simultaneous multi-channel measurements*
- *High data acquisition rate*
- *Leading-edge technology*



DEA 288 *Ionic,* Rack version

Cutting-Edge Technology – The Benchmark for Process Control

Two versions of the DEA 288 *Ionic* are available:

Portable Version

With up to seven channels, this DEA is the flexible version for your day-to-day work. It can be easily transported between different measurement locations.

Rack Version for Integration into an Industrial Process

The 19" Rack version is designed for an electrical cabinet. It supports 8 simultaneous measuring channels which can be extended up to 16 modules.



DEA *Ionic*, Portable version with TMCc sensor and adaptor box for the connection of all disposable sensors

The DEA 288 *Ionic* covers a wide range of measurement frequencies (from 1 mHz to 1 MHz) 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 fast 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.

Key Technical Specifications

DEA 288 *Ionic*	
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	Shielded 4-wire technique (compensation of resistivity and capacity of the wire as a prerequisite for precise measurements)
DEA modules	▪ Portable version: All-purpose version, up to 7 channels ▪ Industrial Rack version: up to 8 channels (extension possible for up to 16 channels)
I/O ports	Input and output of measuring signals or signals from peripheral devices such as pressure or temperature sensors. DEA allows for triggering by manufacturing machines.



Adaptor box – fast, easy and reliable connection of all disposable sensors, thermocouples or RTD sensors

DEA 288 *Ionic*

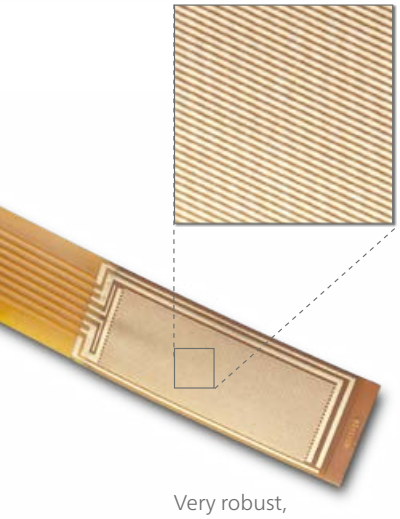
Raises Your Process to the Next Level

High Flexibility

BY MEANS OF SENSITIVE AND VERSATILE SENSORS FOR ANY APPLICATION



Reusable Coated Tool Mountable Comb Electrode for in-mold applications



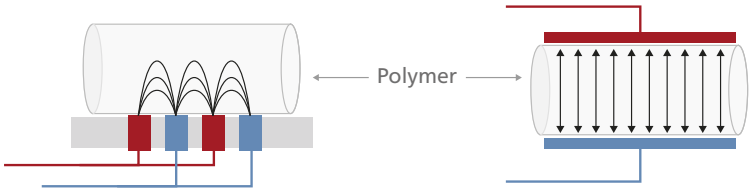
Very robust, implantable standard sensor (IDEX) with comb structure and an electrode distance of 115 µm

In order to meet the requirements of a multitude of polymer processing applications, NETZSCH offers a great variety of dielectric sensors. These can be classified as disposable and in-mold sensors. 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 IDEX (interdigitated electrode) sensor.

Most sensors are composed 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.

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.



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

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.



DEA furnace with installed Coated Tool Mountable Comb Electrode

Specifications for Available Sensor Types

Sensor Type	Sensing Area	Max. Temperature	Electrode Spacing	Main Application	
Micron Sensor (MS)	2.5 mm^2, 26 mm^2, 70 mm^2	200°C or 350°C*	1, 5 or 25 µm	Paints, inks, adhesives	
Mini-IDEX (Interdigitated Electrode)	33 mm^2	275°C	100 µm	All resins (small cavities)	
IDEX (Interdigitated Electrode)	233 mm^2	200°C or 275°C*	115 µm	All resins (epoxy, polyester PES, polyurethane PUR, etc.)	
IDEX, filtered	233 mm^2	200°C or 275°C*	115 µm	Carbon fiber-reinforced polymers (CFRP)	
Tool Mountable Monotrode (TMM)	13 mm^2, 79 mm^2, 707mm^2	220°C	–	Especially for SMC/ BMC, PUR foams	
Tool Mount Sensor (TMS)	214 mm^2	220°C	500 µm	All resins (EP, PES, PUR, etc.)	
Coated Tool Mountable Comb Electrode (TMCc)	254 mm^2	220°C	500 µm	All resins, composites and other polymers with electrically conductive fillers	

* depending on the wiring of the sensor head

Smart Accessories

WHICH BRIDGE THE GAP BETWEEN PROCESS DEVELOPMENT AND PRODUCTION

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 with cooling, laboratory press, and UV lamp for fast curing reactions.



DEA 288 *Ionic* with accessories

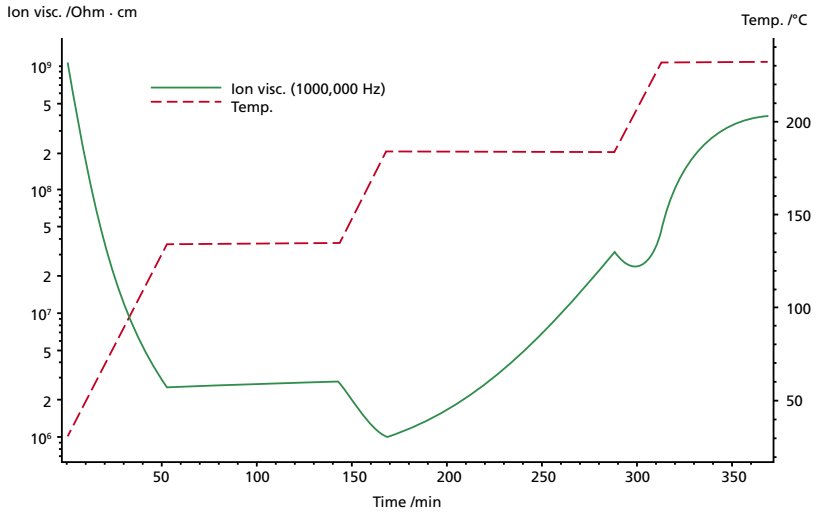
LAB PRESS

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 plates (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 from room temperature up to 350°C. The maximum force that can be applied amounts to 10 kN.

MULTI-FUNCTIONAL LAB FURNACE

With the easy-to-operate lab furnace, it is possible to carry out heating, isothermal or cooling steps in the temperature range from -140°C to 400°C by using either two IDEX (or MS) sensors or a single TMS sensor. Cooling can be realized via air compressor or liquid nitrogen (LN_2). To establish a defined gas atmosphere inside, two purge gases can be attached; these can be switched by magnetic valves. The furnace is designed to be connected to the fiber light guide of a UV lamp.





With the DEA furnace, multiple temperature steps can be realized

UV LAMP

The DEA 288 *Ionic* 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.

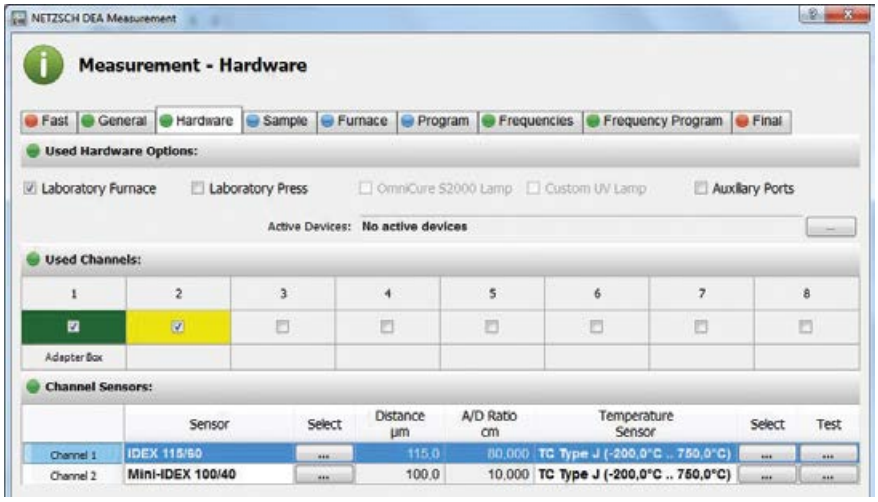
Proteus® Software

Powerful and Easy to Use

Comprehensive Measurement and Evaluation Software

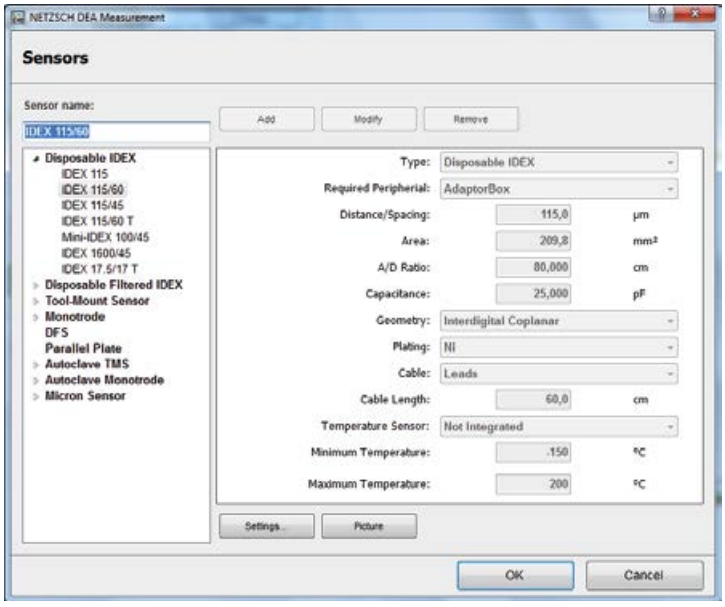
The measuring part of the software provides the user with a modern, user-friendly operating interface. *Proteus*® now offers a quick and convenient input assistant for programming all relevant measurement parameters. Color-coded tabs facilitate data entry and guarantee that no important parameter is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

Segments can be adapted (time, temperature, frequency) during a running measurement. In addition, a snapshot can be taken to analyze the data recorded up until that point.



User interface for programming a test run

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.



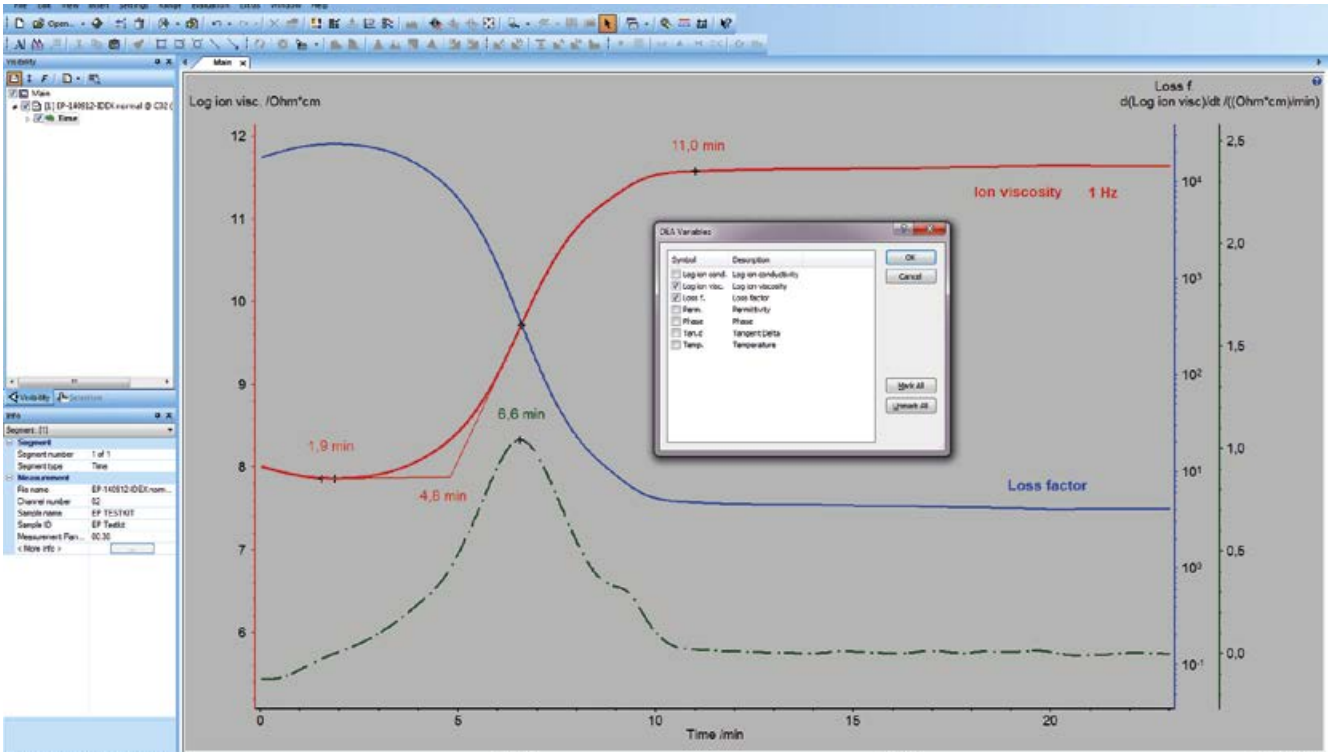
The desired channels can be easily enabled by selecting the appropriate check box. Active channels are colored green.

Selection of a suitable sensor is very easy. The software contains a complete list of all available sensors, including their particular technical specifications. 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, sensors may be defined by the user.

The well-proven *Proteus*® software ensures comprehensive analysis. It allows for easy inputting of a measurement's parameters and features routines for data acquisition and evaluation with maximum flexibility.

General Software Features

- DEA variables: ion viscosity, ion conductivity, loss factor, permittivity phase, tanδ as a function of time/temperature
- Multiple-method plot – comprehensive evaluation and presentation of, for example, DEA, DSC and DMA curves in a single graph for detailed material characterization
- Picture-in-picture (PIP), 3-D plot
- Snapshot for evaluation of a measurement in progress
- Determination of characteristic values such as peak or extrapolated onset or endset, 1st derivative on a single curve or on a curve family, degree of cure, percent cure, conversion curve, delta step
- Comparative analysis of up to 64 curves or segments from the same or different measurements
- Raw data preservation – original measurement data is always available
- Data and graphic export
- The software activates communication with accessories by mouse click. It controls the temperature profile of the lab furnace and lab press and triggers the UV lamp.



Screenshot of the analytical software



Various Applications

In-Process Characterization of a Sheet Molding Compound (SMC)

The term SMC (Sheet Molding Compound) refers to a reinforced composite material created by a specific process.

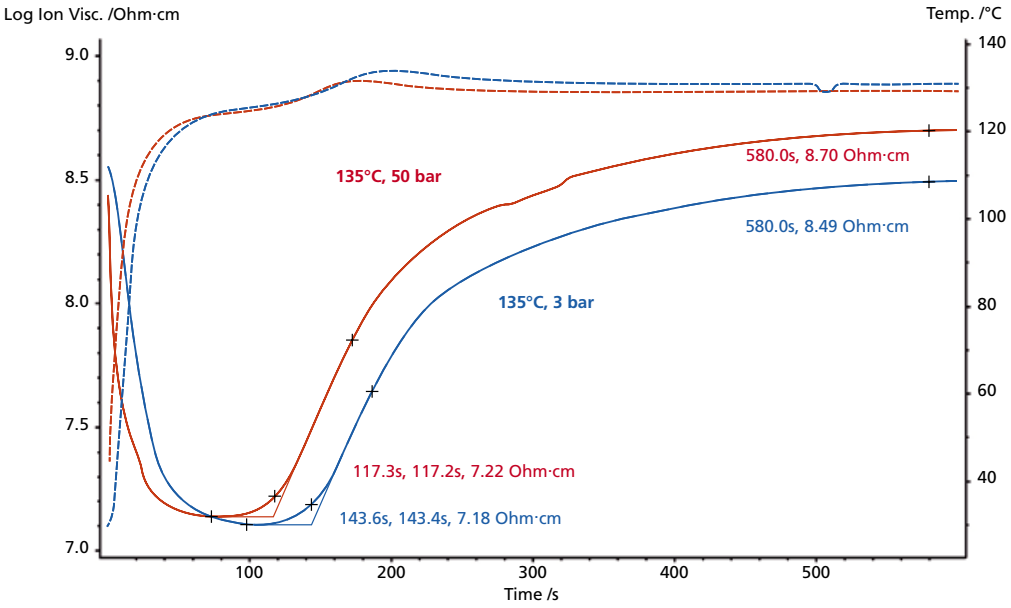
A fiber-matrix semi-finished material, consisting of a resin (typically polyester or vinyl ester resins), chopped glass fibers, mineral fillers and additives, undergoes a compression molding process and cures under elevated temperature and pressure. The properties of SMCs are defined in the European 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:

- 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 solid 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 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.



Real-Time Analysis of the UV Curing Behavior

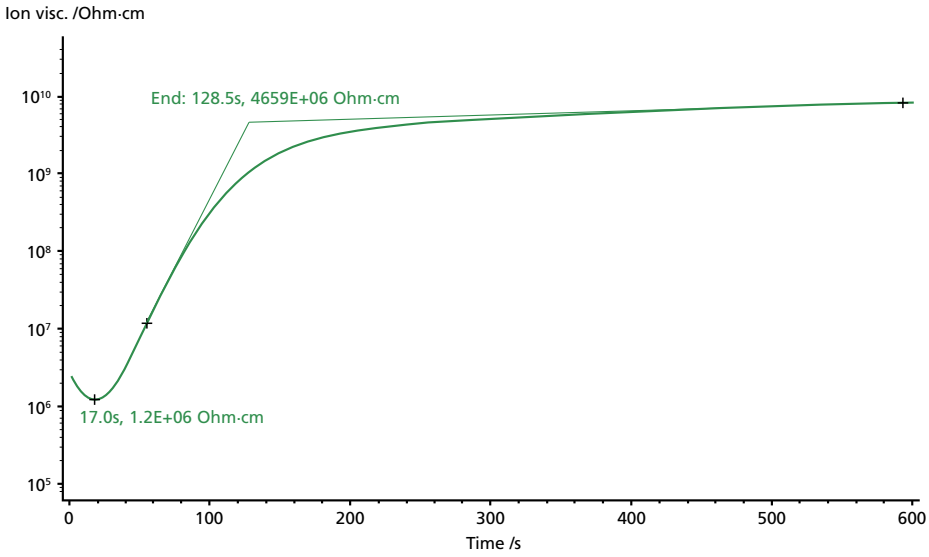
The light-induced curing of paints, inks, varnishes, adhesives, casting compounds and composites is a young but quickly growing technology. It is frequently applied in the automotive industry, in electronics, in medical engineering, in metal processing, and in machine and plant manufacturing.

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 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)



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

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/cm^2 UVA at room temperature. The employed frequency was 1000 Hz. During UV treatment, only 17 s passed before the ion viscosity curve began to rise, 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.



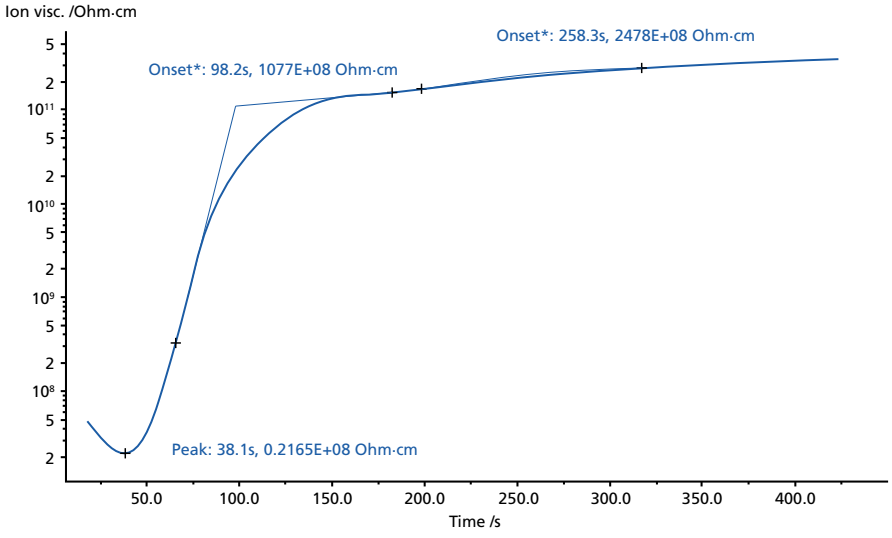
Resin Transfer Molding (RTM)

Resin Transfer Molding (RTM) is another closed molding technique for producing complex three-dimensional 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.

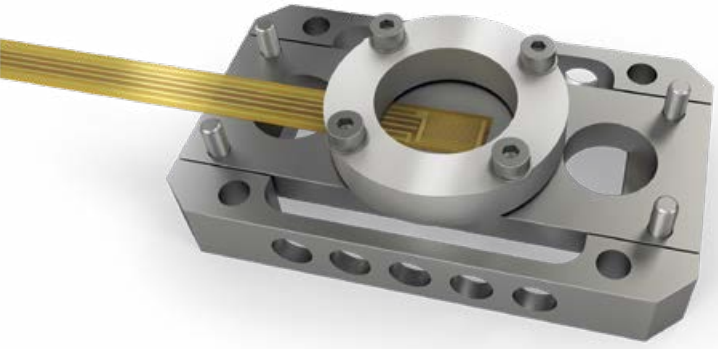


DEA result of a measurement on an epoxy based CFRP material

In this example, a carbon fiber-reinforced epoxy resin was measured in a mold using a coated Tool Mountable Comb Electrode (TMCc) at 80°C.

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 after approximately 170 s. A second curing step was observed after 258 s.

Simultaneous DEA-DMA and DEA-Rheology



Sample holder for simultaneous DMA-DEA with Mini-IDEX sensor

Advantages of Simultaneous Measurements

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

Comprehensive Material Characterization via Coupling of DEA 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.

To address this issue, the DEA 288 *Ionic* can 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 a Mini-IDEX sensor in an appropriate DMA container. 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.

Combining dielectric (thermal) analysis with rheology expands the accessible frequency range from 10^{-3} 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 *Ionic* with reusable TMCc sensor (comb sensor with 0.5-mm electrode spacing), integrated in a MARS III Rheometer (plate-plate, gap >0.6 mm)

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 3,500 employees at 210 sales and production centers in 35 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) 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.

Proven Excellence.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

NETZSCH®

www.netzsch.com

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