Following Cross-linking

Optimized Paint Curing by Means of Dielectric and Kinetic Analysis

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The course of paint curing or diffusion processes in cured paint - as for the investigation of water absorption, for example - can be sensitively measured by means of Dielectric Analysis (DEA). Unlike alternative methods such as DSC (Differential Scanning Calorimetry) or DMA (Dynamic Mechanical Analysis), this technique does not require complicated sample preparation and is suited for all types of paint systems. Moreover, modeling of the test results allows effective optimization of the curing process.

After what amount of time or at what temperature does the curing reaction of the paint start?

Is the paint already entirely cured or is there a post-curing?

Which type of paint shows higher reactivity?

When is the paint entirely dried?

Such or similar questions are those which paint developers and users would like to answer comprehensively. Thermal Analysis offers an appropriate tool for this [1], but there can be certain restrictions depending upon the situation. DSC (Differential Scanning Calorimetry), for example, can be excellently employed for powder paints [2], but often fails for liquid, solvent-containing paint systems since the exothermal reaction is overlapped by the endo - thermal peak of the solvent. Moreover, DSC cannot be employed for very fast curing processes (e.g. for UV reactions) or multi-component paints where reaction already begins upon mixing and weighing of the sample. Changes in the stiffness and damping behavior can be investigated by means of dynamic-

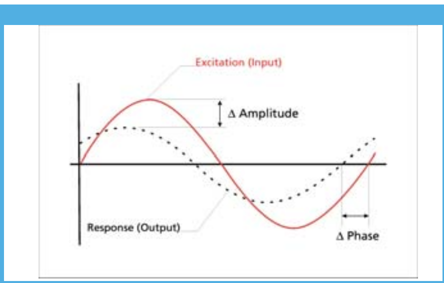

Fig. 1: Measuring principle of dielectric analysis

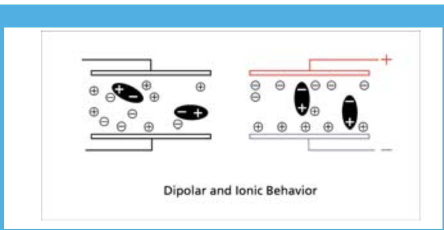

Fig. 2: Behavior of the dipoles and ions prior to curing (left) and after curing (right)

mechanical analysis (DMA). For liquid paints, however, an appropriate container is required, resulting in long times for measurement and preparation. In [3], natural silk was soaked with the paint. During curing, an increase in the E modulus was measured in the tension mode.

Dielectric Analysis (DEA) - Measuring Method

These problems can be avoided when using Dielectric Analysis (DEA). The measuring principle is based on the sample being in direct contact with a dielectric sensor that consists of two electrodes. The electrodes can be arranged either as a plate capacitor or in a fringed design. A sinusoidal voltage (input signal) is applied to one electrode. The second electrode acts as a receiver for the resulting current. Due to the influence of the sample as a dielectric, the measuring signal is phase-shifted to the input signal and attenuated in amplitude (fig. 1). This depends on the ionic mobility (solvents, impurities) and the alignment of the dipoles in the sample.
During the curing of a reactive resin, both the ionic mobility (ion conductivity) and the alignment of the dipoles in the alternating current field decrease (fig. 2).
The change in dielectric properties (dielectric constant (permittivity) and loss factor) is then evaluated from the measuring signal. In practice, presentation of the so-called ion viscosity, the reciprocal value of the ion conductivity, has proven itself worthwhile.

Measurement Examples from Paint Practice

Liquid UV paint on a PUR acrylate basis

The UV curing of liquid polyurethane-(PUR)-acrylate paint was investigated using a DEA instrument with a fast data acquisition rate. The paint was applied at the sensor surface of a 25-µm MS sensor (see box), dried for approximately 5.5 min at 130°C, and then exposed to a UV light at 120 W/cm. The measurement was made at a frequency of 1000 Hz and a data acquisition rate of 55 ms/data point. Figure 4 depicts the rapid increase in the ion viscosity by 2.5 orders of magnitude from 10^8 Ωcm to $10^{10.5}$ Ωcm. The entire UV curing occurred within 7 to 8 s.

Apparatus Technology and Sensor Types

Various DEA systems are available; these are not restricted only to laboratory use, but are primarily intended for in-situ curing processes in the oven or painting line.

High Performance

The most efficient instrument, the DEA 230/2 Epsilon, has two external interfaces for measuring two sensors in one experiment and is the only DEA which can be equipped with the highly sensitive and highly accurate Integrated Circuit (Chip) sensor. This is ideal for very weak or slow reactions and also for very low conductivity materials. Multi-frequency measurements can be carried out between 10^{-3} and 10^{5} Hz. Two other versions of this instrument are available measure only one sensor or up to 10 sensors. These two versions of the instrument can be operated between 10^{-1} and 10^{5} Hz. Each DEA 230 can be connected to a dynamic mechanical analyzer so that both the dielectric and visco-elastic properties of a resin during curing can simultaneously be determined in one experiment.

High Speed

For very fast curing processes (< 3 min), the single-channel DEA 231/1 Epsilon or its 4-channel version, both of which work at a freely selectable frequency of up to 10^{4} Hz, are recommended. Due to their considerably faster data acquisition rate in the millisecond range, they are, for example, also used for UV curing processes. With the CPC (Critical Point Control) software under MS® Windows™, four critical points for the quantitative description of the curing for quality control and assurance are determined and stored in a database for statistic evaluation.

In-line Measurement

The DEA 234 CurePak is a 4-channel, battery-operated instrument which can be introduced, along with up to 4 dielectric sensors and thermocouples, into a tunnel oven for the painting of car bodies, for example. The electronics are protected by an insulated box and can therefore withstand the process temperatures (e.g. 150°C) and times (e.g. 40 min) several times over. After recording the data - it is possible to use the multi-frequency mode here as well - the measured values are read out and evaluated on the PC.

Disposable and Reusable Sensors

The systems can be equipped either with the disposable sensors IDEX (Interdigitated Electrode) or MS (Micron Sensor), depicted in figure 3, or with the reusable, firmly mounted TMS™ (Tool Mount Sensor), DFS (Dielectric Fluid State), or Monotrode sensors for in-situ curing.

The IDEX sensors have proven ideal for paints and coatings. These robust standard sensors consist of nickel-coated fringe electrodes applied onto a polyimide substrate. Since the distance between the electrodes is 115 µm, the electric field also penetrates approximately 115 µm into the paint layer. Versions of up to 200°C and 375°C are available. For thinner paint layers (max. 80 µm), MS sensors are recommended. These are fringe-designed chrome electrodes on a quartz substrate. The MS sensors are available in three versions: 1-µm, 5-µm and

Fig. 3: MS, Chip and IDEX Sensors for DEA

Liquid 2C-PUR paint

A liquid 2-component (PUR) clear coat, used as a topcoat in automobile painting, was investigated using a high-performance DEA instrument and IDEX sensors (see box) [4]. After mixing the two liquid components - resin (polyole and additives) and hardener (isocyanate) - in a stoichiometric ratio of 3:1 - the paint was applied at the sensor surface with a scraper. The thikkness of the wet paint layer was 150 mm. After a flash off time of 7 min at room temperature, the sensor with the paint film was put into a furnace and heated to 140°C at different heating rates. Finally it was held isothermal for 2 h, so that an almost complete curing could be presented.

Shown in fig. 5 are the ion viscosity (blue curve), the loss factor (green curve) at 1, 10 and 100 Hz, and the temperature ramp (red curve) with an initial heating rate of 15 K/min as function of time. Due to the temperature increase, the ion viscosity initially decreases. The shape of the curve correlates extremely well with the dynamic viscosity from conventional rheometer measurements. The critical starting temperature for the drying and curing of the paint is reached after 7 min or 90°C. The ion viscosity curve increases three orders of magnitude from 10^{8} Ωcm to approx. 10^{11} Ωcm after 120 min and then remains nearly horizontal, since the paint is then entirely cured.

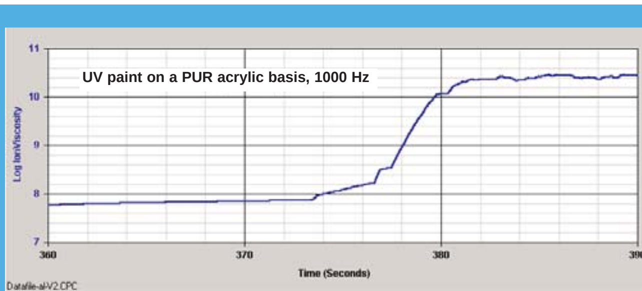

Fig. 4: UV curing of a PUR acrylic paint, measured with the DEA 231/1 at 1000 Hz

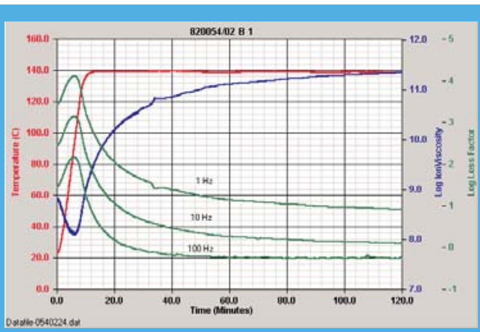

Fig. 5: Ion viscosity, loss factor and temperature for a PUR paint as a function of time

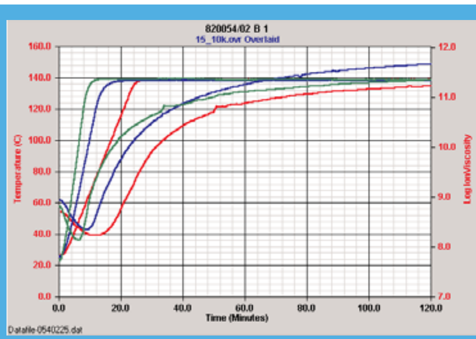

Fig. 6 : Comparison of the DEA measuirng results for a PUR paint at different heating rates: 15 K/min (green), 10 K/min (blue) and 5 K/min (red)

Fig. 6 shows the ion viscosity for three different heating rates at a measuring frequency of 1 Hz. As expected, the fastest heating rate (15 K/min) caused the earliest onset of paint drying. This can also be seen in the sharpest increase in the ion viscosity (green curve). Unexpected, however, is the intersection of the blue and green ion viscosity curves during the isothermal curing. This may be due to the varying layer thicknesses of the wet paint as well as a variation in the mixing ratio.

Results at a Glance

- Dielectric Analysis (DEA) delivers significant results for the drying and curing process of liquid paints by means of the so-called ion viscosity curve.
- It can be employed not only on a laboratory scale, but also for in-situ paint processes and presents itself as the ideal tool for quality control and assurance.
- Even continuous painting processes in a conveyer oven can be recorded and evaluated with the appropriate equipment.
- Besides determinating the kinetic parameters, a kinetic analysis of the measured data can also yield predictions for any temperature/time program, and thus optimization of the curing is possible.
- The diffusion properties of a cured paint film can be determined via the dielectric constant.

Modeling and Predicting the Curing Speed

The curing behavior of the PUR paint was investigated with the NETZSCH Thermokinetics software [5], which is described in more detail in [6]. After the DEA-measured data were converted into ASCII format and a model-free estimation of the kinetic parameters was made, the reaction model was fitted to the measured data with the help of non-linear regression. Figure 7 shows the best fit of a subsequent reaction model with steps of the n-th order (solid curves) for the logarithm of the ion viscosity (symbols). The correlation coefficient for the fit quality was calculated at 0.9984.

It is now possible to make predictions of the ion viscosity rate for each temperature/time program.

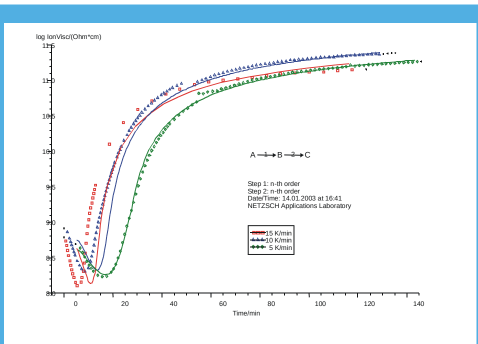

Fig. 7: Fit of the kinetic parameters of a two-step following reaction to the

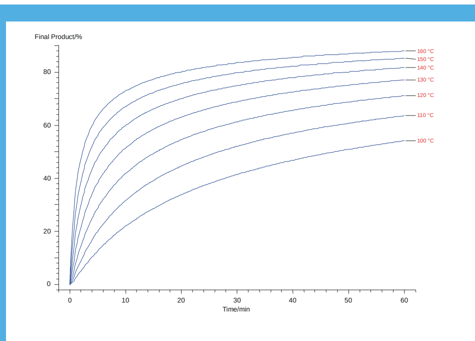

Fig. 8: Decree of curing of the PUR paint at different temperatures

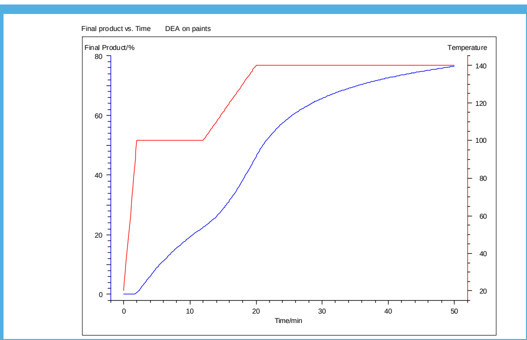

Fig. 9: Predictions of the degree of curing (blue curve) of the PUR paint at a two-step temperature/time program (red)

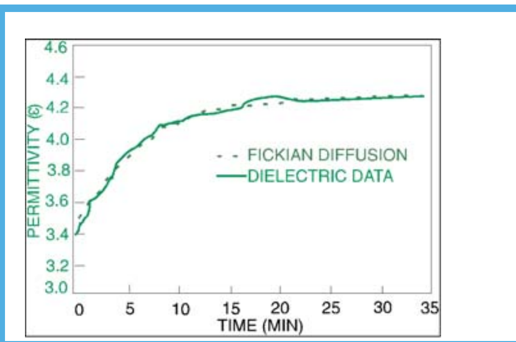

Fig. 10: Increase of the dielectric constant (permittivity) during the water adsorption of a paint film

Figure 8 depicts the curing process to the cross-linked PUR paint (final product in %) with an increasing temperature. After a curing time of 45 min at 140°C, which was recommended by the paint manufacturer, the degree of curing was only approx. 80%. This means that for practical use, the post-curing was taken into consideration. A curing of 100% would obviously cause a lower flexibility and toughness of the paint film, which is not desired.
Simulations showed that, even after 48 h at 140°C, only a 95% degree of curing could be reached.

Depicted in fig. 9 is the result of another practice-related simulation. An additional isothermal step at 100°C was provided in order to guarantee evaporation of the solvent. After 50 min, a degree of curing of 80% was achieved for this temperature/time program with isothermals at 100°C and 140°C.

Diffusion in cured paints

The usage properties of cured paints and coatings, such as scratch resistance, are strongly dependent on their diffusion properties. These can easily be measured by means of DEA, by bringing the sensor - with the cured paint film applied - into the practice-relevant environment at a defined humidity level. Water penetrates via time into the paint layer and causes an increase of the dielectric constant e' (fig. 10). With an automatic curve fit of the evaluation software, the Fickian diffusion coefficient can quickly be calculated. Various publications like in [7] demonstrate this additional application field for DEA for paints.

Literature

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