Simultaneous multi-frequency dielectric measurement technique for fast curing reactions

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Abstract. Dielectric Analysis has proven to be an important tool in various industry and research sectors. But new developments, in particular, highly reactive thermosetting resins and adhesive systems with UV radiation activation reveal limitations of commercially available measurement systems. These systems achieve dynamics which reach a conversion rate of up to 90% in less than one second.

In dielectric analysis the material properties are determined by measuring the reaction current and the corresponding phase angle as a result of an input voltage signal. By determining the complex impedance and phase angle, different material properties, such as relative permittivity or ionic conductivity, can be calculated to evaluate the material conditions. In order to be able to adequately evaluate manufacturing processes and curing processes, a broadband measurement of the electric variables mentioned before is necessary. Unfortunately, commercially available systems achieve spectroscopic results only by the use of a frequency sweep, which is not applicable to monitor properly the behaviour for highly dynamic UV-curable resins. Likewise, this is similar for rheological measurement methods, which are equally limited in their measurement point rate and dependent on the applied excitation frequency.

To attain sufficient resolution in the time domain even for highly reactive systems, a system which offers the possibility of spectroscopic examinations combined with an extremely high measuring point density was developed. The actual simultaneous recording of all applied frequencies (up to 20 different ones) reduces significantly the measurement time per measurement point. Thus creating the potential to analyze extremely dynamic reactive systems in detail even at low frequencies. Limits in speed are only given by the lowest frequency monitored. In addition, the measurement points are recorded time-synchronously for all frequencies, allowing immediate spectroscopic analysis. Overall, this opens up the potential, especially in the area of UV-curing highly reactive resin systems, both in the laboratory and in the process environment, to realize material characterization and condition monitoring.

Introduction

Dielectric analysis (DEA) has become a popular tool not only in science but in industry as well. Nevertheless, it has long been used to investigate dielectric dispersion phenomena for colloidal solutions [1, 2] and still is a standard method for this purpose [3]. In biology, the
use of dielectric analysis for the evaluation of dielectric behavior of the human or any other biological tissue and the interactions on a cellular level can be found in literature [4-6]. For some time, the use of dielectric analysis for industrial applications has become more common. In the aerospace industry, the method was used to monitor the curing process of fiber reinforced plastics within the resin transfer molding (RTM). In [7] a process control device based upon the dielectric analysis for an epoxy based resin is presented. Shepard et al. [8] demonstrate the feasibility for the cure monitoring and process control via DEA for polyester based sheet molding compound (SMC) respectively for bulk molding compound. More recently, the DEA was used to examine the curing behavior of a b-stage resin [9] and the phase change in neat as well as fiber reinforced PA6 [10].

An interesting application is the use of DEA for ultraviolet (UV) curable resins. Only little literature can be found investigating the conversion behavior at low frequencies [11-14]. The main reason are the fast curing cycles which can be less than one second. Therefore spectroscopic data is difficult to obtain. Hence, the standard procedure monitoring fast conversions for UV-curable resins was demonstrated by a solution based upon IR spectroscopy [15].

In this paper the concept for a device capable of quasi-spectroscopic monitoring for low frequencies using DEA is presented. With this approach, the use of DEA for highly reactive UV-curing systems shall be demonstrated obtaining synchronous data for up to 20 discrete frequencies within a bandwidth of 4 decades.

1. Methods

In the 1880’s, Oliver Heaviside first introduced impedance spectroscopy (IS), thoroughly discussed in [16]. The basic idea behind IS is to apply an electrical (voltage or current) stimulus (periodically or non-periodically) to a specimen and observe the resulting signal. Usually the relations between the specimen properties and the response signal caused by periodic excitation is difficult to formulate within the time domain, often involving a complex solution of a system of differential equations. In this respect the Fourier transformation allows significant simplification by transferring the problem to the frequency domain. This allows a simplified calculation of the impedance magnitude by measuring the current and voltage signal, and subsequently calculating the phase difference between them for arbitrarily selected frequencies.

This more general concept is the basis for the DEA. Even though it is counted to the thermal analysis methods it has a special status among these. Classical thermal measurement techniques like differential scanning calorimetry (DSC) or rheological investigation, focus on the chemical conversion rate, respectively the mechanical stress within a specimen. Contrarily DEA examines the interactions between ions and molecules due to a changing electric field between the electrodes of a sensor. An excitation voltage is applied to the test specimen. By measuring the phase shift and amplitude of the current response signal and the known geometrical parameters of the used sensor, the conductivity, permittivity and further derived quantities can be obtained. These properties may be represented as a function of frequency, temperature and/or time, depending on the conducted experiment.

1.1 Basic schematic circuit layout

In the literature different approaches for the electrical circuit layout for the measurement and processing of the created voltage and current signals can be found, each with its own benefits and purpose [17, 18].

The chosen approach features a transimpedance amplifier (TIA) for the current-to-voltage conversion. The corresponding circuit diagram is shown in Fig. 1. The excitation of the
capacitive sensor drives an input current into the inverting input of the op amp. The output of this circuit is an amplified and inverted current-proportional voltage signal according to the formula $V_{out} = I_{in} \cdot Z$. Similar circuit designs for different applications have been introduced by [18], [19] and [20].

![Diagram](image_url)

**Fig. 1:** Schematic representation of the basic circuit layout featuring a transimpedance amplifier.

1.2 Signal

Most commercial systems use pure sine waves as excitation signals as they provide the best signal quality [21]. For a spectroscopic analysis a frequency sweep needs to be conducted. For slow curing resins this method has proven great success as the changes in material properties proceed at an even slower rate than the sweep time. However, for highly reactive UV-curable acrylate based materials the curing cycles might be shorter than a full frequency sweep over the chosen bandwidth. Therefore another excitation signal is needed. Recently, multi-frequency simultaneous (MFS) measurement techniques have become more popular. Using broadband excitation signals comprised of multiple discrete frequencies and evaluating the signal response by means of spectral analysis applying the fast Fourier transformation (FFT), the time to obtain the complete IS result is dramatically reduced.

Different signal types used for MFS measurements have been reported in literature, e.g. binary sequences as maximum length binary sequences (MLBS), discrete interval binary sequences (DIBS) [22, 23], sine based signals as chirp [24] or multi-sine signals [25, 26]. Each signal comes with certain advantages as well as disadvantages and has to be carefully chosen for the intended application. The signal used in the presented work is a multi-sine, combining the possibilities of a simultaneous capturing of several discrete frequency components with a satisfying signal quality for a real-time monitoring application [21]. The signal is generated by adding up multiple sine waves, while each wave can be chosen with its particular frequency $f_n$, amplitude $a_n$ and phase $\phi_n$ according to the following equation:

$$u(t) = \sum_{n=1}^{N} a_n \cos(2\pi f_n t + \phi_n)$$

(1)

Metrics are needed to evaluate the quality of the generated signals and the corresponding impedance spectra. To determine the signal quality in the time domain the crest-factor (CF) is used to determine how much signal amplitude is needed to introduce a certain amount of energy into a system. The CF is the ratio between the peak value of a signal and the effective root-mean-square value of the signal [21]. For a signal $s(t)$ measured over a time interval $[0; T]$ the CF is calculated by:

$$CF(s) = \frac{\max_{t \in [0,T]} |s(t)|}{\sqrt{\frac{1}{T} \int_0^T |s(t)|^2 dt}}$$

(2)

Complimentary to the crest-factor, the root mean square (RMS) voltage of the multi-sine for a limited voltage level is used as a metric for the energy density as proposed by [27]. For
further insight, the signal-to-noise ratio (SNR) is applied. The SNR is the ratio between the power of a signal and the power of present background noise. The more frequencies are incorporated in the multi-sine signal, the better the spectral resolution of the impedance spectrum. However, the amount of energy being introduced to the system for a single frequency component is inversely proportional to the number of excited frequencies \( N \). It was found during the research of this project that for a satisfying frequency resolution at least 10 different frequencies are needed. For \( N > 25 \), the single amplitudes, especially for the low frequencies, drop below a level where they cause a measurable effect in the specimen as the maximum value of the applied voltage signal was limited to 10 V\(_{\text{PP}}\). A number of 20 frequencies has proven to be a good compromise between spectral resolution and sufficient energy input. The signal was additionally optimized in terms of amplitude, phase angle and frequency distribution. The parameters indicate that the combination of a second order power function and phase offsets calculated according to Newman give the best result with the lowest CF (3.32) and simultaneously the highest RMS voltage (1.5091 V). Fig 2 shows the corresponding FFT spectrum of the created signal. Due to the repeating nature of the signal higher frequency components appear more often than low frequency components. To keep the energy input for each frequency component at a similar level, the amplitude decreases with rising excitation frequency.

![Fig. 2: FFT spectrum of the created multi-sine signal with decaying amplitudes.](image)

1.3 Analysis

For the interpretation of the results, sensor parameters as the A/D ratio and the substrate capacitance \( C_{\text{sub}} \) are needed. Both parameters are unique to the used sensor. The A/D ratio is obtained by the data sheet while the substrate capacitance is measured and calculated according to [30]. The system specific gain and phase information for the TIA as well as the following analog filtered outputs is determined by a circuit simulation using SPICE software. Additionally, information about the used excitation frequencies is necessary for the calculation of the characteristic values later on and for the interpolation of the simulation data to fit the values of interest in the data analysis.

In terms of measurements, the excitation voltage signal and the converted current proportional voltage signals are necessary for the analysis. These signals, so far only time dependent, are Fourier transformed to gain access to the frequency related information. Further the impedance \( Z \), respectively its inverse, the admittance \( Y \), as well as the phase angle \( \theta \) between current and voltage are calculated. From these two fundamental values, \( Z \) and \( \theta \), material specific parameters, among others conductance and capacitance are derived. This procedure is repeated for every single time sample. To assess the quality and information density of the acquired data the SNR is determined from the FFT data. As soon as the last data set is analyzed, the data is sent to plots for graphical interpretation of the results.
2. Experimental

2.1 Materials and sample preparation

During this investigation, a commercially available UV-radiation curable system provided by DELO Industrie Klebstoffe GmbH & Co. KGaA (DELO®) was examined. The type used within this research was the standard DELO® Photobond® PB437 (PB437). The PB437 is a one-component and solvent-free UV- and light curing adhesive based on a modified urethane acrylate. Typical fields of application are the bonding of plastics (PMMA, PC) but also glass or metal. Detailed information can be found on the DELO® website. To avoid interference, the sensing electrodes were cleaned upfront using acetone and isopropanol. Any remaining solvent was removed by heating up the sensing electrodes to fully vaporize it. The use of a planar interdigitated sensor for the measurement requires the thickness of the sample to be greater than the spacing between the electrodes in order to avoid measurements of air or material on top of the sample. Further, only shielded wires were used as long and unshielded wires pick up electrical interference and noise from nearby devices.

2.2 Test setup

The experimental investigations were conducted using three different methods, differential scanning calorimetry (DSC), shear rheology and the proposed simultaneous multi-frequency dielectric measurement technique. The first two methods are used to provide comparability of the measurement results to commonly used material characterization techniques and demonstrate the capabilities of the developed measurement system.

2.2.1 Differential Scanning Calorimetry (DSC)

The DSC measurements were performed with a Netzsch DSC 204 Phoenix photo-DSC setup. This setup consists of a light source (OmniCure S2000SC) and fiber optics which are connected to the DSC furnace. The optics are placed into the top cover of the furnace to ensure reproducible distances between sample and reference. Samples with masses between 9 – 13 mg of the adhesive were placed into aluminum pans and both, sample and reference, were irradiated simultaneously. During this procedure, the sample temperature and the heat flow difference were recorded.

2.2.2 Rheology

Oscillating rheology measurements were conducted using an MCR302 rheometer from Anton Paar GmbH. The MCR302 is equipped with a parallel plate setup. The bottom plate consisted of a highly UV penetrable glass plate. As a light source, the same OmniCure S2000SC and fiber optics were used as in the DSC and DEA measurements. The measurements were conducted within the linear region of the storage modulus, which allows only for a maximum measurement frequency of 1 Hz.

2.2.3 Multi-frequency dielectric measurements

For the dielectric measurements the interdigitated sensors were placed in an aluminum pan and fully covered with the PB437 adhesive. As radiation source the OmniCure S2000SC was used with the fiber optics placed above the resin in the same distance as for the DSC and rheology measurements.
Fig. 3: Schematic depiction of the signal processing chain

Fig. 3 shows the schematic signal processing chain. The signal chain starts at the function generator (Agilent Trueform Series Waveform Generator 80 MHz), which provides the excitation signal $V_{exc}$. The excitation voltage causes a response current $I_{res}$ in the capacitive interdigitated sensor. This current is subsequently converted into a voltage by the circuitry on the measurement board. The voltage $V_{meas}$ is then forwarded to an oscilloscope (Keysight Infinium S Series 500 MHz) where the analog current-proportional signal is converted to digital information for further data analysis. The same analog-to-digital conversion is performed for the excitation voltage $V_{exc}$ that is measured at the function generator.

3. Results

Fig. 4 shows the calculated results of the electrical impedance generated with the developed system as a function of frequency $f$ and time $t$. From the impedance data as a function of $(f, t)$ and the phase angle as a function of $(f, t)$ the relative permittivity $\varepsilon'$ and the loss factor $\varepsilon''$ can be derived according to [30]. In addition, the dissipation factor $\tan \delta$, the ionic conductivity $\nu$ and its inverse, the ionic viscosity $\sigma$, can be calculated as well. This data is more appropriate for further material analytics than only the purely electrical parameters impedance and phase angle.

Due to this representation, the impedance changes at higher frequencies are hard to determine. Nevertheless, the signal to noise ratio is much better at higher frequencies and the relative change for the derived quantities is in the same order of magnitude.
Fig. 5: Relative permittivity $\varepsilon'$ for several frequencies. All frequencies were recorded simultaneously.

Fig. 6: Loss factor $\varepsilon''$ for several frequencies. All frequencies were recorded simultaneously.

Fig. 7: Dissipation factor $\tan \delta$ for several frequencies. All frequencies were recorded simultaneously.

Fig. 8: Ionic viscosity $\nu$ for several frequencies. All frequencies were recorded simultaneously.

As can be seen from Fig. 5 depending on the frequency different behavior within the reaction can be observed. While the behavior of the relative permittivity is constant for all frequencies monitored, except for an offset between the different frequencies. Nevertheless, the progression of the offset can be an indicator, as well being now accessible for further analysis.

Fig. 7 and Fig 8 show the dissipation factor $\tan \delta$ and the ionic viscosity $\nu$ for the same 10 frequencies used in the figures above. As the dissipation factor is $\varepsilon''$ divided by $\varepsilon'$ the curve characteristics show similarities to Fig. 5 and Fig. 6. In Fig. 8 the frequency dependency of the ionic viscosity of the material becomes quite obvious.

This data was then used to compare the proposed monitoring system with the rheology and DSC measurement. In Fig. 9 the heat flow measured with the DSC, the storage modulus from the rheology measurements and the loss factor $\varepsilon''$ for 10 different frequencies are displayed. With $f(1)$ at a low frequency of 5 kHz and $f(10)$ with 380 kHz, the other frequencies are equally distributed. Each mark represents a distinct data point. The amount of data captured by the rheology setup is limited to the linear region of the complex viscosity, which is up to 1 Hz for the PB437. The heat flow from the DSC setup represents an integrated signal of the energy converted within the reaction. This allows a good distinction of different reactions if they take place after one another or differ strongly in time.

The system presented in this paper offers additional information as the short signal rise directly after the start of UV radiation, which could be reproduced for all other measurements of the PB437. Further, the data obtained from the DEA yield a more distinct representation of the reactions during the curing process, compared to rheology and DSC.
Fig. 9: Comparison dielectric measurements for 10 different frequencies with the storage modulus from the rheology and the heat flow from the DSC.

4. Conclusion

The presented device has proven its feasibility for the spectroscopic monitoring of reactive UV curing resins. Now the frequency dependent behavior becomes accessible in real-time. Because 20 data points over the entire bandwidth of the system are captured time synchronously a curve for each time step can be created. The lowest frequency used to monitor the reaction limits the time resolution. Therefore, the proposed system overcomes the limitations typically accompanied by the standard DEA systems commercially available. The same is true for commercial vector network analyzers or LCR-meters, which both use frequency sweeps for spectroscopic analysis.

The time synchronous data opens up new possibilities of reaction monitoring, e.g. to determine the conversion of reaction partners by the use of the frequency dependent permittivity.

Further development of the system will focus on the extension of the measuring range and a miniaturization of the system to avoid additional equipment for signal generation and acquisition. Additional signal processing optimizations are ongoing and other fields of application are currently considered.

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References