Design, Calibration and Validation of 24 GHz Resonators for Epoxy Resin Cure Monitoring Systems in the Fibre-Reinforced Plastics Fabrication

Jannis GROH 1, Jan SCHÜR 1, Mehdi JAVDANITEHRAN 2, Gerhard ZIEGMANN 2, Martin VOSSIEK 1

1 Institute of Microwaves and Photonics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany
2 Clausthal Centre of Material Technology, TU Clausthal, Clausthal-Zellerfeld, Germany
Contact e-mail: jannis.groh@fau.de

Abstract. The quality and the mechanical properties of fibre-reinforced plastics (FRP) are strongly dependent on the processing of the matrix during the curing process. The exact analytical process control is difficult due to the complex relationships between the geometry and reaction kinetics. Therefore, an on-line monitoring of the curing process is necessary to reach a higher quality and reproducibility in FRP-fabrication.

Besides a variety of non-destructive testing methods, the examination of materials based on their dielectric properties has established itself as a reliable method in various applications. State of the art dielectric methods used for measuring such curing processes use frequencies up to a couple of GHz or in the IR range.

To develop printed circuit sensors that are integrable in FRP, it is necessary to focus on small wireless chipless sensors operating in the microwave range e.g. at 24 GHz. The measured permittivity offers information about the polarizability of the examined medium. The main polarization effects in this frequency range are dipolar and lattice polarization. Thus, the permittivity is directly related to the cross-linking level of the matrix composites and thereby also to the curing level. The dielectric behaviour around 24 GHz of epoxy resins during their curing process has not yet been investigated adequately up to now. This fact makes it difficult to design optimized sensor structures.

This paper will present and discuss several methods to accurately measure the dielectric properties of epoxy resins at 24 GHz during the curing process of FPRs. The used measurement systems allow for reference measurements and also for validation of future integrable chipless wireless sensors. A comparison and evaluation of a hemispherical open resonator and an open coaxial resonator is given. The pros and cons and the technical limitations of both designs are discussed. Furthermore the progression of measured dielectric properties as a function of the temperature is correlated with corresponding isothermal differential scanning calorimetry measurements. The shown response surface and the correlation function strongly underpin the usefulness of microwave sensors for FRP-applications.
Introduction

Fibre-reinforced plastics (FRP) are becoming one of the most important materials in the present time. The rotor blades of wind turbines for example are almost exclusively build of fibre glass reinforced plastics. FRP are also indispensable for the aircraft, automotive and ship building industry. Due to the stability and lightness the popularity as construction material is steadily increasing. As especially the stability depends strongly on the curing process and the resulting cross-linking level, the non-destructive monitoring possibilities are restricted. The differential scanning calorimetry (DSC) method is one of the widest-spread techniques for cure monitoring of epoxy resins. Therefore the heat flow, which is associated with the transition in the material as a function of time and temperature [1], is measured. This method is applied on very small samples in a temperature controlled surrounding. So it is not directly applicable on an industrial process and only representative for isothermal curing.

An alternative obvious approach to determine the cross-linking level of epoxy resins is to measure the mobility of the epoxide groups and the reactive hydrogen, which are the reaction partners providing the cross-linking. This mobility can be measured as polarizability in terms of the dielectric properties. Thus a dielectric measurement in the GHz frequency region allows access to the information about the lattice and dipolar polarizability and therefore is directly related to the cross-linking level respectively the degree of curing. To determine also small changes of the cross-linking level the paper focus is on resonant measurement methods.

1 Hemispherical Open Resonator Method

1.1 Principle and Setup of Measurement

The characterization of the dielectric properties by measurements in a hemispherical open resonator is based on the description of the electromagnetic field distribution in terms of the Gaussian beam theory. The technique is well known [2-4] and established itself as a precise approach to measure the permittivity and loss tangent of low-loss materials. It is applicable for single layered as well as for multi-layered substrates [5-6].

The employed resonator was developed in [7-8]. It consists of a planar and a spherical mirror facing each other (Fig. 1). Both mirrors are made of aluminium and have been polished after fabrication. Two small coupling holes with an aperture diameter of 2.5 mm are located in the centre of the confocal mirror. Both holes interface with two WR-42 rectangular waveguides at the backside of the mirror as feed and extraction ports for the RF test signal. Due to the position of the coupling holes and the limitation of the beam radius with an absorbing aperture only TEM$ _{00p}$ modes are supported by the resonator. The resonant frequency of an empty hemispherical open resonator with a distance D between the two mirrors is

$$f_r = \frac{c_0}{2D} \left[ p + \frac{1}{\pi} \arctan \left( \frac{D}{r - D} \right) \right], \quad (1)$$

where p is the number of half wavelength in the resonator and r is the radius of the concave mirror. For the measurements presented in this paper a spherical mirror with a radius $r = 0.249$ m was placed in a distance of $D = 0.189$ m from the planar mirror. Considering TEM$ _{0030}$ as the resonant mode to be evaluated, the resulting resonance without sample is in
dependency of the applied temperature at around 24 GHz and has a quality factor $Q$ around 100,000.

By inserting a dielectric sample into the Gaussian beam, additional losses will occur and therefore an extension of the electric length of the resonator, caused by the shorter wavelength in the sample. This leads to a lower resonance frequency $f_r$ and lower quality factor $Q$ as a function of permittivity $\varepsilon_r$ and loss tangent $\tan\delta$. The maximal change and therefore also the highest sensitivity is achieved if the sample is located in a maximum of the electric field intensity. At the plane mirror the electric field of the Gaussian beam has to vanish (Fig. 2) due to the conducting nature of the metallic material. This leads to a decreased sensitivity if the sample is simply placed on top of the mirror. In addition measurement errors easily appear if the sample is not placed perfectly plane on the mirror.

![Fig. 1. Hemispherical open resonator with sample and sample holder](image)

To maximize the sensitivity and minimize inaccuracies caused by divergences of actual surface geometry and the assumed computation model of the sample, the dielectric properties are determined with the approach presented in [8]. This approach is based on the evaluation of the variation in resonant frequency and quality factor while the sample is moved from the plane mirror to the first maximum or minimum of the electric field in z-direction (Fig. 2).

![Fig. 2. Electric field intensity in z-direction](image)

Taking into account that the epoxy resin is liquid at the beginning and therefore will have a curved surface due to its surface tension, it is self-evident to choose an approach that is robust against surface geometries which differ from plane samples. In addition this approach offers the opportunity to adjust the measured thickness $d_{\text{MUT}}$ of the sample by evaluating differences in curve shapes of simulated and measured change of resonant
frequency and quality factor, which are related to the thickness $d$ of the air gap below the sample.

In principle the only necessary calibration for this approach is the measurement of the resonant frequency and quality factor of the resonator without a sample. In addition a normalisation was carried out to improve the dynamic range. This normalisation is simply realized by inserting absorbers into the Gaussian beam path.

For measuring liquid samples it is indispensable to use a sample holder. Therefore the multi-layered approach described in [7-8] was used for the determination of the dielectric properties of the epoxy resin. To keep the additional losses as low as possible a sample holder made of a low loss microwave circuit substrate (Rogers RO4003) with the thickness of $d_{Sub} = 0.2$ mm was designed. Therefore the substrate was fixed in a frame made of aluminium with adjusting screws to maintain tension of the substrate and improve planarity. The measurements were performed in a heating chamber to guarantee stable conditions for the whole resonator setup at the desired reaction temperature. To obtain the permittivity and the loss tangent of a single layer in a multi-layered sample, the geometrical and dielectric properties of all other layers have to be known. Therefore the dielectric properties of the sample holder substrate were determined for each measurement separately in advance.

1.2 Measurement Results

The examined matrix consist of EPIKOTE™ epoxy resin RIMR 135 and the curing agent RIMH 137. In a first step the evaluation of the parameters of the empty resonator, normalisation and measurement of the RO4003 substrate in the heat chamber were conducted. Then three gramm of the mixed and vacuum degassed composites were dispensed on the sample holder to an approximately 0.2 mm thin layer ($d_{MUT}$). Despite the low loss substrate and the very thin layer of epoxy resin a reduction of the measurement bandwidth of the used vector network analyzer to 1 Hz was necessary, to reduce the noise floor and to identify the resonance frequency. This leads to an extension of acquisition time up to 15 minutes for each measurement comprising one frequency sweep at 11 different distances $d$ on the way to the first maximum of the electric field intensity.

The obtained permittivity $\varepsilon_r$ and the related loss tangent $\tan\delta$ during the curing process at 60°C, 70°C and 80°C are depicted in Fig. 3 and Fig. 4. The decrease of $\varepsilon_r$ and $\tan\delta$ is caused by the continual reduction of the dipolar and molecular mobility by the increasing cross-linking level of curing agent and resin and is therefore directly related to the degree of curing.

![Fig. 3. Permittivity $\varepsilon_r$ of epoxy resin during the curing process](image)
To validate the correlations between the obtained dielectric properties and the degree of curing, these results were compared to results obtained by the isothermal curing kinetics modelling developed in [1]. This model is based on differential scanning calorimetry (DSC) measurements. With an excellent accordance between model and measurements, the DSC measurements have been replaced by the model based results in this paper. To express $\varepsilon_r$ in the manner of the curing degree $\alpha$ it is normalized by

$$\alpha = \frac{\varepsilon_r(t_0) - \varepsilon_r(t)}{\varepsilon_r(t_0) - \varepsilon_r(t_{\text{end}})} \quad \text{(2)}$$

The comparison of the curing degree obtained from the permittivity measurements with the open resonator and the isothermal curing model is depicted for the different temperatures in Fig. 5. In Fig. 6 the model and $\tan\delta$ based curing degree is compared, whereby the normalization of $\tan\delta$ can be achieved just as for $\varepsilon_r$ resulting from equation (2).

Fig. 5 also shows that especially the permittivity is a good indicator for the degree of curing. The loss tangent can also be used as a tracer but an exact determination of $\tan\delta$ gets more difficult with additional losses at higher temperatures. This results in a higher uncertainty for higher temperatures in the obtained results which becomes obvious in Fig. 6.
Fig. 6. Degree of curing determined from the standardized loss tangent \( \tan \delta \) in comparison with the data obtained from the according DSC-model

2. Open Coaxial Resonator Method

2.1 Principle and Setup of Measurement

The second way to determine the dielectric properties of the epoxy resin presented in this paper is an open coaxial resonator. The measurement principle is therefore based on the change of the terminating impedance at the open end of the resonator in dependency of the material placed in the electromagnetic field fringing out of the resonator. The fringing field results in an electrically longer resonator [11]. Shortened on one side and open on the other, the total effective electrical length \( l_{\text{eff}} \) of a coaxial resonator has to be an integer multiple of a quarter wavelength for the resonant frequency \( f_r \). An equivalent circuit of the resonator and the added components representing the fringing field is depicted in Fig. 7.

Fig. 7. Equivalent circuit of the open coaxial resonator

According to [11] the resonant condition for a radiating open coaxial resonator can be expressed as

\[
\Delta G + j \omega \Delta C = Y_0 \tan(\gamma \Delta l),
\]

(3)

where \( Y_0 \) is the characteristic admittance in the resonator, \( \omega \) is the circular frequency, \( \Delta G \) and \( \Delta C \) are the conductance and capacity added by the fringing field and \( \gamma \) is the propagation constant in the material at the open end of the resonator. If the total admittance at the terminal pair of the open resonator is \( Y = G + jB \), the quality factor can be calculated by [12]

\[
Q = \frac{\omega}{\frac{\partial B}{\partial \omega}}.
\]
Evaluating (3) makes it obvious that the additional length $\Delta l$ depends on $\Delta G$, $\Delta C$ and $\gamma$ respectively which are all determined by the dielectric properties of the material. The terminating impedance and according to equation (3) the additional length can be calculated analytically for various geometries, if the field distributions are known. The hypothetical field distributions inside and outside the resonator therefore have to be matched at the boundary between resonator and MUT with respect to all boundary conditions, the dielectric properties of the MUT and the applied electromagnetic field. Solving the matched field equations for the corresponding reflection coefficient, the terminating impedance can be calculated and applied to the resonant condition (3) and the calculation of the quality factor (4). The obtained resonant frequency and quality factor in dependency of the dielectric properties than have to be compared with the measured parameters.

With respect to later applications, the resonator was constructed for the use in a reaction chamber made of aluminium which is filled via vacuum infusion. So the leakproofness and stability of the resonator is very important to avoid bubbles in the resin. A spatial limitation of the fringing field to a small region of measurement is also of interest, to realize a local measurement and avoid the stimulation of substrate modes propagating through the whole reaction chamber. Therefor the last sections of the inner and outer conductor are tapered to achieve a higher sensitivity with a significant higher concentration of the electric field in a small area at the end of the conical waveguide section. The designed resonator is depicted in Fig. 8. The conical shape of the outer conductor leads to an also conical shaped teflon filling that is the dielectric of the resonator. This conical shaped teflon covers the 0.1 mm shorter inner conductor, in order to obtain a thin layer of Teflon between the inner conductor and the MUT. This causes a high leakproofness if there is a depression at the tapered side of the resonator.

The resonator is only weakly coupled with two UT-85 semi-rigid coaxial waveguides, which are short-circuited at the end. The coupling of the electromagnetic field between the waveguides and the resonator is achieved by two 0.2 mm high and 1.5 mm wide coupling slots placed at the end of the waveguides. The geometrical length of the outer conductor is $l = 9.7$ mm. The resulting resonant frequency of the supported TEM-mode can be measured in dependency of applied temperature and MUT between 24.5 GHz and 25 GHz. The effective length of the resonator corresponds to five times the quarter wavelength of this mode. The coupling aperture between resonator and MUT has a radius of $r_c = 0.5$ mm. At the cylindrical part of the resonator the radii of the inner and outer conductor are $r_i = 1$ mm and $r_a = 3.5$ mm respectively and the space is also filled with teflon as dielectric.
To guarantee an isothermal curing the height of the reaction chamber was set to $d_{\text{MUT}} = 2\,\text{mm}$ for the measurements presented in this paper. The reaction chamber with the resonator was placed in a temperature controlled oil bath which was maintained at the desired reaction temperature for at least one hour before measurements have been started.

The mounting support for the resonator was designed with a screw thread for height adjustment. This setup provides a regulation for the distance between the resonator and the aluminium wall of the reaction chamber at the other side. It can be set to $d_{\text{MUT}} = 0$ at measurement conditions without removing the resonator from the oil bath. This leads to the highest possible capacitive load for this resonator. A contrary measurement is achieved by adjusting the distance to a height of $d_{\text{MUT}} = 2\,\text{mm}$ in accordance with the height of the reaction chamber. The evaluation of the measured data was performed with the 3D electromagnetic field simulation program CST. With the two data sets described before an iterative adaption of the geometric parameters in the CST simulation model is possible to obtain a model that represents the behaviour of the resonator for the exact conditions of the measurement to be evaluated.

To remove influences of standing waves and cable losses in the feeding coaxial lines, a TRL-calibration has been carried out prior to the measurements. The TRL-calibration standards have been implemented by coaxial lines - connector assemblies analogue to those used for the resonator. The exact lengths of the coaxial lines for the TRL-calibration have been determined by reflection measurements in the time domain. Additionally a controlled heating of the lines was implemented to reproduce the measurement conditions for the TRL-standards at different temperatures.

2.2 Measurement Results

In Fig. 9 and Fig.10 the evaluated dielectric properties during the curing process for the same kind of epoxy resin and curing agent are shown for reaction temperatures of 60°C, 70°C and 80°C. The obtained results from the coaxial resonator measurements are in good consistent with those obtained with the spherical open resonator. At the beginning measurements were recorded in 30 seconds intervals. Therefore and in contrast to the open spherical resonators the results also show the heating of the epoxy resin, after it has been infused with room temperature. The quick acquisition of measurement data enables the monitoring of temporally short events like the heating at the beginning or the short temperature increases in thicker samples caused by the exothermic reaction.

![Fig. 9. Permittivity $\varepsilon_r$ of epoxy resin during the curing process](image)

8
To correlate the obtained results with the curing degree based on the DSC-model developed in [9] the permittivity and loss tangent were normalized analogue to the open spherical resonator measurements before. It should be noted that the value at $t_0$ in Equation (2) has to be a theoretical value representing the dielectric properties of the resin starting to cure on the designed reaction temperature without heating up. In this case it was calculated by replacing the dip at the beginning with a curve extrapolation to the zero point of the time axis. In Fig. 11 and Fig. 12 the curing degree calculated from the DSC-model is compared to the one computed from the permittivity and quality factor of the coaxial resonator measurements.

Fig. 11: Degree of curing determined from the standardized permittivity $\varepsilon_r$ in comparison with that obtained from the according DSC-model

Fig. 12. Degree of curing determined from the standardized loss tangent $\tan\delta$ in comparison with the data obtained from the according DSC-model
In comparison to the spherical resonator measurement, a lower correlation to the DSC-model can be observed. Nevertheless the relation between the determined dielectric properties and curing degree is obvious. A reason for the differences may be the analysis with the 3D simulation solver which is supposed to be replaced by an analytical model of the resonator in the future. This avoids inaccuracies caused by the quantisation of the 3D-model when the mesh is adapted to the geometry.

3. Discussion

The open resonator proved to be a precise and powerful tool to obtain the dielectric properties of planar material samples. The obtained results are in a good agreement with the curing degree maintained by models and measurements with state of the art techniques. Because of the high losses of fluid epoxy resin and curing agent a very thin and continuous layer is needed as sample. If this condition is not guaranteed the determination easily collapses. To enable measurements applying this technique a very small measurement bandwidth and thus a long data acquisition time is required. A snapshot especially of fast changing properties is consequently not possible. Due to the geometry dependent reaction kinetics the spherical open resonator method is hence only representative for very thin components with absolutely isotherm curing and slowly varying properties. In contrast the open coaxial resonator method can be applied to most applications but the sensitivity is considerable lower in comparison to the spherical open resonator method. However the sensitivity is way enough for a precise cure monitoring. The simulative determination of the dielectric properties can be applied, but is not sufficient for a quick and precise real time evaluation of the composite matrix’s dielectric properties and therefore should be replaced by an analytical description of the terminating impedance for advanced applicability.

4. Acknowledgement

The authors acknowledge the financial support provided by the DFG (Deutsche Forschungsgemeinschaft) (Project VO 1453/12-1, ZI 648/34-1).

References


