10th International Conference on Composite Science and Technology
ICCST/10
J.Schmidt, M.Opitz, N.Liebers

EVALUATION AND CALIBRATION OF TOOL INDEPENDENT CURE MONITORING SYSTEMS FOR EPOXY RESINS

J. Schmidt[*] , M. Opitz[†], N. Liebers[†]

[*†]German Aerospace Center, Institute of Composite Structures and Adaptive Systems
Braunschweig, Germany
jochen.schmidt@dlr.de

mark.opitz@dlr.de, nico.liebers@dlr.de

Key words: Composites, Epoxy resin, Degree of cure, Process monitoring.

Summary: *There is a strong demand for cure monitoring solutions to improve the manufacturing processes for FRP components made from thermoset polymers. Piezoelectric ultrasound sensors and dielectrical analysis are systems that do not require major modifications to the molds. Both systems proved to be able to monitor the curing process and to determine the earliest point in time when the component may be demolded. To link the sensor values conductivity and signal velocity to the degree of cure a lookup table for the individual resin system is necessary.*

1 THE INCREASING NEED FOR CURE MONITORING SOLUTIONS

The cure monitoring of FRP components is a well-established field of research since decades. The main aims are to improve manufacturing processes to make them more efficient and to assure the quality of the FRP components. S. Konstantopoulos, R.Meier and N. G. Pantelelis showed in previous publications that there are various measuring principles to monitor the curing process especially of epoxy matrices. Those systems which partly reached maturity phase include direct current resistivity measurement, the dielectrical analysis, ultrasound analysis, spectroscopy and thermography [1,2,3]. Some of those systems are restricted concerning the implementation in closed molds or proven tooling concepts. Therefore for this survey the ultrasound cure monitoring and the dielectric analysis have been chosen as they do not require major modification to the mold. Besides the process optimization for economic reasons another area of application occurred in the recent past. Since the curing process has a significant influence on the mechanical properties of the FRP component and on its geometrical accuracy it is mandatory to monitor it to be able to manufacture high accuracy FRP parts [4]. There grew a strong request for such components along with the research on UAVs especially for natural laminar flow and low radar signature applications. Therefore there is a need for advanced manufacturing processes based on process monitoring and control. Regular single step manufacturing processes using temperature as sole input value do often result in FRP components with poor geometrical precision. Internal research on laminar wing leading edges revealed that it is promising to use two-tier processes with an initial cure at a low temperature and a free standing post cure to reduce those deviations. For further improvement of this manufacturing approach it is important to monitor the degree of cure to

be able to determine when the first step is completed and the composite part can be demolded. It is even more important to monitor the degree of cure during the post curing process to make sure that the curing temperature does not come too close to the current glass transition temperature of the composite part to avoid plastic deformation.

2 APPLIED MEASUREMENT PRINCIPLES

2.1 Acoustic cure monitoring

The ultrasound measurement process chosen for this test series is the transmission technique. Piezoelectric elements are attached concentrically to opposite sides of the tooling. One of the elements is connected to a signal generator the other one is connected to an oscilloscope. The signal run time through the tooling and therefore through the resin specimen is measured. It declines with an increasing degree of cure as the resin gains stiffness during this process. This means the signal velocity calculated from the run time and the width of the mold cavity increases as the vitrification of the epoxy resin is ongoing [5,6]. Figure 1 shows the type of discoidal piezoelectric sensors that were used to perform the cure monitoring on the samples. In order to avoid unstable acoustic coupling to the tooling those piezoceramics were bonded directly to the mold using a conductive temperature resistant adhesive [6,8]. The thermal extension of the tooling can be determined using the echo from the inner mold face. Therefore the extension of the signal runtime due to the elongation of the distance is considered in the calculation of the signal velocity.

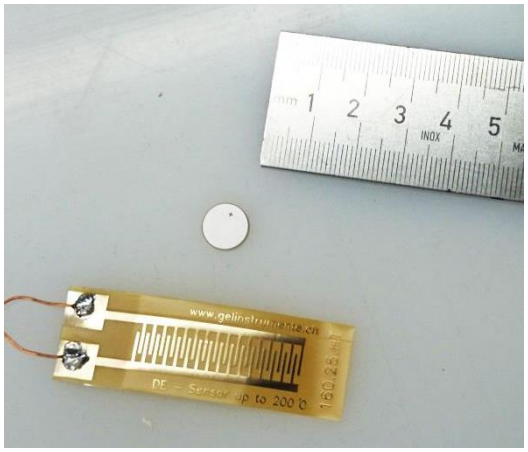

Figure 1: Flat interdigital sensor and above discoidal piezoelectric sensor

2.2 Dielectric cure monitoring

The dielectrical value conductivity can be used to monitor the curing of thermoset polymer materials. During the ongoing cross linking process within the resin the viscosity increases constantly. This leads to an impeded mobility of the charge carriers. Reaching the end of a curing process when there is a solid composite structure both dipoles and ions are not able to align themselves anymore. This means they are in an unaligned state which avoids any conductivity [5,7]. The most important advantage of the dielectric system is its ability to perform measurements without any mechanical influence to the specimen. Furthermore it is possible to attach the thin film sensors to a specific layer within a stacking. The equipment used for this study was a PDE-1 provided by Gel Instrumente.

2.3 Differential scanning calorimetry

The curing of epoxy resins is an exothermal reaction. Thermal energy is emitted during the process and the amount of energy can be measured. The degree of cure is defined as the rate of thermal energy a pre cured resin specimen emits compared to the total amount of thermal energy an uncured resin specimen emits. This means with an increasing degree of cure less thermal energy is emitted by the specimen [5]. According to this the degree of cure determined by DSC analysis is the ratio of the total conversion enthalpy which is a specific resin value to the residual enthalpy of the specimen. *Table 2* shows the previously determined average total conversion enthalpy for both epoxy resin systems used for the specimen.

$$\boldsymbol{A}_{\mathrm{DSC}} = \mathbf{100}\% \cdot \left(\mathbf{1} - \frac{\Delta \boldsymbol{H}}{\Delta \boldsymbol{H}_{\boldsymbol{t}}}\right) \tag{1}$$

Epoxy resin	**Parameter**	**Temperature Gradient**	**Maximum Temperature**
Hexflow RTM6-1	conversion enthalpy $\Delta \boldsymbol{H}$	2 K/min	250 °C
	glass transition temperature $\boldsymbol{T_g}$	10 K/min	250°C
Araldite LY564 / Aradur 22962	conversion enthalpy $\Delta \boldsymbol{H}$	2 K/min	225°C
	glass transition temperature $\boldsymbol{T_g}$	10 K/min	225°C

Table 1: Differential scanning calorimeter setup

The determination of the glass transition temperature and the measurement of the conversion enthalpy were performed according to ISO 11357. All tests were performed using a differential scanning calorimeter DSC822^e provided by METTLER TOLEDO.

Epoxy resin	**Number of samples**	**Average total conversion enthalpy $\Delta \boldsymbol{H_t}$ [J/g]**	**Standard deviation**
Hexflow RTM6-1	5	456,19	19,68
Araldite LY564 / Aradur 22962	3	473,52	10,89

Table 2: Overall conversion enthalpy of both resin systems

3 EXPERIMENT SET-UP AND EQUIPMENT

3.1 Test schedule and procedure

As it was expected that there may occur different results depending on the resin system tested it has been decided to choose two epoxies with different characteristics. The first one is Huntsman Araldite LY564 combined with the hardener Aradur 22962. This difunctional resin cures in a wide temperature range from room temperature up to 150°C. It is commonly used for fast resin transfer molding applications. An initial cure at around 60°C allows the manufacturing of composite parts with very small deviations but with some restrictions concerning the mechanical properties.
The second resin system that has been chosen is Hexcel Hexflow RTM6-1. This one is tetrafunctional and it is commonly used for aircraft applications. It has to be cured at 180°C to achieve optimum mechanical properties and a high glass transition temperature. The lowest curing process to manufacture composite parts in a reasonable time from this resin is at 130°C. It is a single component system which means it is premixed and has to be stored at subzero conditions to avoid any curing reaction during storage time.
The following table shows the temperatures defined for the isothermal curing processes of the specimen and the corresponding curing times.

Epoxy resin system	Sample Name	Curing temperature	Curing time [min]
Araldite LY564 / Aradur 22962	LY564_040_01	40	165,4
	LY564_060_01	60	59,4
	LY564_090_01	90	38,3
	LY564_090_04	90	19,7
	LY564_120_01	120	6,9
	LY564_150_01	150	15,1
Hexflow RTM6 1K	RTM6_120_01	120	268,0
	RTM6_140_01	140	130,7
	RTM6_170_01	170	41,8
	RTM6_200_01	200	30,9

Table 3: Test schedule and sample names

The curing time starts when the resin is poured into the mold and it ends when the cool down is initiated. To achieve a smooth and steady temperature curve especially at higher curing temperatures and to avoid measurement errors resulting from a temperature gradient it has been decided to preheat the mold to the specific process temperature. The LY564 resin has been prepared at room temperature and poured into the mold within three minutes after mixing. The RTM6-1 has been preheated at 80°C for 30 minutes to achieve a viscosity low enough to be able to pour it into the mold. The measurement of all sensor systems was started before pouring the resin into the tooling.

3.2 Temperature controlled mold

As shown in *Figure 2* the mold consists of two halves made from aluminum that are clamped to each other in an upright position. The parting line is sealed with a rubber piping. A landing around the tooling face creates a mold cavity with a width of exactly 5mm. Both thermocouple and interdigital sensor as shown in *Figure 1* were installed inside the mold whereas three pairs of the piezoceramic sensors were attached to the outer faces of the halves.

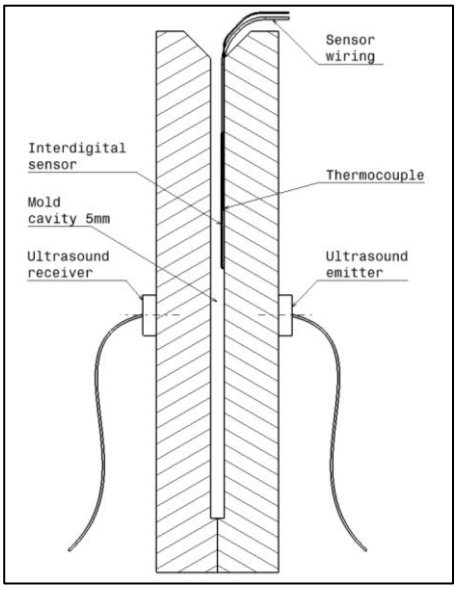

Figure 2: Cross section of the tooling and sensor positions

The resin temperature has a great influence on its reaction rate. This means the higher the resin temperature is the faster the curing will be completed [5]. To be able to control this temperature the mold as shown in *Figure 3* was connected to a closed water circulation temperature control unit. The maximum cool down rate of this test set-up was determined to be 17 K/min in previous test run. This is particularly important to avoid significant further curing during cool down which would lead to incorrect results from the DSC analysis.

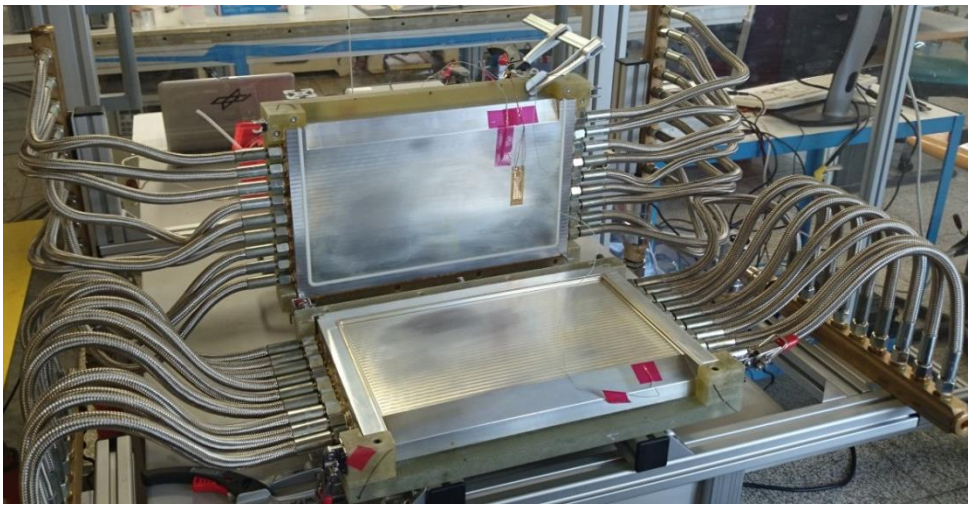

Figure 3: Opened temperature controlled tooling with sensors attached to the tooling face

4 TEST RESULTS

The figure below shows the sensor data acquired during the curing cycle of the specimen *RHPW_LY564_090_04.* It is used as an exemplary chart to discuss the characteristic attributes in the following section.

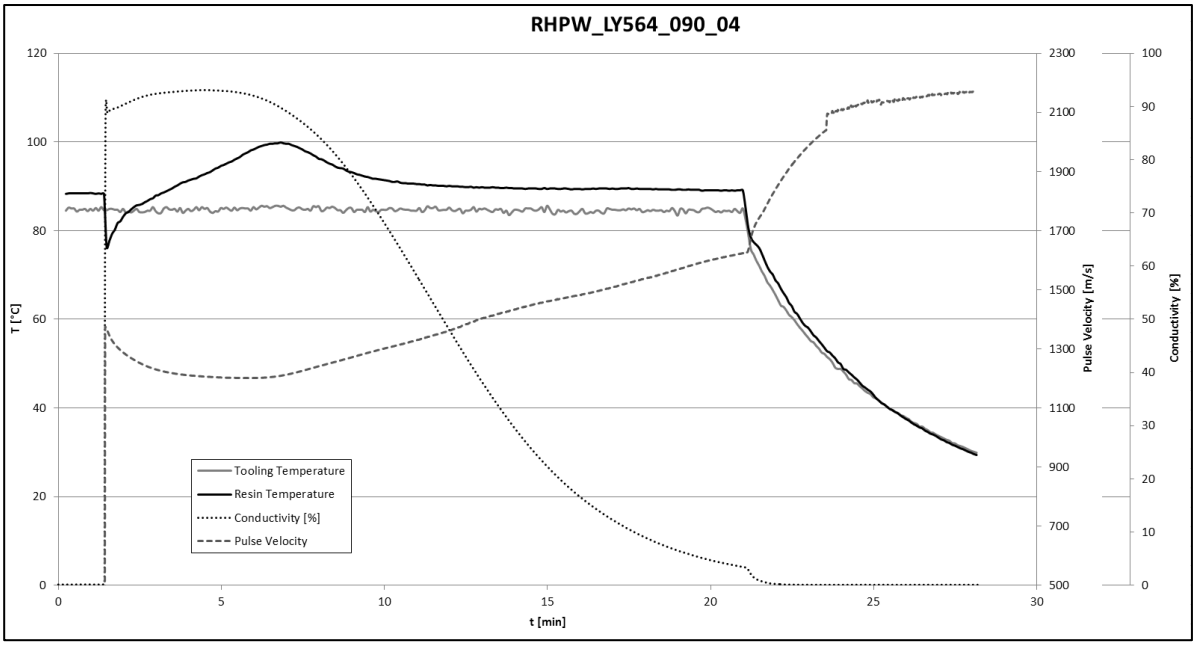

Figure 4: Exemplary curing chart of RHPW_LY564_090_04

The curing process starts at 1:45 min when the resin was poured into the mold. The pulse velocity starts from zero because of the missing acoustic coupling and jumps up to approximately 1400m/s as soon as there is resin in the cavity between the ultrasound sensors. This starting value depends on the resin`s viscosity and its temperature when it is poured into the mold. The conductivity changes from total insulation to a conductivity of about 90% as soon as the interdigital sensor comes in contact with the resin. At the same time the resin temperature drops for a short period because the epoxy was prepared at room temperature to avoid any curing in advance.

After that the pulse velocity decreases and conductivity increases because the resin becomes less viscous. This happens for a few different reasons. At first the resin is heated up through the tooling. In addition there is also the energy emitted by the exothermal reaction of the epoxy resin systems and especially of Araldite LY564. There occurred temperature peaks within the specimen whereas the largest temperature difference that was measured occurred at both samples *LY564_120_01* and *LY564_150_01* and was 55 K in average. Another reason for the decreasing viscosity of Araldite LY564/Aradur 22962 is a thinning agent that starts working after mixing both components.

After that temperature peak the ongoing cross linking between the epoxy reactants leads to an increasing viscosity and to a decreasing mobility of the charge carriers within the resin. Therefore the measured conductivity is falling whereas the signal velocity is rising.
At 21min the cool down of the tool is beginning while the conductivity is at 3,38% and the pulse velocity is at 1655m/s. During the cool down the signal velocity increases rapidly and the conductivity drops to total insulation. As the temperature of the specimen falls below its current glass transition temperature which is depending on its degree of cure the material properties change from viscoelastic to glass hard and brittle [1, 6, 7]. *Table 4* shows the characteristic data for all manufactured specimen.

	Dielectric System		**DSC Analysis**					**Piezoelectric System**		
Sample	Conductivity at Cool Down [%]	**Dielectric Degree of Cure [%]**	Average Residual Reaction Enthalpy [J/g]	**Average Degree of Cure from DSC [%]**	Standard Deviation	**Average Tg from DSC [°C]**	Standard Deviation	Normalised Pulse Velocity Start [m/s]	Normalised Minimum Pulse Velocity [m/s]	**Normalised Pulse Velocity at Cool Down[m/s]**
LY564_040_01	5,69	**0,94**	114,74	**0,758**	12,47	**62,11**	0,03	1355	1305	**1605**
LY564_060_01	5,52	**0,94**	103,69	**0,781**	13,22	**62,86**	0,07	1355	1255	**1605**
LY564_090_01	0,10	**1,00**	25,03	**0,947**	1,08	**88,89**	1,39	1355	1255	**1705**
LY564_090_04	3,38	**0,96**	100,41	**0,788**	2,41	**65,96**	0,25	1355	1195	**1605**
LY564_120_01	4,77	**0,95**	23,11	**0,951**	2,38	**100,00**	3,59	1355	1105	**1585**
LY564_150_01	9,84	**0,90**	0,00	**1,000**	0,00	**123,23**	0,18	1355	1055	**1225**
RTM6_120_01	6,19	**0,94**	178,91	**0,608**	5,39	**64,13**	2,14	1383,75	1258,75	**1728,75**
RTM6_140_01	5,11	**0,94**	117,17	**0,743**	4,81	**111,35**	0,74	1383,75	1183,75	**1683,75**
RTM6_170_01	3,33	**0,96**	66,26	**0,855**	1,79	**150,93**	1,96	1383,75	1123,75	**1813,75**
RTM6_200_01	24,08	**0,74**	17,25	**0,962**	0,58	**211,18**	3,62	1383,75	1133,75	**1723,75**

Table 4: Compilation of all test results

To find out if there is a direct link between the sensor values conductivity and pulse velocity and the degree of cure a DSC analysis has been performed after the demolding of the specimen. The table above shows degree of cure determined following (1) and the glass transition temperatures of the samples. As one can see neither the dielectric degree of cure nor the pulse velocity at cool down correlate with the increasing average degree of cure from DSC. The values of both cure monitoring systems depend on the viscoelastic behaviour of the resin and therefore on its temperature. This becomes particularly obvious when the cool down starts and both measurements show a large gradient.

1 CONCLUSIONS

Both cure monitoring systems proofed to be able to determine the vitrification of both resin systems independent from the curing temperature. Further evaluation of the results from the trial shows that there is no obvious direct link between the velocity of sound and the degree of cure determined by the DSC analysis. The same applies to the dielectric conductivity of the resin. For both monitored sensor values a lookup table for the individual resin is necessary to be able to make a statement concerning the degree of cure.

Furthermore the acquired data should be reassessed to find out if the pulse velocity or the conductivity directly describes the ratio between the current glass transition temperature of the resin and the effective temperature of the sample.

At higher curing temperatures close to the maximum reachable glass transition temperature of the individual epoxy resin system there may occur problems with the ultrasound cure monitoring. As those temperatures lead to higher curing reaction rates chemical shrinkage within the resin increases. For this reason the resin sample can lose the close contact to the tooling face in some areas which means the acoustic coupling is not granted anymore. In this case the waves can propagate between the sensors and the measurement is interrupted. This took place during the curing processes of *LY564_150_01* and *RTM6_200_01* but it never happened to all three pairs of piezoceramics.

After the initial cure process the interdigital sensors are firmly attached to the specimen or composite structure. This means one could reconnect them to the data acquisition after demolding the structure. Further tests have to be made using initially cured sensor equipped specimen to find out if the sensor data delivered during free standing post cure can be used to improve the manufacturing process.

As it is possible to attach the piezoelectric sensors directly to the composite structure after demolding, the ultrasound system may also allow a monitoring of a free standing post cure process. Further tests have to be made to show that the quality of the sensor data acquired this way is sufficient for a closed loop control of the post cure process.

REFERENCES

[1] S. Konstantopoulos, E. Fauster, R. Schledjewski, *Monitoring the production of FRP composites:A review of in-line sensing methods.* eXPRESS Polymer Letters Vol.8, No.11, 2014

[2] R.Meier, S.Zaremba, O*nline process monitoring systems – benchmark and test study.* FPCM-11, Auckland, 2012

[3] N. G. Pantelelis, E. Bistekos, *Process monitoring and control for the production of CFRP components.*SAMPE, Seattle, 2010

[4] M. Kleineberg, *Präzisionsfertigung komplexer CFK-Profile am Beispiel Rumpfspant.* PhD thesis, Braunschweig, 2008

[5] G. Gkikas, D. G. Aggelis, *Simultaneous acoustic and dielectric real time curing monitoring of epoxy systems.* Smart Sensor Phenomena, Technology, Networks, and Systems Integration, 2012.

[6] N. Liebers, *Sensor guided cure Processes – a Study of productivity and quality optimization potential.* The 19th international conference on composite materials, 2013.

[7] C.G.W. Ehrenstein, *Duroplaste. Aushärtung - Prüfung Eigenschaften. Composite Structures*, München, Hanser, 1997.

[8] N.Liebers, *Effective and flexible ultrasound sensors for cure monitoring for industrial composite production.* Deutscher Luft- und Raumfahrtkongress, Berlin, 2012