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Article

A Novel Approach to Monitor the Curing of Composite Materials in Closed Tools by the Use of Ultrasonic Spectroscopy

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Abstract: With an ever broadening use of composite materials manufacturers are in high demand of efficient curing cycles to reduce costs and speed up production cycles. One method to to archive this goal is active cure monitoring to determine the exact time of curing needed. This article provides a novel method to measure the cure inside of closed tools by using ultrasonic spectroscopy. For this a simple experiment is used to show the change of the ultrasonic spectrum during the cure of an epoxy. The results clearly show a direct correlation of amplitude and state of cure where the amplitude reaches a global minimum at the glass point.

Keywords: ultrasonic; cure monitoring; resonant ultrasonic spectroscopy

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1. Introduction

Composite materials are the basis of many constructions of our times. They offer high stiffness at low weight. That makes them the ideal material for aerodynamic and space applications where weight is a serious concern. As a result of the growing ecological awareness of the population the demand of composite materials has grown significantly not only in the aerospace industry. Especially the automotive industry sees them as a way to reduce fuel consumption by lowering the general weight. The broader application has resulted in a high demand for large quantities of lower priced composite materials with a consistent quality. The result of this development has set new challenges on manufacturers. Especially the inconstancy of curing times are a big challenge for faster production cycles.

Currently most manufacturers use the standard curing times with high security factors to determine the cure duration. By doing so they accept unnecessary high curing times and thus a lower productivity or face the danger of not fully cured products. A possible solution is the use of cure monitoring. This would allow manufacturers to optimize curing cycles, resulting in higher production values.

There are many different cure monitoring techniques on the market like dielectric cure monitoring ([1] & [2]), which is already well established, and fibre optic cure monitoring ([3] & [4]). A limited number of cure monitoring techniques is able to detect cure changes without direct contact between sensor and composite material. Direct contact may result in unnecessary wear of the sensor and the tool, reducing the overall lifetime and the creation of unwanted visible production marks. Ultrasonic is one of the few techniques that can detect cure changes without direct contact. On of those techniques is ultrasonic cure monitoring. [5]

Ultrasonic waves detect the change of acoustic impedance and damping during the curing process. This paper is focused on a new approach on ultrasonic cure by the active use of acoustic tool resonances similar to [6] but with a low energy and low price approach on the subject.

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2. Materials and Methods

To test the viability of ultrasonic spectroscopy to monitor the curing of epoxy materials a simple experiment is prepared. In this experiment a general epoxy (RTM 6 of Hexcel) is applied to a aluminium plate. This epoxy stands as an example for many matrix systems with similar properties. The plate has the dimensions of 250x250x20 [mm].
On the backside of this plate two piezos made of PIC255 are applied close to the centre with 40 [mm] distance to each other. One functions as a transmitter, the other one as a receiver. The epoxy used to fix the sensor and actuator is RTM 6 as well. It was cured before at 180 [C] under vacuum.
On the front side a pool is created using a general vacuum sealant. In the pool centre a standard thermal sensor is applied. The plate is than heated to 80 [C]. Afterwards the cold (25 [C]) epoxy is filled in the pool and the setup is placed in an oven with 180 [C] where it is left until it is fully cured. This setup is displayed in figure 1.

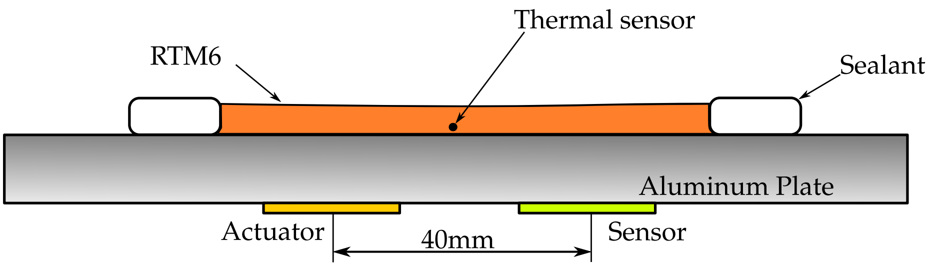

Figure 1. Test setup for ultrasonic spectroscopy cure monitoring

During the whole time the ultrasonic spectrum is measured using a 65 [kHz] and 90 [kHz] discrete 300 point swept sine actuation with 20 [V] peak to peak amplitude. This frequency range is in direct proximity to the first resonance frequency in the direction of the plate thickness direction.
The resonance frequency range was calculated using the following formula

$$f_n = n \cdot \frac{c}{2d} \qquad (n = 1, 2, 3 \ldots) \tag{1}$$

Where f is the resonance Frequency, c is the speed of sound and d is the thickness of the plate and n a numeric to determine the resonance order. By using the known sound parameter for aluminium and the thickness of 20 [mm] the first resonance frequency is calculated at 77 [kHz] for shear waves.

3. Results

Figure 2 shows the results of a single cure measurement using ultrasonic spectroscopy in a range of 65 [kHz] to 90 [kHz] during the cure of RTM6. The horizontal axis shows the Frequency [Hz], the vertical the time [s] and the color represents the amplitude [V] of the harmonic response signal.

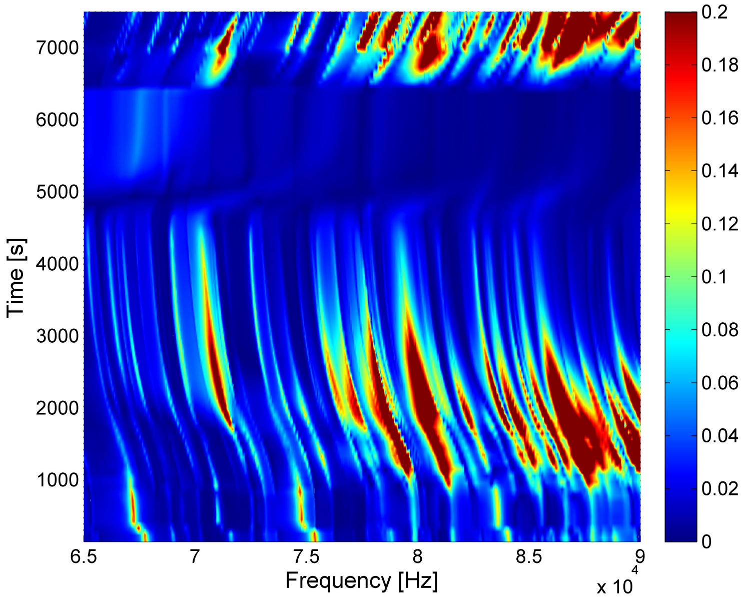

Figure 2. Change in the response spectrum during cure over time

Figure 2 shows a number of interesting points in time. The first one can be seen at the very bottom. At 400 [s] a significant and very fast shift of most resonance frequencies can be seen. At this point in time the epoxy was applied. The fact that not all resonances are affected in the same way is a clear indicator for the different resonance types. The resonance spectrum itself is a result of all resonances of the sensor-actuator-plate-system. This implies that it contains the resonances of the actuator and the sensor as well. Their frequencies are not affected by the epoxy on the other side of the plate. Nonetheless their amplitude is affected by the amplitude of the reflected waves as well.

The second interesting point in time is the frequency shift which starts at 1000[s]. It is the result of a rise in temperature in the pre-heated oven. It affects all frequencies in the same way. The really interesting part are the amplitudes. Most resonance amplitudes are growing at the beginning while they are decreasing to the end. This is a result of the change in epoxy parameters as well as sensor-glue parameters. A temperature induced reduction of the glue stiffness results in a reduction of the resonance of the actuator/glue system, bringing it closer to the measured frequency band. This leads to an increase in sensivity as well as actuator output. While the impedance of the aluminum doesn't change much during heating, the acoustic impedance of the epoxy is sinking as a result of the decrease in density. This explains the high amplitude change during the heating process but not the diminishing resonance signals as time goes on. The diminishing is a result of another effect, which cannot be explained by temperature changes. It is a direct effect of the slowly progressing cure. While the temperature rise results in a thermal expansion, the cure progressively shrinks the epoxy, adds an increasing stiffness and adds a significant damping because of the ever increasing viscosity.

This directly leads to the third interesting point of time. At 5000 [s] the glass transition takes place. The epoxy has nearly no fluid properties anymore. The glass transition point can be accurately pinpointed by measuring the viscosity or approximated by calculating the degree of cure as done later. The viscosity on the other hand directly effects the damping of the material. As the fluid parameters decrease, the damping is increasing, climaxing in an absolute maximum in the glass transition point. This effect affects all sound waves hitting the boundary line between epoxy and metal, diminishing them to a global minimum. As clearly visible all resonance amplitudes are affected in the same way. The frequency shift is a result of the change in boundary conditions.

After the glass transition the inner viscosity of the newly formed solid body are falling again to its final, far lower value. This change can be seen in the resonance spectrum as well where the resonance

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amplitudes are returning and a new weaker resonance spectrum becomes visible. This is a clear indication for the "after cure" region.
The fifth change in the impedance spectrum occurs when the oven is opened at 6500[s] and the system is rapidly cooled. Because of the difference in the specific thermal expansion parameters, a high shearing force between the metal and the epoxy occurs, leading to complete detachment. This is clearly indicated by the jump in amplitude and was visibly confirmed during the experiment.

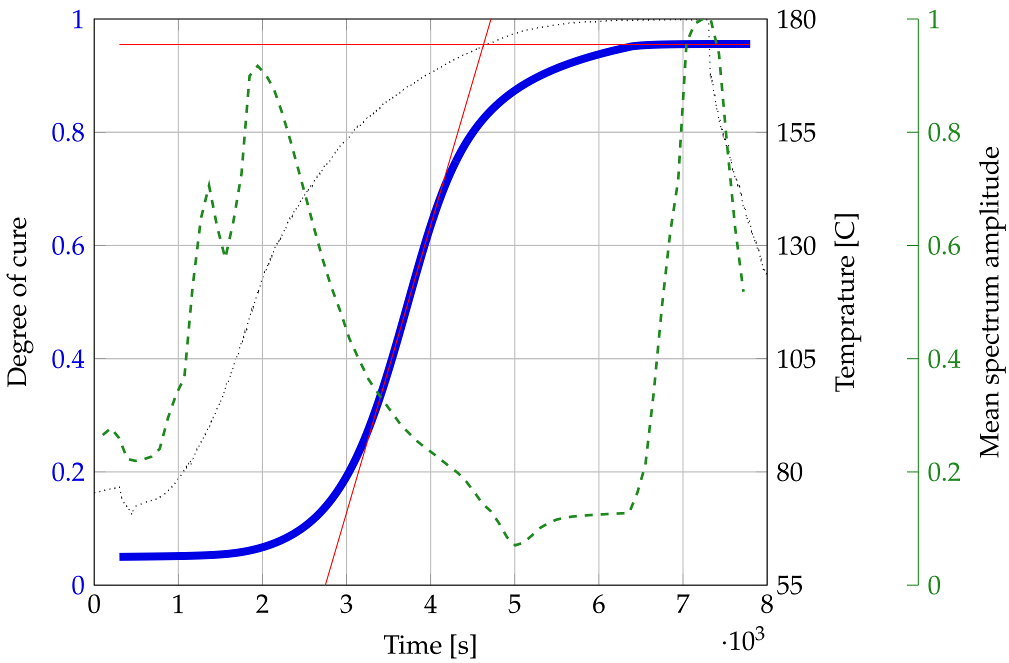

Figure 3. Measured temperature (black-dotted) and calculated degree of cure (blue) of the epoxy during the experiment with added support lines (red) to determine glass transition point (intersection), Mean spectrum amplitude of figure 2 green-dashed

Figure 3 shows the measured temperature change and the calculated curing of the epoxy and the change of the mean value of the amplitude of figure 2. The calculations are based on the Dissertation of Panagiotis l. Karkanas [7]. The figure clearly shows a similar point of cure at the measured temperature profile. The bump in the temperature profile at around 300 [s] is a result of the epoxy being pured in. The epoxy was kept at room temperature. The results clearly show, that the minimum of the mean spectrum is very close to the calculated point of cure. Differences can be a result of calculation, and epoxy variations.

4. Discussion

The results presented in chapter 3 clearly show a very clear correlation between amplitude and point of cure visible in figures 2 and 3. There is a small deviation between calculation and measurement. A possible reason for this deviation is a wrong temperature measurement. The temperature sensor was very close to the aluminium plate. This might have created a faster temperature rise. Another possibility is a fitting error for the curing lines. The deviation is however quite small and can be ignored.
The results of the experiment clearly show the effectiveness of the presented method. Measuring the resonance spectrum allows a good detection of the glass transition point. This allows the tracking of epoxy cure even in closed tools without a direct contact between the epoxy and sensor. By removing a need for a direct sensor epoxy contact, high abrasion before, after or during the cure are possible

allowing far rougher environments, which are quite common in the industry especially at tool cleaning. It also allows sensing without leaving any extra production marks.

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Conflicts of Interest: The authors declare no conflict of interest

1. Garden, L.H.; Hayward, D.; Pethrick, R.A. Dielectric non-destructive testing approach to cure monitoring of adhesives and composites. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering* **2007**, *221*, 521–533.
2. Maistros, G.M.; Partridge, I.K. Dielectric monitoring of cure in a commercial carbon-fibre composite. *Composites Science and Technology* **1995**, *53*, 355–359.
3. Chen, J.Y.; Hoa, S.V.; Jen, C.K.; Wang, H. Fiber-Optic and Ultrasonic Measurements for In-Situ Cure Monitoring of Graphite/Epoxy Composites. *Journal of Composite Materials* **1999**, *33*, 1860–1881.
4. Buggy, S.J.; Chehura, E.; James, S.W.; Tatam, R.P. Optical fibre grating refractometers for resin cure monitoring. *Journal of Optics A: Pure and Applied Optics* **2007**, *9*, S60–S65.
5. Liebers, N.; Raddatz, F.; Schadow, F. Effective and flexible ultrasound sensors for cure monitoring for industrial composite production. *Deutscher Luft- und Raumfahrtkongress 2012* **2012**, *9*.
6. Whitney, T.M.; Green, R.E. Cure monitoring of carbon epoxy composites: an application of resonant ultrasound spectroscopy. *Ultrasonics* **1996**, *34*, 347–353.
7. P. Karkanas. Cure Modelling and Monitoring of Epoxy/Amine Resin Systems. *Phd Thesis* **1998**.