Application of Ultrasonic Cure Monitoring of Thermosets in Research and Production

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Abstract
The characterisation of the curing process of epoxies by ultrasonic is a well known diagnostic /1, 2, 3, 4/. Meanwhile this diagnostic is used to study the cross linking process in some other materials, such as rubber or EVA for solar cell encapsulation. An outstanding application is the diagnostic of the curing process in composite materials applied in aviation and automotive industries consisting of carbon or glass fibre matrix and B-stage resin.
This paper presents a comparison of ultrasonic measurements and usual laboratory diagnostics as Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and oscillating rheology demonstrating the effectiveness of ultrasonic diagnostic in production and research. The application for different materials is shown.

Keywords: curing process, epoxy resin, rubber, prepreg, ultrasound

1. Introduction

Thermoset materials play an important role in modern industry. The main reason for applying such materials is the need to reduce the weight of the produced work pieces. Examples can be found in aircraft and automotive industries.
The transition from a production of small quantities such in aircraft industry to bulk production needed in automotive industry requires not only adequate materials but also direct information about the curing process for having stability in production.

2. Experimental set up

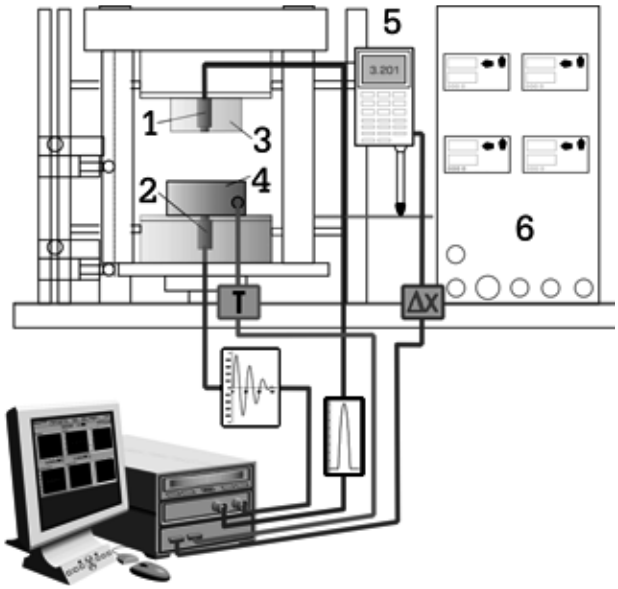

Fig. 1: Principle of measurement
1, 2 sensors, 3, 4 mould, 5 thickness gauge,
6 temperature controller

Some diagnostics for the curing process (such as DMA and DSC) are well known but their application is restricted to research and development. Since some years ultrasonic diagnostic is used in the lab and there were some activities to apply it in production [1,2].

In the past SLT developed a new hardware and adequate software for ultrasonic diagnostic of the curing process. It is as well suited for industry as for application in a lab.

A sophisticated excitation is used for reaching a high efficiency. The frequency and the duration of the excitation pulse can be adapted to material and type of measurement. Within some limits given by the transducers the frequency can be shifted in such a range where the attenuation in the material is low. For the frequency range from 500 kHz to 10 MHz high temperature transducers are commercially available. The principle of excitation and detection apparatus is shown in Fig.1.

Normally two different principles of measurement are possible: the pulse-echo modus and the transmission modus. In most cases we use a sample thickness of some millimetres and through transmission. We measure a reference signal (without or with known material between the sensors) and determine the transit time by a comparison with this reference. The electronic hardware uses an ADC with a clock rate of 100 MHz. For increasing the time resolution a dedicated fit procedure is included.

Most of the studied materials show a very strong damping of the ultrasonic signal especially during the softening of the material. Thus it is necessary to cover a wide range of amplitudes. The included automatic control of the amplifier covers a range of 80 dB.

3. Results and Discussion

The aim of this article is to demonstrate the application of ultrasonic diagnostic for curing processes in production and to present a comparison with other diagnostics. A typical dimension of the sample we used is 2 cm x 2 cm and the thickness is determined by an electronic thickness measurement or it is fixed by end plates to a defined value (typical 1,5 mm). The velocity of sound is determined using the sample and the transit time, on the other side $v_s=\sqrt{(L`/\rho)}$, were L` is the storage modulus for longitudinal waves and ρ is the density holds. L` depends on the compression and the shear modulus. So the velocity is directly coupled with the mechanical properties and hence it correlates with the curing process.

The velocity of sound is for all studied samples a function of temperature $v_s = v_s(T)$. In the following text we decide between isothermal and non isothermal (temperature ramp) processes.

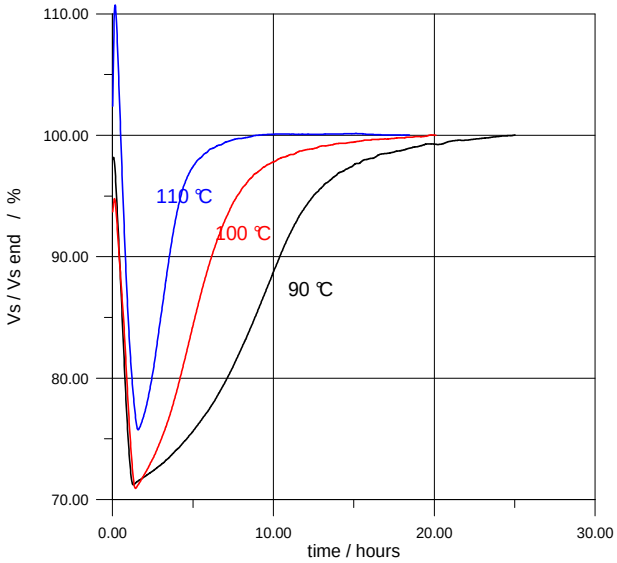

Fig 2: Isotherm curing process of epoxy resin for three different temperatures.

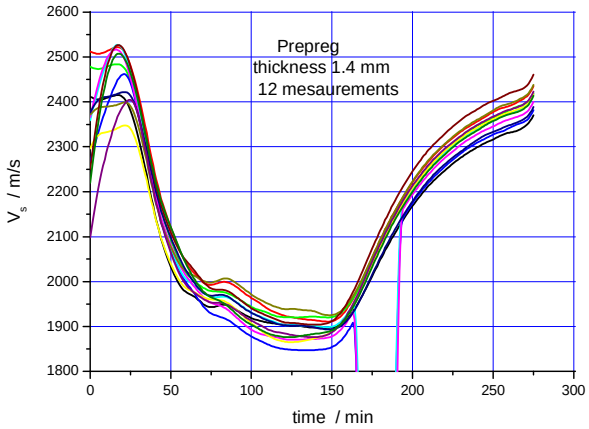

Fig. 3a: Velocity of sound versus time (temperature as function of time in Fig. 3b) for epoxy resin prepreg: 12 separate measurements at the same material showing differences in the absolute value (+/- 50 m/s), but the same characteristic behaviour.

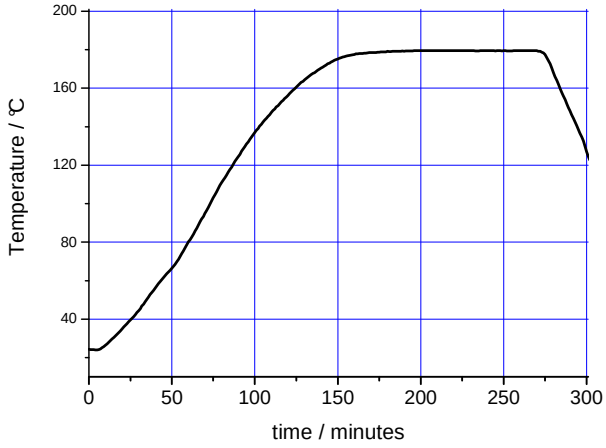

Fig. 3 b: Temperature ramp used for Fig. 3 a.

For isothermal processes only the heating of the sample up to a constant value is influenced, but for temperature ramps we find a competition between a velocity increase caused by curing and a velocity decrease caused by an increase of the temperature. For all isothermal processes the interpretation of the ultrasonic signals is easy; the temperature has only influence as an additional parameter for each measurement. In Fig. 2 an example is given for epoxy resin for 3 different temperatures. After reaching the final thickness the output data are stable. The velocities are normalized to the final value. It is obvious that the curing process is faster and begins earlier for higher temperatures.

Figs. 3 and 4 demonstrate the influence of the temperature for a non isothermal measurement. In Fig. 3a and b the results for a (high temperature) epoxy are shown. In this case the cross linking starts after reaching 180 °C (after 2.5 hours heating ramp). The increase of the velocity is very notably.

Fig. 4 depicts the curing process for an epoxy resin and an epoxy prepreg during the T-ramp. Curing starts at about 100 °C and is completed at 130 °C. The further increase of the temperature reduces the velocity of sound of the totally cured material mainly by passing over the glass temperature.

For all different epoxies the increase of the velocity of sound during the cross linking phase is so significant that the T-dependence of v_s plays a minor role.

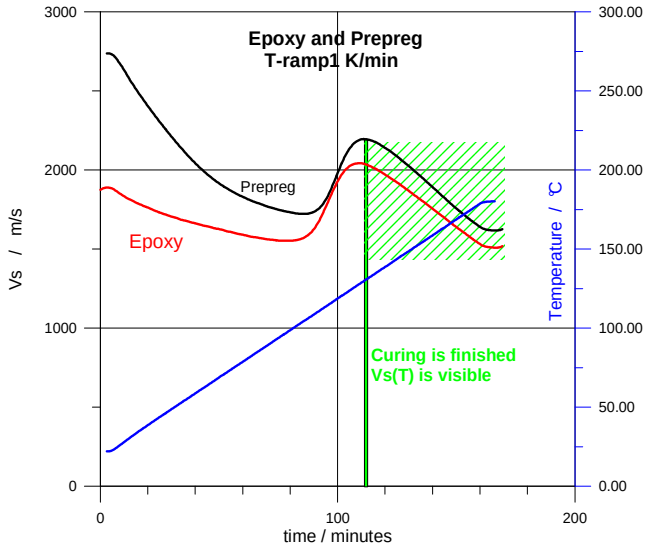

Fig. 4: Velocity vs. time for a T-ramp of 1 K/min. The pure epoxy and a prepreg made with the same epoxy show the same behaviour. Cross linking begins at about 100 °C and is finished at 130 °C.

In commonly used rubbers the change of v_s during vulcanisation is generally lower than in epoxies. Fig.5 depicts v_s versus time for an isothermal process (T=170 °C). It is seen that the increase of v_s depends on the type of rubber, but the isothermal measurement gives a clear information about the beginning and the typical duration of the cross linking process. The results are in agreement with vulcameter measurements. Similar results were achieved for EVA foil playing an important role in solar cell production.

For a measurement with a T-ramp (or for very bulky parts where the temperature increases slowly) the vulcanisation process in rubber can be totally covered by the T-dependence of v_s

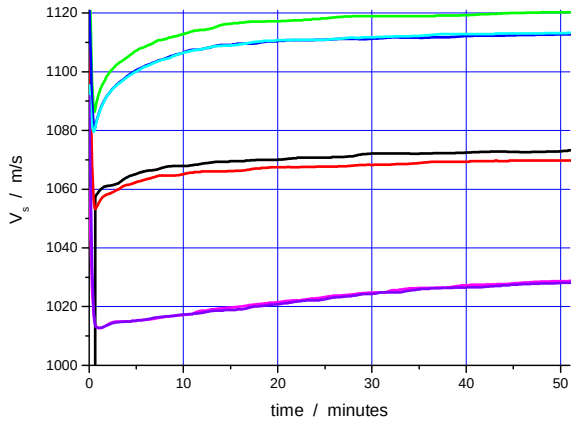

Fig. 5: Isothermal vulcanisation for 3 different rubber samples.

during a T-ramp. For such application a more dedicated interpretation is necessary**.**
The temperature dependence of v_s prevents a direct relation between v_s and the degree of cross linking. For many applications the absolute value of the degree of cross linking is not of

interest. In this case dv_s/dt can be used and it has an additional advantage: changes of the absolute value of v_s caused by (stationary) inhomogeneities in the material (as seen in Fig. 3a) are not visible. Fig. 6 depicts dv_s/dt for 8 samples of the same material showing nearly the same behaviour. During the first 10 min the thickness of the samples changes as a consequence of the softening of the material. After this time the curves are nearly identical. Such information can be used to control and optimize the cycle time.

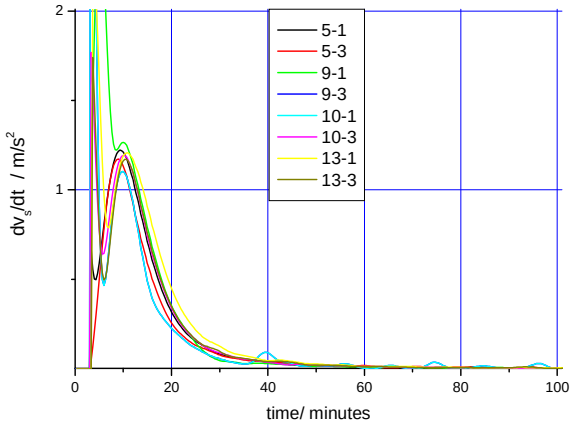

Fig. 6: First deviation of the velocity (dv_s/dt) as a function of time. Often it is called "reaction rate".

If it is necessary to archive all curing data including the degree of cross linking for having a quality document one can trace the ultrasonic data to DSC results. In Fig. 7 a DSC signal is shown for a T-ramp of 1 K/ min for an epoxy resin. The reaction integral (integral over the specific heat flow) is direct information for the degree of curing for this T-ramp. An ultrasonic measurement under the same conditions yields the following curve (Fig. 8).

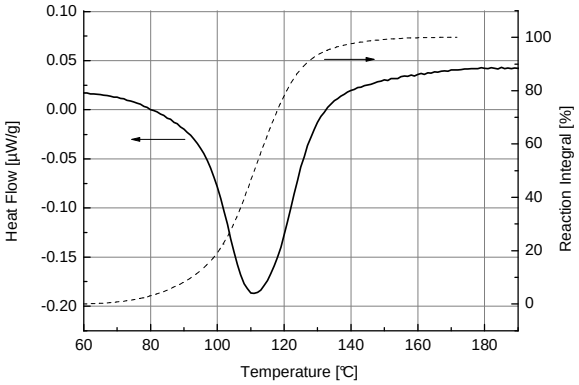

Fig. 7: Heat flow vs. temperature for a T–ramp (1 K/min). From this heat flow the reaction integral is determined.

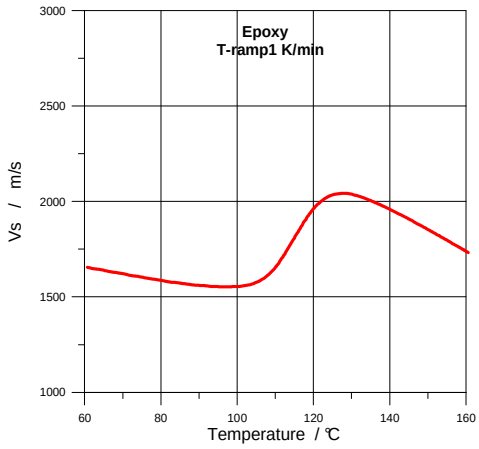

Fig. 8: Ultrasonic speed vs. temperature for the same epoxy resin as in Fig.7

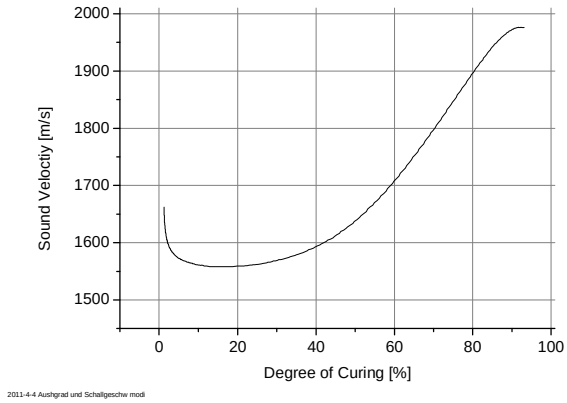

Fig. 9: Velocity of sound vs. degree of curing for a fixed temperature. Data from Fig. 8 and Fig. 7.

A combination of these two curves provides the relation between ultrasonic measurement (v_s) and degree of curing, seen in Fig. 9.

From the shape of the curve one can see that a determination of small curing degrees is connected with a larger error, but it should be pointed out, that the relation between v_s and the degree of curing for value >30% is significant; consequently ultrasound diagnostic can be used up to the end of the curing process (what is not possible with a dielectric diagnostic).

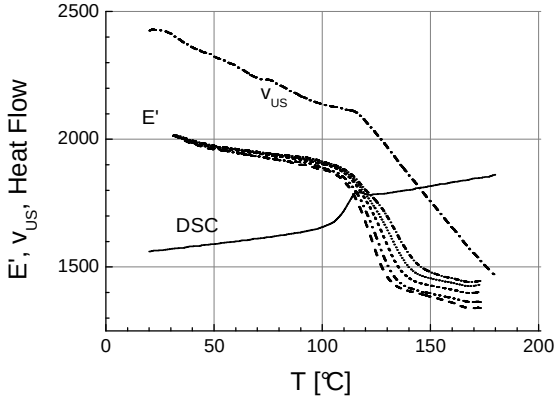

Fig. 10: Signals of three diagnostics vs. time for a T-ramp (1 K/min). T_g is indicated by all methods.

The comparison of the different diagnostics gives an answer to the question if ultrasound diagnostic can be used for the determination of the glass temperature (T_g), describing the transition from glass to rubber. This temperature is an indicator for a correct technological procedure and directly connected with the mechanical properties. Fig. 10 depicts the results for DMA, DSC and ultrasound diagnostic using the same heating ramp 1 K/min: DSC gives clear information - the change of the specific heat is connected with the transition from glass to rubber state. The storage modulus E' determined by DMA (here for 5 frequencies 0.3 to 33.3 Hz) is affected by this transition, too, but the temperature range is broader. The ultrasonic signal consists of two nearly linear parts having the point of intersection at T_g.

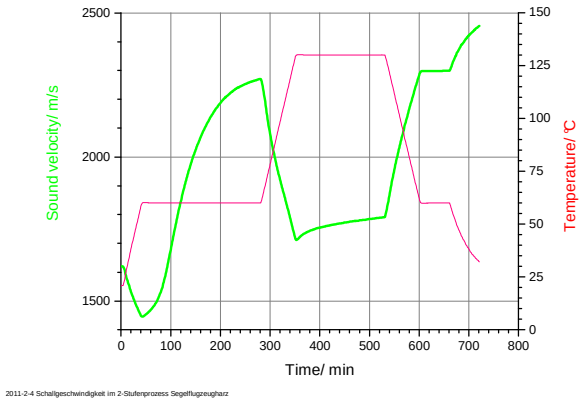

Fig.11: Velocity and temperature vs. time for a two step curing of epoxy resin. Temperature: red, v_s: green.

In Fig. 11 the measurements for an epoxy resin for sailplane application are shown. The two step heating procedure is done according to the data sheet. It is clearly seen that v_s increases strongly during the first T-plateau. A temporary decrease of v_s at the beginning of the second T-level is again caused by $v_s(T)$. The following increase is relatively low and doesn't reach a stationary value. So not full curing is reached.

4. Summary

The presented results demonstrate a wide field of application of ultrasonic diagnostic reaching from a direct registration of the curing process for different materials to the quality check of incoming goods. This information can be used for the control of cycle time and are a quality document for each part.

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