Chapter 7: Non-destructive evaluation (NDE) of polymer matrix composites:
Using ultrasound to monitor the curing of composites
in: Non-destructive evaluation (NDE) of polymer matrix composites, Edited by Vistasp M. Karbhari,
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1. Introduction

For all means of transportation the requirements to increase of energy efficiency are immense. That means beside improvements in engine and drive train a dramatic weight reduction by maintenance of the strength properties. In air craft industry a considerable change comes from use of carbon fibre composite structures in the airliners. A carbon fibre fraction of more than 50% in weight is the aim for the Boeing 787 Dreamliner and the Airbus A350 XWB. Also for the automotive industry requirements for weight reduction are very ambitious. This is extremely important for electric cars where the high weight of the batteries

can only be resolved by a consequent light weight construction in components especially for the car body.

Materials which fulfil the demands of high strength in combination with low weight are the composites. Typical for a composite is the combination of fibre enhancement – typical carbon or glass fibre – and a polymer matrix. This matrix can be built up of thermoplastic or thermoset material. At present thermoset materials carry the greater weight because they give more freedom for building complex parts. Thermosets are characterized by mixtures of reactive resin and hardener. They are liquids with low viscosity at room temperature or slightly increased temperatures. So they can infiltrate a fibre structure (fabric) easily. The reactivity of the resin and hardener comprises the possibility to change the state of matter from a liquid to a stiff solid by the chemical curing reaction which is a crosslinking process. The reaction is started mainly by higher temperatures, but the chemistry can be set to run at room temperature, too.

The most widely used thermoset matrix for cured composites are epoxy and unsaturated polyester resins. In advance are polyurethane resins. Typically resin and hardener are shipped separately. They are mixed in the prescribed ratio resin to hardener by the processor and then infiltrated into the roving. A more bygone processing method is the application by hand. A modern method is the resin transfer moulding (RTM) technique. Here the fabric is placed in a closed mould. The fresh mixed resin-hardener-mixture is pumped into the mould. The mould is preheated to curing temperature. It may be evacuated. In a special form the upper part of the mould may be a vacuum tight foil. After a definite time, sufficient to reach the required degree of curing, the mould will be opened and the part removed from the mould.
An alternative process starts with so called prepreg material. Here the impregnation of the fabric with the resin-hardener mixture is already done by the prepreg manufacturer. The reactive prepreg must be stored at typically -18 °C to avoid precuring before processing. Prepregs are shipped as coil. With spreading machines many layers are put one upon the other until the default thickness is reached. This final thickness can be few centimetres. Such prepreg stacks are wrapped by a vacuum tight foil. They are cured for many hours in great autoclaves with pressures up to ten bar and high curing temperatures. These parts can have dimensions as large as 5 m x 20 m.

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The final properties of composite parts are strongly dependent on the degree of curing reached in the manufacturing process. In the aerospace industry a curing degree close to 100 % is pressed for and has to be checked and documented during production process.

2. Thermosets– from liquid or low temperature melting material to solid, high temperature stable material

Thermosetting materials have the advantage to reach their final properties to become a solid and stiff material by a technical cross-linking reaction. Before cross-linking they are liquid or low melting materials. The most popular systems for composite manufacturing are epoxy resins. Epoxy resins are characterized by an oxygen atom connected with two adjacent carbon atoms in a chemical compound. This ring with oxygen also named oxirane ring builds approximately an equilateral triangle. It is highly strained and therefore epoxy resins are highly reactive. Necessary for a meshwork formation are two oxirane rings at either ends of the basic molecule. Crosslinking can be carried out by special hardener as anhydrides, amines and phenols. In Fig. 2.1 the formula for the wide-spread epoxy bisphenol A diglycidyl ether (produced from a reaction between epichlorohydrin and bisphenol-A) and a diamine hardener are given.

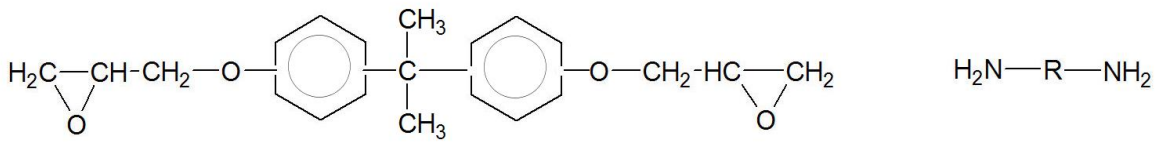

Fig. 2.1: Epoxy bisphenol A diglycidyl ether and diamine hardener

In the crosslinking reaction the oxirane ring is opened and an OH-group is formed with a hydrogen from the NH-group of the amine. The amine molecule is joined up with the free valence of the CH_2-group. By additional reaction of the second part of the diamine a chemical bridge between adjacent epoxy molecules is formed – see Fig. 2.2. Using polyfunctional amines three dimensional networks are the result. Such a heavily crosslinked polymer is rigid and strong. The crosslinking process is named curing. Depending on the kind of resin, hardener and activators curing can proceed at room temperature but many formulations need high temperatures for the reaction.

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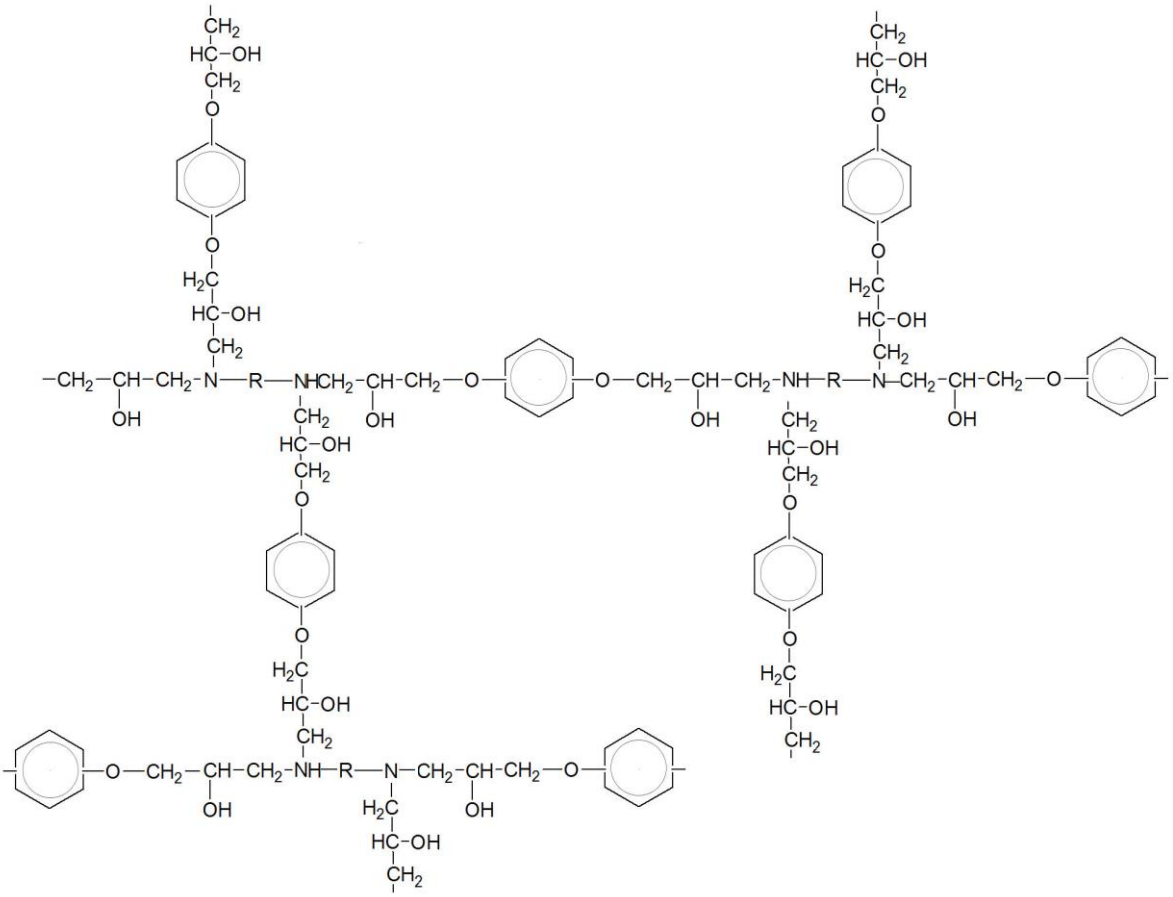

Fig. 2.2: Illustration of the crosslinked network structure of bisphenol A diglycidyl ether and diamine hardener

For practical use of epoxy the knowledge of the curing process is of great importance. On the one hand the final properties in particular the glass-rubber transition temperature (T_g) are determined by the chemical structure and the curing conditions. On the other hand optimization of the process, especially knowledge of the time for gelation and vitrification, are of great importance. At gelation the molecular weight has increased so far that the viscosity becomes infinite and the resin can no longer flow and fill the mould. At vitrification the reaction comes to a standstill because the dramatic molecular mobility reduction disables that the reactants come into close contact. Other classes of resins with similar use as epoxy are unsaturated polyester (UP) and polyurethane (PU). A specific class of UP based compounds are the bulk moulding compound (BMC) from UP with short glass fibres and sheet moulding compound (SMC) with glass fibre matting.

A special kind of thermosetting materials are moulding compounds. The well known phenolic resin based Bakelite is used in techniques for more than 100 years. Beside phenolic resin with hexamethylenetetramine hardener (PF) have melamine-formaldehyde (MF), urea-formaldehyde (UF) found a widespread application.

Other than thermosets but also a cross-linked polymer are elastomers (rubber). As distinguished from thermosetting materials the number of crosslinking bridges is rather low. First rubber cross-linking was performed by sulfur.

3. Scientific methods for investigation of crosslinking reaction and determination of degree of curing

3.1 Rheology

Rheology is the science of the flow of matter. The measuring principle is to enclose the material in the gap between two plates or cones and to rotate or oscillate on of the plates – insert in Fig. 3.1. For curing materials only the oscillating modus is of interest. Measured parameters are the torque, the amplitude and the phase between both. Including the gap geometry from torque and deformation angle the complex shear modulus can be calculated. It is combined from storage modulus G' and loss modulus G''. From both an effective viscosity ($|\eta^*|$) can be a calculated using the Cox-Merz rule [1].

In Fig. 3.1 the crosslinking reaction of epoxy resin registered by an oscillating rheometer is demonstrated.

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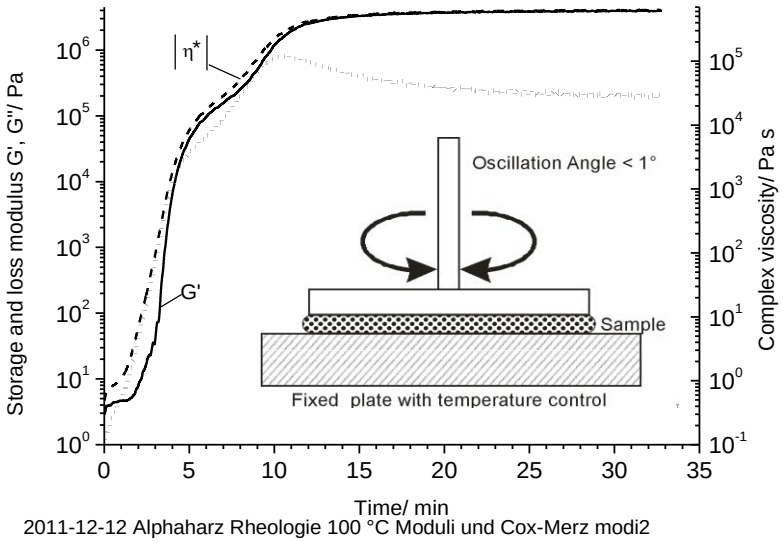

Fig. 3. 1: Storage and loss modulus and calculated complex viscosity vs. curing time from rheological measurements, isothermal epoxy resin curing at 100 °C, logarithmic y-axis

A sharp rise of viscosity is found to start at about two minutes. The rise of viscosity comprising more than three orders of magnitude is an indication for gelation. G' and G'' approach each other and are equal at about four minutes. This characteristic point is often used to define it as gel point (Winter [2]). At ten minutes a maximum in loss modulus G'' appears. This is a typical indication for passing a rubber to glass transition [3-5]. In the consequence the compound solidifies. In Fig. 3.2 an example of basic investigations on the influence of process temperature on epoxy resin curing is summarized.

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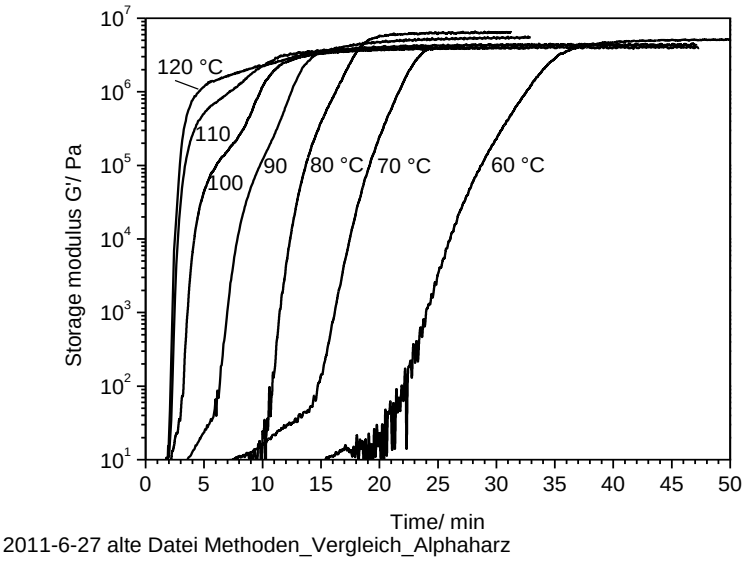

Fig. 3.2: Storage modulus vs. curing time from rheological measurements, epoxy resin curing, influence of process temperature, logarithmic y-axis

3.2 Differential Scanning Calorimetry DSC

DSC is a method to detect the heat flow rate between two crucibles with high accuracy – see insert in Fig. 3.3. One of them contains the material to investigate, the other is normally empty. The temperature of the chamber can be either constant or a heating/ cooling ramp with definite temperature changing rate is realized. For polymers characteristic physical conversions as melting, crystallization, evaporation and glass transition lead to a heat flow between both measuring positions. Crosslinking reaction is exothermic and can therefore be detected eminently good by DSC.

In Fig. 3.3 the DSC curve for an reactive epoxy is given. The crosslinking reaction provides an exothermic peak with a maximum at 140 °C. The reaction enthalpy measured in J/g can be calculated from time integral of the peak.

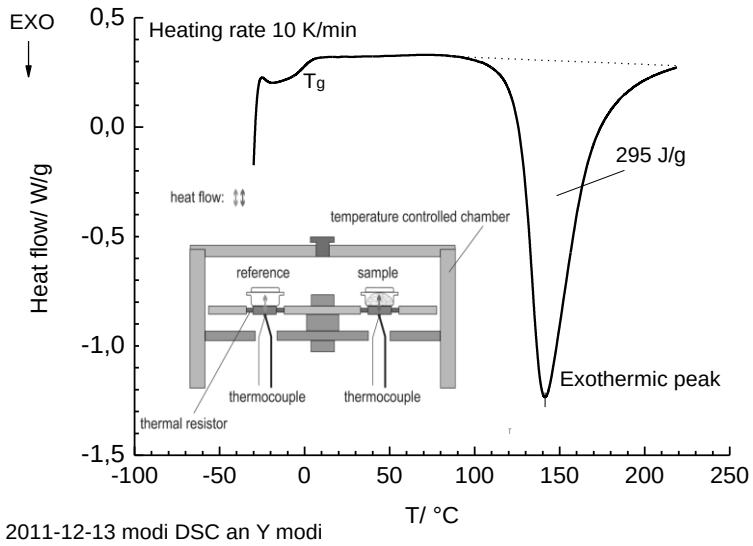

Fig. 3. 3: DSC heat flow vs. temperature, epoxy resin, starting from the frozen state to a temperature of full crosslinking

DSC is the most popular method to find out the degree α of curing:

$$\alpha_{DSC} = 1 - \frac{\Delta H_r}{\Delta H_t}$$

ΔH_r – remaining reaction enthalpy, ΔH_t – total reaction enthalpy

3.3 Dynamic Mechanical Analysis DMA

The measuring principle of Dynamic Mechanical Analysis (DMA) is the excitation of a sample by a sinusoidal mechanical deformation and the detection of the answer. The amplitude of the force and the deformation and the phase relation between both are measured. In the result the storage modulus E' and the loss modulus E'' can be calculated. A sketchy drawing of the working principle is given in the insert in Fig. 3.4. In tis figure the storage and loss modulus as function of temperature for a sample prepared from an cured epoxy are shown as example.

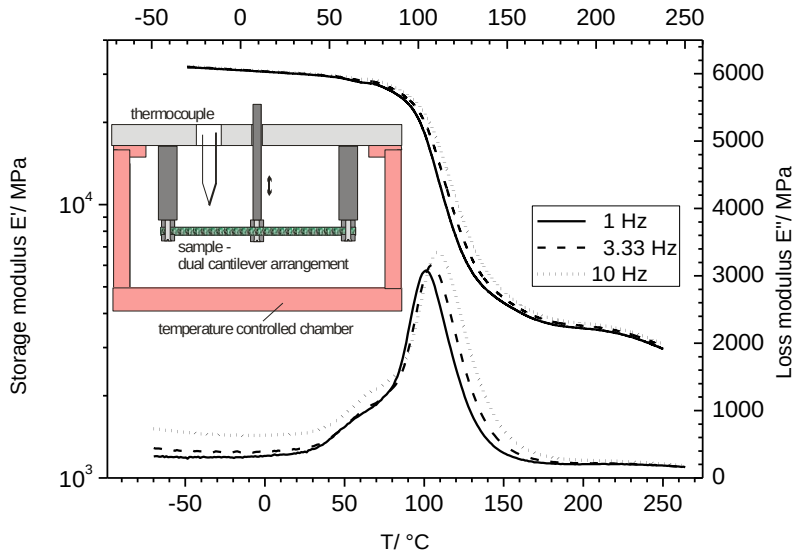

Fig. 3.4: DMA, storage and loss modulus vs. temperature, sample from epoxy, heating rate 1 K/min, (E' – logarithmic axis)

The storage modulus (E') changes in the temperature range from about 80 to 150 °C where a decrease of about one order of magnitude appears. This change is accompanied by a peak in loss modulus. The higher the frequency the more the transition is shifted to higher temperatures. All these facts illustrate passing through the glass-rubber transition of the cross-linked resin. The glass temperature T_g can be defined as peak of the loss modulus or half height of the step in storage modulus [5].

Only at full curing the final glass transition temperature ($T_{g\infty}$) can be reached. Therefore, at damage events DMA analysis is a reliable method to find out by looking for $T_{g\ actual}$ if curing was well done.

4. Correlation between degree of curing and mechanical properties

Curing increases the glass transition temperature and produces the final mechanical properties. In Fig. 4.1 the change of T_g by stepwise curing is shown.

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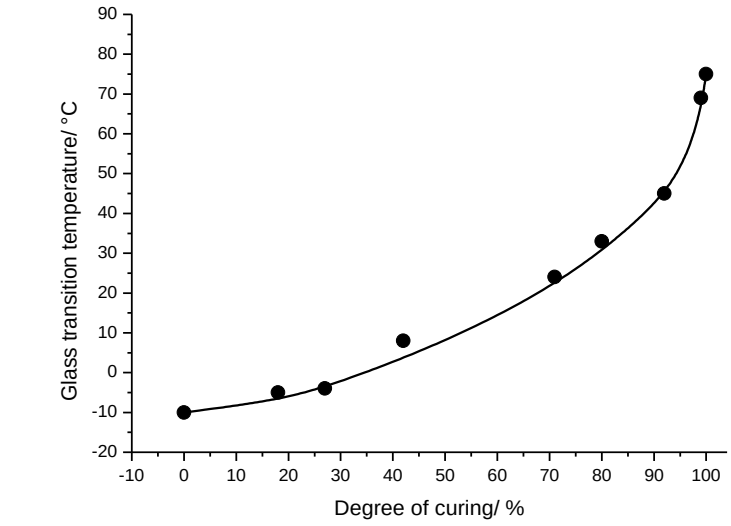

Fig. 4. 1: Epoxy resin, glass transition temperature vs. degree of curing, DSC

A typical error at thermoset curing is a wrong curing time. In the case of phenolic resin a too low degree of curing and consequently a too low glass transition temperature leads to bladders after demoulding - see in Fig. 4.2 a photograph of a defective PF-part.

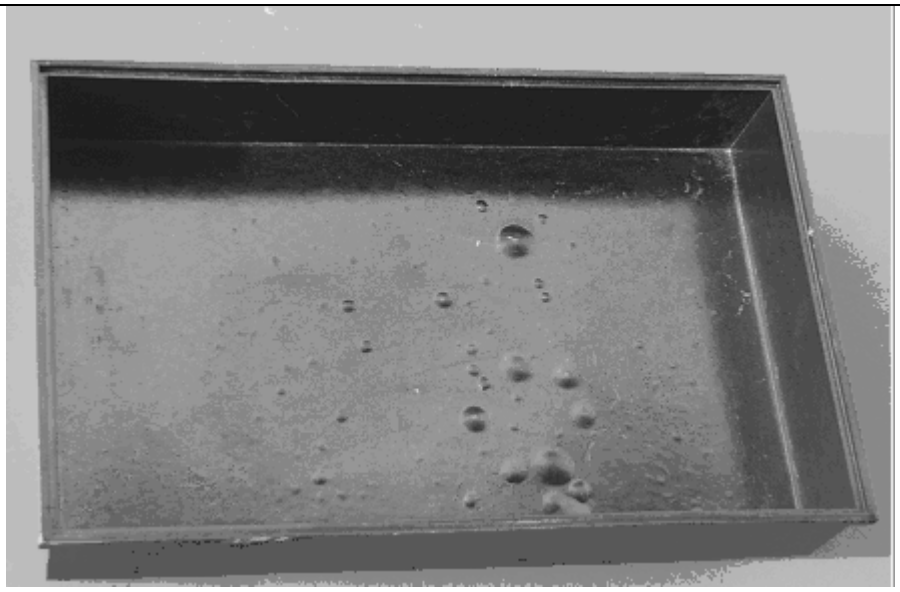

Fig. 4.2: PF-part (Bakelite) taken from the mould in an incomplete state of crosslinking. Such manufacturing defects can easily be avoided by utilisation of online process monitoring.

As a rule wrong crosslinking process can not be seen so easily by viewing and analytic methods must be utilized. For a broken carbon composite bicycle fork a too minor degree of curing was detcted by DMA – see Fig. 4.3. In the first measurement of the part a T_g of 111 °C was detected. By increasing the temperature up to 250 °C in the DMA run the part got the chance to post-cure. In the second measurement this sample showed a notable increase of T_g from 111 °C to 141 °C and the imperfect curing was proven. In practice the dramatic consequence of reaching a very high curing often is underestimated.

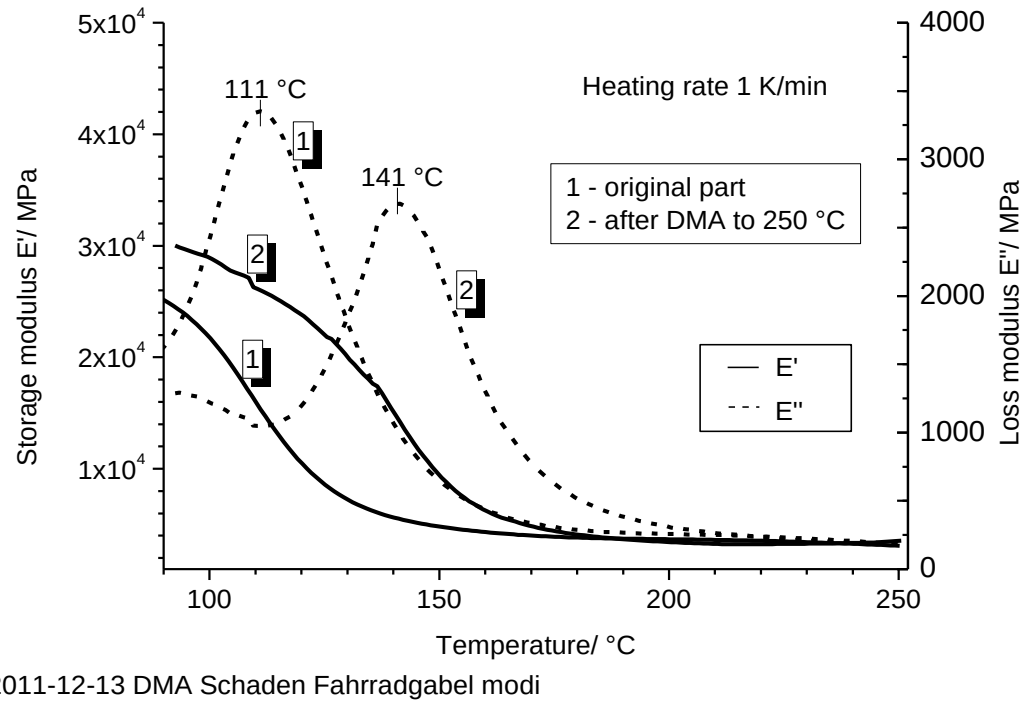

Fig. 4.3: Incorrect bicycle part, storage and loss modulus vs. temperature

We verified for example that for UF-moulding compound the impact strength rises steadily with curing time [6] - see Fig. 4.4.

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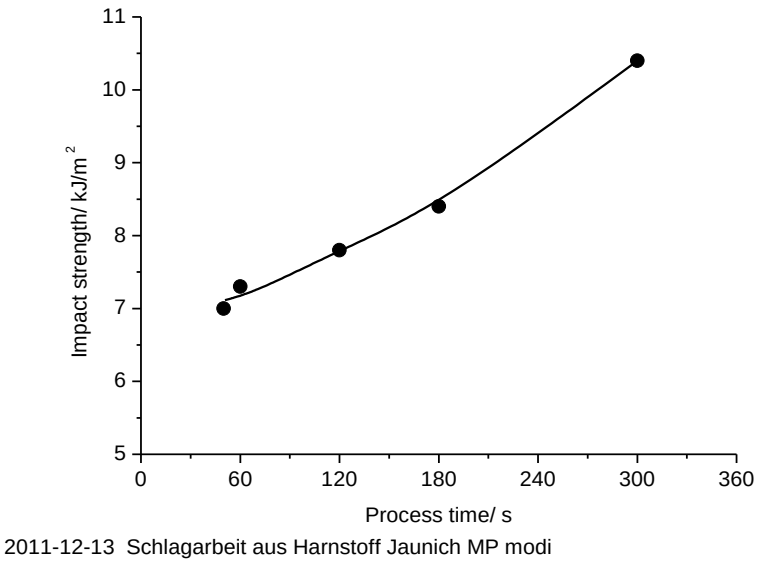

Fig. 4.4: Impact strength vs. process time, parts from UF-moulding compound

Wolfahrt et al. [7] changed the degree curing of epoxy prepregs from 68 to 100 % and found that the fracture toughness increased with degree of curing and remained nearly constant from 90 %. A distinct correlation between degree of curing and crack propagation speed for glass fibre epoxy composite was reported by Trappe et al. [8]. A change of degree of curing from 92 % to 96 % produced a decrease of crack propagation speed by a factor 10. For dental composites a correlation between degree of curing and fracture toughness [9] wear depth [10] was published.

5. Technique for online process monitoring by ultrasound

In the 1940s first successful experiments were done using ultrasonic as diagnostic tool. In the following years the enormous potential of ultrasonic for non-destructive testing was realized (see e.g. Krautkraemer[11]). Consequently it is not surprising that the idea to use ultrasonic for a study of curing processes was realized rather early [12]. A lot of basic works was done by Alig et al. [13-19], Challis et al. [20-24]. A good overview on methods for cure monitoring including ultrasound is given by Lodeiro and Mulligan [25].

The idea behind ultrasonic cure monitoring is that the experimental values, the sound velocity of a longitudinal wave v_s^{long} in a media and the damping of this wave α^{long} are

connected with the longitudinal storage modulus L' and the longitudinal loss modulus L'' as follows:

$$L' = (v_s^{long})^2 \cdot \rho \qquad \text{and} \qquad L'' = 2(v_s^{long})^3 \cdot \rho \cdot \alpha^{long} / \omega \tag{5.1}$$

where ρ is the density , ω the angular frequency and α the damping
L' and L'' can be summarized as the complex longitudinal modulus L*:

$$L^* = L' + iL''$$

The longitudinal wave modulus is connected with the compression modulus K* and the shear modulus G* and finally also with the modulus of elasticity E* and the shear modulus G*:

$$L^* = K^* + \frac{4}{3}G^* = \frac{4G^* - E^*}{3 - \frac{E^*}{G^*}} \tag{5.2}$$

The crosslinking process causes a characteristic change of the modulus of elasticity and shear modulus. Hence also a characteristic change of the longitudinal wave modulus exists and can be used for characterization of crosslinking. You might say that ultrasound brings the DMA-methods into the mould.

5.1 Working principle and Transducers

In Fig. 5.1 the principle of an ultrasonic measurement is depicted. In Fig.5.2 the propagation of a longitudinal wave is exemplified.

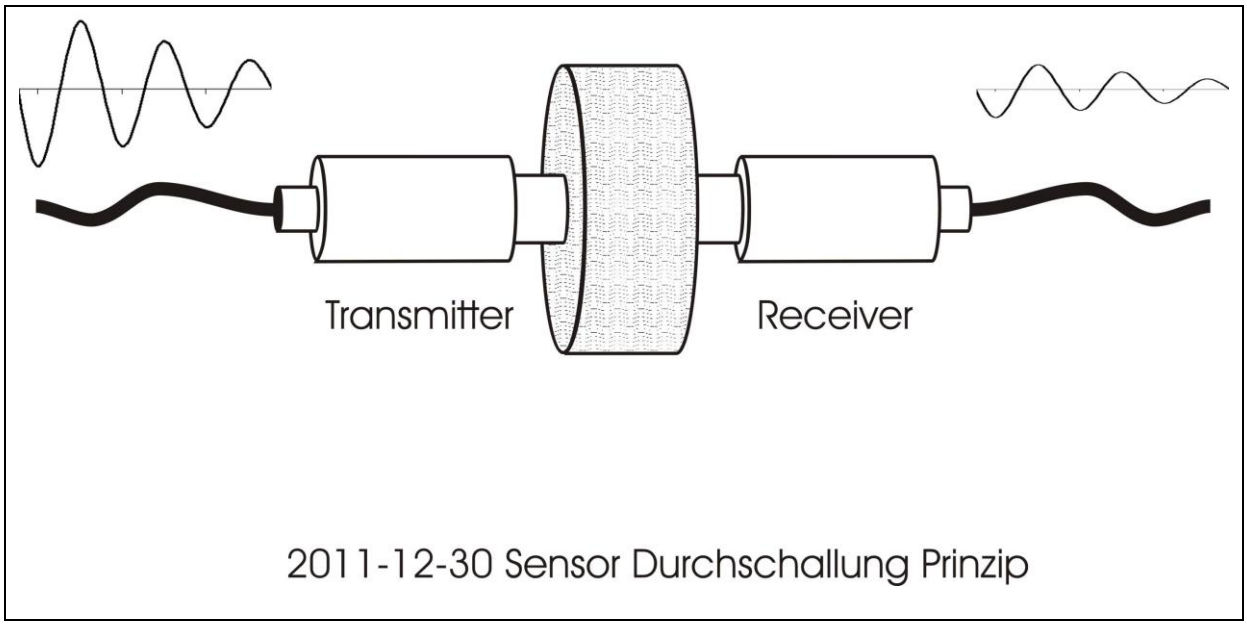

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Fig. 5.1: Scheme of an ultrasonic measuring arrangement - through transmission

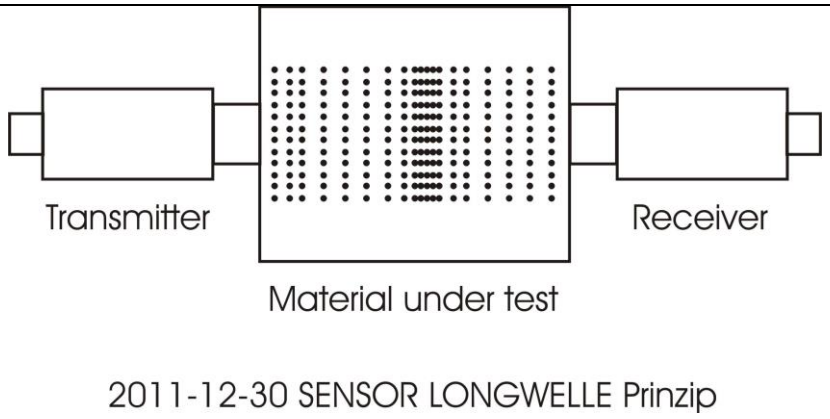
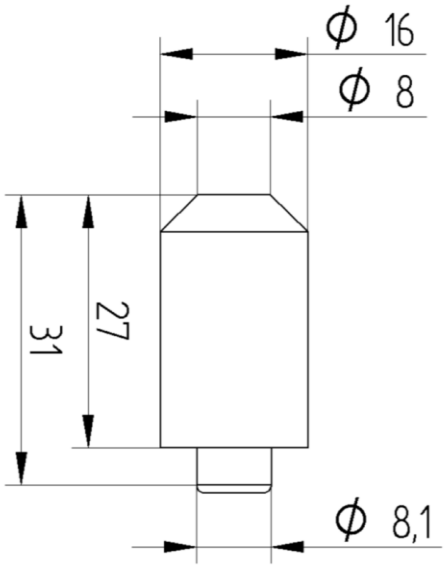


Fig. 5.2: Illustration of the propagation of longitudinal waves (compression waves) between the sensors.

The working principle of the ultrasonic sensors rests upon the electrical excitation of a piezoelectric ceramic. Its orientation is chosen such that longitudinal waves are emitted by thickness oscillations. On the other side a thickness change of a piezoelectric material generates a voltage, thus the same sensor can be used as transmitter or receiver.
In Fig. 5.3 such a transducer is shown. The typical dimensions are given in Fig. 5.4. The relatively small sensors can be included into a mould or a test set up easily.

5.3: Photo of an ultrasonic transmitter (GE company)



5.4: Technical drawing of an ultrasonic sensor

5.2 Necessary values to be measured

For a determination of the sonic parameters in the media under test two parameters are needed, the sound velocity and the damping.

To determine the sound velocity the thickness of the material where the ultrasonic wave is travelling through and the pulse transit time have to be measured.
Many methods to determine the thickness of the material between fixed or variable plates are known, but most of them suffer from more or less temperature dependent mistakes. In certain limits it is possible to increase the material thickness to reduce the influence of this inaccuracy. Our compression mould was completed with a dial gauge with USB data output. It works successfully for a probe thickness between 1 and 5 mm. For a given mould cavity the thickness of the cavity can be measured or is known from construction.

For determination of the travelling time the easiest way is to measure the difference between a reference signal – transmitter in direct contact to the receiver without a material - and the signal having passed the material under test. In this way the travelling times in both sensors (and in the wall in front of the sensors) must not be known.

A correct determination of the damping (sound attenuation) in the material is a complex task. The damping is influenced by different parameters: acoustic impedance mismatching between sensor and material and its change during curing, scattering of the incident wave, voids in the material [26]. For prudential reasons it is helpful to normalize the measured amplitude by the amplitude of the reference signal.
In principle it is possible to use through transmission (two sensors in a line) or to measure the echo from the opposite wall using one sensor only. The second method demands a short excitation pulse for a clear separation between excitation and reflection. This is always difficult for a sample thickness in the order of millimetres. Furthermore, reflections in the sensor presuppose a more complicated data evaluation.

The sensors can be fixed in a hidden position or they are arranged in the surface of the mould having direct contact to the material under test. The second method delivers higher amplitudes but normally it is used in the lab where an imprint on the sample is accepted.
The widely-used arrangement of hidden transmitter and receiver is shown in Fig.5.5.

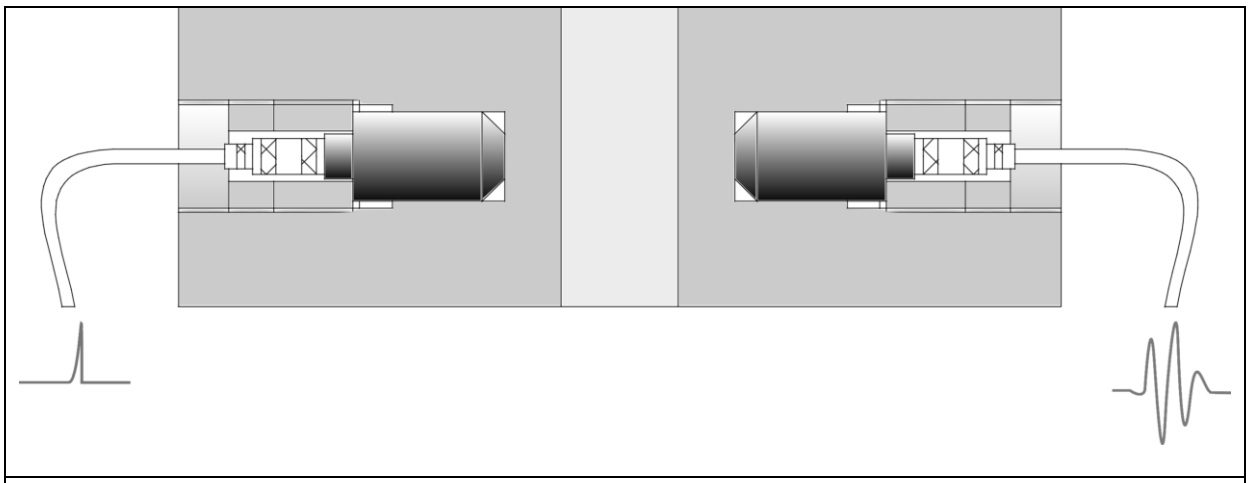


Fig.5.5: Typical measuring set up for hidden ultrasonic sensors in the wall of the mould

5.3 Excitation of the transmitter

There are different possibilities for the electrical excitation of a piezoelectric transducer in the kHz or MHz region (see e.g. [11]). From NDT applications it is known that a continuous excitation leads to interferences between the incoming and reflected signals arising from all boundary layers and thereby it is difficult or impossible to find the correct information caused by a complicated structure of the received signal.

For avoiding such problems adequate sensors and often a short excitation pulse are used. For such a type of excitation the analysis of the beginning of the signal is expedient because the influence of interferences increases during the duration of the excitation. Two methods for excitation are well known: The excitation with a single pulse having a rise or fall time in the 10 to 100 ns-regions and an amplitude in the range between some 10 and less than 500 V. This pulse can be generated by switching on (or switching off) a static voltage at the sensor or by an external pulser. In such a case the free oscillation of the sensor is mainly determined by its resonance frequency. An additional damping of the piezo ceramic element reduces the duration of oscillation. But one can't expect that for such an excitation a narrow banded signal is created. It always features a frequency spectrum. The appearance of multiple frequencies can cause problems because there is an influence of the frequency on the sound velocity (dispersion) and on attenuation.

Another possibility is the burst excitation using a group of positive and/or negative rectangular pulses forming the excitation signal or an excitation using a free programmable pulse generator. The effective frequency of excitation is determined by the duration of each pulse and can be varied. For example a central frequency of 4 MHz is generated by

rectangular pulses with alternating polarity having the same duration of 125 ns. Changing the duration of each pulse the central frequency is shifted. Using this method for excitation the frequency of the transducer signal can be varied within the limits given by the datasheet of the sensor. For instance, a transducer with a central frequency of 4 MHz can be stimulated to transmit signals between 3 and 6 MHz. The frequency spectrum broadens when the number of burst pulses decreases as is illustrated by a Fourier transformation.

Such an excitation offers the possibility to apply such a frequency where the damping in the material under test is more favourable. In Fig.5.6 the output signal of a transmitter for different excitation pulses is depicted.

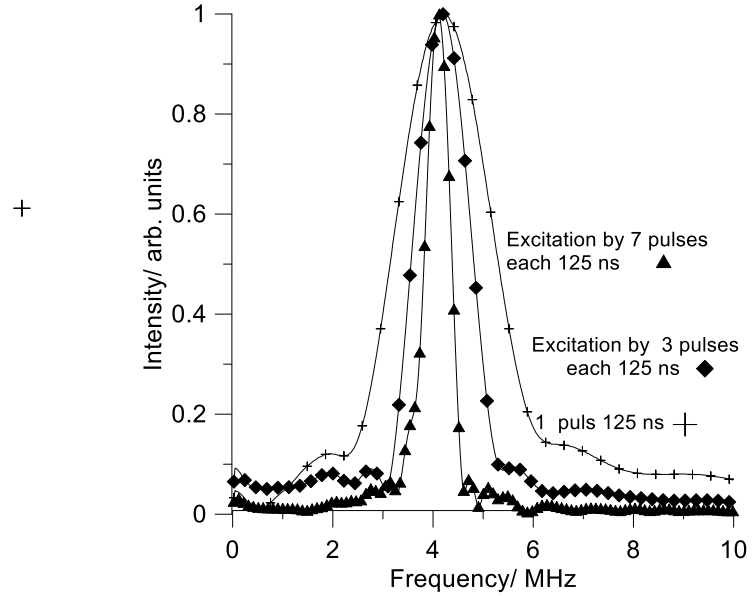


Fig. 5.6: Output signal for different numbers of excitation pulses. One burst pulse consists of a rectangular pulse having a duration of 125 ns, 3 burst pulses means a group of 3 pulses with alternating polarity each pulse 125 ns. (1/250 ns=4 MHz)

The damping of the excitation pulse in the test material is a critical parameter, as will be shown later. It depends as well on the amount of carbon or glass fibres as on the concentration of gas bubbles in the material and on a strong loss process during the softening of the material and becomes stronger if the material thickness increases. In nearly all practical applications we will see that the loss of intensity caused by these effects is the most critical influence. There are limits for increasing the excitation power of the transmitter (durability) and consequently the detection system has to be optimized to reach a good signal to noise ratio. Another way to reduce the influence of losses in the material is, to reduce the excitation frequency. It is well known that the damping increases when the

frequency rises. Concentrating on short time windows where the internal reflections have no influence the excitation frequency cannot be too low.

An additional effect appearing in composite materials having influence on the received signal is the reflection of the ultrasonic wave at intern interfaces in the material (transition from resin to fibre) or at intern gas bubbles [14, 27] . These reflections generate signals with an additional delay and consequently interferences. Its influence increases with pulse duration too.

5.4 Signal detection

The “efficiency” of ultrasonic transducers is low: An excitation of the transmitter with more than 100 volts leads to an output signal at the receiver in direct contact to the transmitter of about 1 V up to 10 Volts. For losses of 50 to 60 dB in the material and additional losses by mismatching an output signal as low as 10 µV can be expected. It’s a big challenge to measure such small signals in the MHz-region. First of all an excellent broad band pre- and post-amplifier system combined with band filters is necessary. The band filters are an effective contribution to improve the signal to noise ratio. Furthermore, an averaging of the measured signals is helpful for increasing the signal to noise ratio. For repetition rates of 1000 groups of excitation pulses per second an averaging using 500 groups delivers two datasets for the calculation of sound velocity and damping per second what is enough for all predictable applications. Every dataset inclosing process time, pulse shape, pulse transit time, attenuation, mould and/or resin temperature, thickness is saved automatically.

The amplifier should have an automatic gain control because the input signal may vary by four to five orders of magnitude. Afterwards an Analogue to Digital Converter (ADC) with at least eight bit resolution and a digitalisation rate of 100 MHz is necessary. Using such components and adequate software the time resolution is in the order of one nanosecond.

5.5 Signal evaluation

Different software methods are known to determine the transit time. The simplest one is the direct determination of the transit time by a comparison between reference and measured signal using maxima or minima or zeros. More sophisticated methods are based on correlation functions or Fourier transformation. The problems arising from data analysis for composite materials and a more sophisticated data evaluation are discussed e.g. in [26, 28].

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5.6 Change of sound velocity and damping during crosslinking – an example

Two main parameters of the cross linking process are of interest: The transit time and the attenuation of the sound wave in the material. The first parameter is often used directly to give an information about the cross linking process. More colourful is the use of the velocity of sound. A strong increase at the beginning and a stationary value at the end of the process is a valuable information about the crosslinking process. A typical dataset for a prepreg curing is depicted in Fig. 5.7: Shown are the sound velocity and the attenuation of the ultrasonic signal together with the linear increasing temperature. The attenuation in the material shows two distinctive regions: a very strong attenuation (up to 75 dB) during the softening of the material (60 to 120 min) and a clear reduction of the damping during crosslinking (130 to 200 min) similar to the increase of sound velocity here.

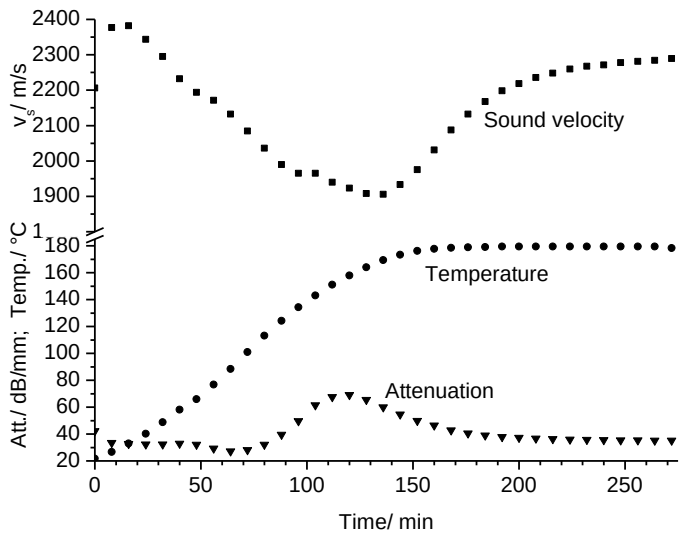

Fig.5.7: Sound velocity, damping and mould temperature vs. process time, curing process for a T-ramp of 1 K/ min up to 180 °C followed by a constant temperature. Illustrated is the strong attenuation during softening (up to 75 dB/mm). The velocity increase at the end of the process is a clear information about the crosslinking process.

5.7 Compression mould for laboratory ultrasound investigations

A small mould developed for use in laboratory is shown in Fig.5.8 It will be fixed in a press and is heated from the backside. The sensors are arranged in both parts in such a way that they are on a line in through transmission arrangement. The aim of this tool is to realize an

incoming goods control and to optimize manufacturing conditions, especially when new basic materials with unknown curing parameters have to be qualified for the production process.

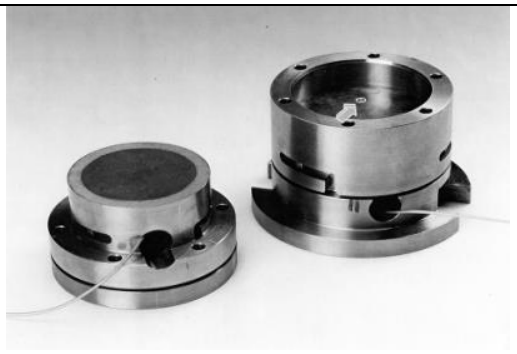

Fig. 5.8: Opened measuring cell : the arrow depicts on the sensor in the lower part

In Fig. 5.9 a scheme of a complete measuring station is depicted, consisting of the mould with two sensors and heaters, a distance measuring system and the excitation and detection unit controlled by a computer.

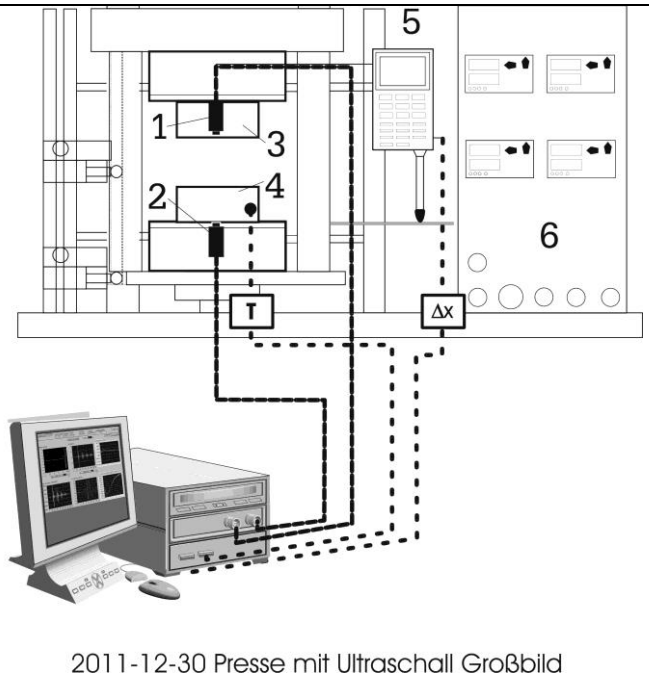

Fig. 5.9: Schematic drawing of the complete computer controlled measuring system consisting of temperature controlled mould, distance measurement gauge, pulse generation and data acquisition

In Fig. 5.10 a photograph of the main components (pulse generation, pulse detection and a 16 channel multiplexer) is depicted. It is controlled by a PC and prepared for application in industry.

The ultrasonic measuring system was developed in co-operation of BAM (www.bam.de), ISK-Iserlohn (www.isk-iserlohn.de) and SLT (www.pyrosensor.de) and named US-plus® [29-32] -

The specific configuration is characterized by:

US-plus® system with single channel set up or up to 16 channels for flow front detection and homogeneity investigations characterized by

• automatic detection of the us-signals

• "online" – information about the curing process with automatic data recording and graphical readout

• comparison of curing curves for analysis of reproducibility, comparison between materials and influence of change of process parameters is visible

• comparison to master curves and automatic alarm when predefined limit values are exceeded

Fig. 5.10 Main item of the US-plus® system designed for use in the production process. For application it has to be completed with a PC

US-plus® is available as single channel system or can be combined with a 16-channel multiplexer. The computer controlled system is designed for use in industry for online logging of the curing process and for flow front detection. It has some input ports for data from the mould and can send signals to stop the curing process. All measured data will be archived automatically. A comparison to a master curve is possible. Different online graphs are available.

In Fig. 5.11. a laboratory device based on the US-plus® system is shown. It includes a small pneumatic press containing sensors for one or some channels. The temperature of the mould is computer controlled : heating ramps or isothermal mode of operation – also in arbitrary combination - are possible (up to 180 °C).Main application is the curing diagnostic of different materials in the lab and the check of incoming goods for different industrial application e .g. injection moulding.

Fig. 5.11:Complete laboratory device for the registration of the curing process, based on the computer controlled ultrasound system US-plus®

6. Examples of usage of the ultrasonic online process monitoring system

The curing process leads to a characteristic increase of storage modulus as measured with a rheometer. The sound velocity is a function of the storage modulus – Eq. 5.1. The idea of ultrasound online cure monitoring is to bring the measurement of storage modulus into the mould with the help of small temperature stable ultrasound sensors. In analogy to storage modulus a distinct increase of sound velocity is expected.
In the following as example ultrasound results for curing of epoxy, unsaturated polyester, phenolic moulding compound and elastomer vulcanization are given as examples for the potential of the method. Consciously in this chapter only examples for material characterization were selected. The data can be attained either by small laboratory tools (typical for incoming goods control) or from production tools.

6.1 Curing of phenolic resin moulding compound PF

The PF-compound type used came from former Bakelite GmbH, Letmathe. Based on a close co-operation it was possible to get the commercial product gratis and also a special mixture without the hexamethylenetetramine hardener. In Fig. 6.1. the results for three millimetres thick plats are presented. In the compression moulding process the change of sound velocity was online registered. The mould was preheated to 160 °C. The room temperature compound was filled in and the mould closed. The results are shown in Fig. 6.1. For the moulding compound without hardener the softening and melting leads to a typical continuous reduction of sound velocity. The melting process is finished after about 70 s. The moulding compound with hardener shows at the beginning the same decrease by softening but from circa 25 s the curing causes an increase of the sound velocity.

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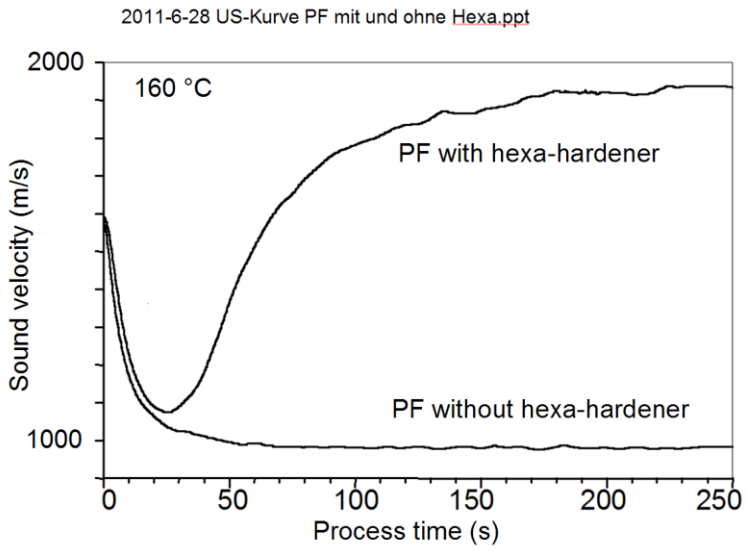

Fig. 6. 1: Sound velocity vs. process time, compression moulding of phenolic moulding compound in commercial mixture and without hardener

To proof the close correlation between the actual sound velocity value and state of curing and reached mechanical properties at four definite times (51, 70, 106, 194 s) the compression process was interrupted and the formed plate quickly removed. From the plate samples for DSC, determination of heat deflection temperature (HDT) (#DIN EN ISO 75) and bending test to destruction were cut. In Fig. 6.2 beside the sound velocity for these four termination times the degree of curing (□-DSC) and the HDT-temperature are summarized. For more clarity the results for room temperature bending test – the flexural modulus from the rise of the stress-strain curve - and the flexural strength are given in Fig. 6.3 separately.

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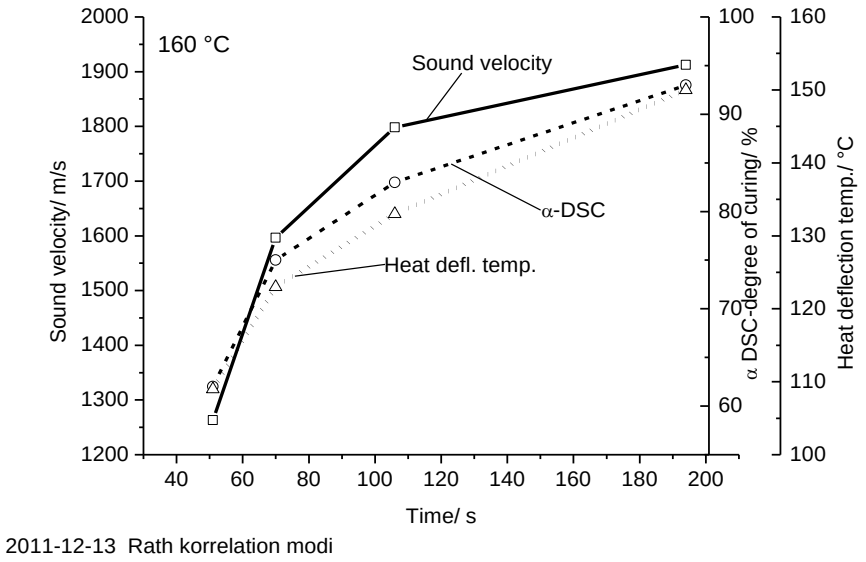

Fig. 6. 2: Sound velocity, degree of curing and heat deflection temperature vs. process time, compression moulding of phenolic moulding compound between curing time sound velocity

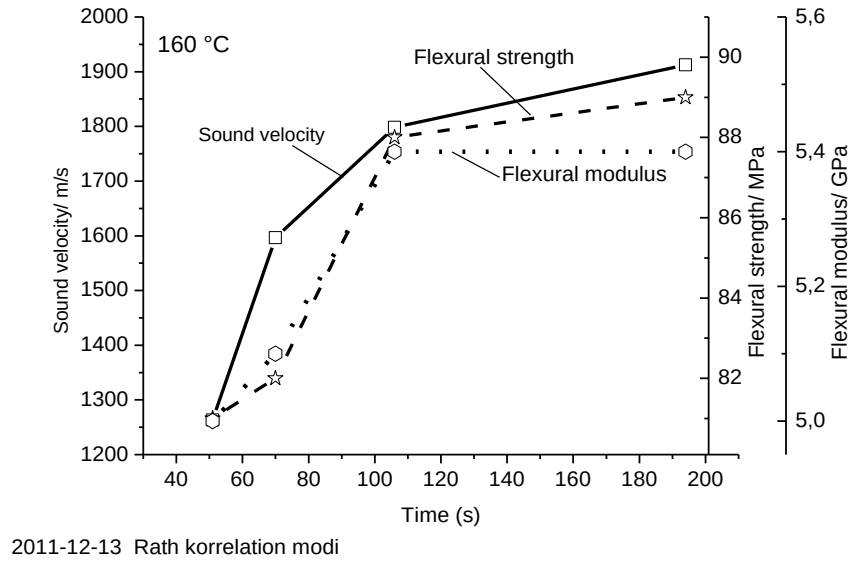

Fig. 6. 3: Sound velocity, flexural strength and flexural modulus vs. process time, compression moulding of phenolic moulding compound

The increase in sound velocity and improvement of HDT-temperature and of mechanical properties correlate well with the rise of the degree of curing. Therefore the progress of

sound velocity rise gives a direct indication on the reached degree of curing and notably to the final properties of the produced parts.

6.2 Curing of liquid epoxy and unsaturated polyester resins

For the investigation of casting resins a measuring cell for liquids was developed. The lower part of the mould was formed as a cavity, the upper part as a stamp. Both parts were encased with heating elements and thermocouples for temperature control were incorporated. The mould could be completely disassembled for remove of the cured block. As examples for measuring results the run of the sound velocity during isothermal curing for two kinds of epoxy resin and unsaturated polyester resin are given. The epoxy resins were selected to have different glass transition temperatures when fully cured ($T_{g\infty}$). Epoxy resins with low T_g (here 120 °C) are used in numerous technical applications from transport sector through to high voltage insulation. The results for isothermal curing at temperatures from 70 to 140 °C are illustrated in Fig. 6.4

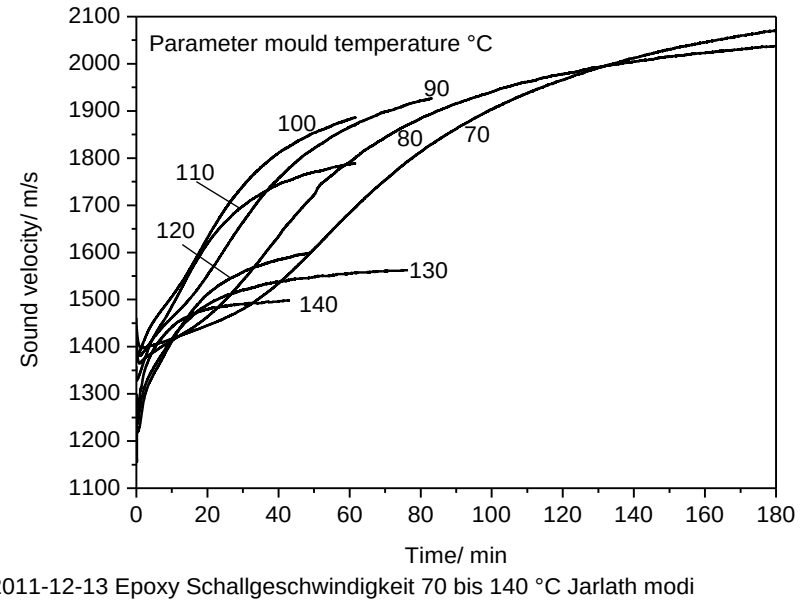

Fig. 6. 4: Sound velocity vs. process time at different temperatures, epoxy resin (low $T_{g\ type}$)

The higher the temperature the faster the marked increase of sound velocity comes to the fore. This illustrates the Arrhenius behaviour of reaction kinetics where an increase of temperature by 10 K increases the reaction speed by a factor of circa two. The lessening of

the end value of the sound velocity with increasing temperature is a result of the general temperature dependence of the modulus of a full cured resin. The greater reduction between 110 and 120 °C has its reason in passing $T_{g\infty}$. At 130 and 140 °C the final state is rubber-like, at 110 and 120 °C it is in the transient.

The epoxy resin from the second example is a high end product for aircraft manufacturing. Its maximal glass transition temperature $T_{g\infty}$ is in the range of 200 °C. In the manufacturing process it is typically used in carbon fibre prepreg lay technology. Curing is carried out in autoclaves at 180 °C for many hours. As an example the results for temperatures from 140 to 180 °C are illustrated in Fig. 6.5. The influence of curing temperature is illustrated very clearly. With rising temperatures the sound velocity at the beginning is reduced, the time for rise and for drop of the curve is also reduced. For 170 and 180 °C a diminution of the final value appears. This is an advice of the proximity of the processing temperature to T_g. Supplementary the times found in rheology experiments for gelation and vitrification are plotted in the description. A famous conformance between ultrasound and rheology data can be stated.

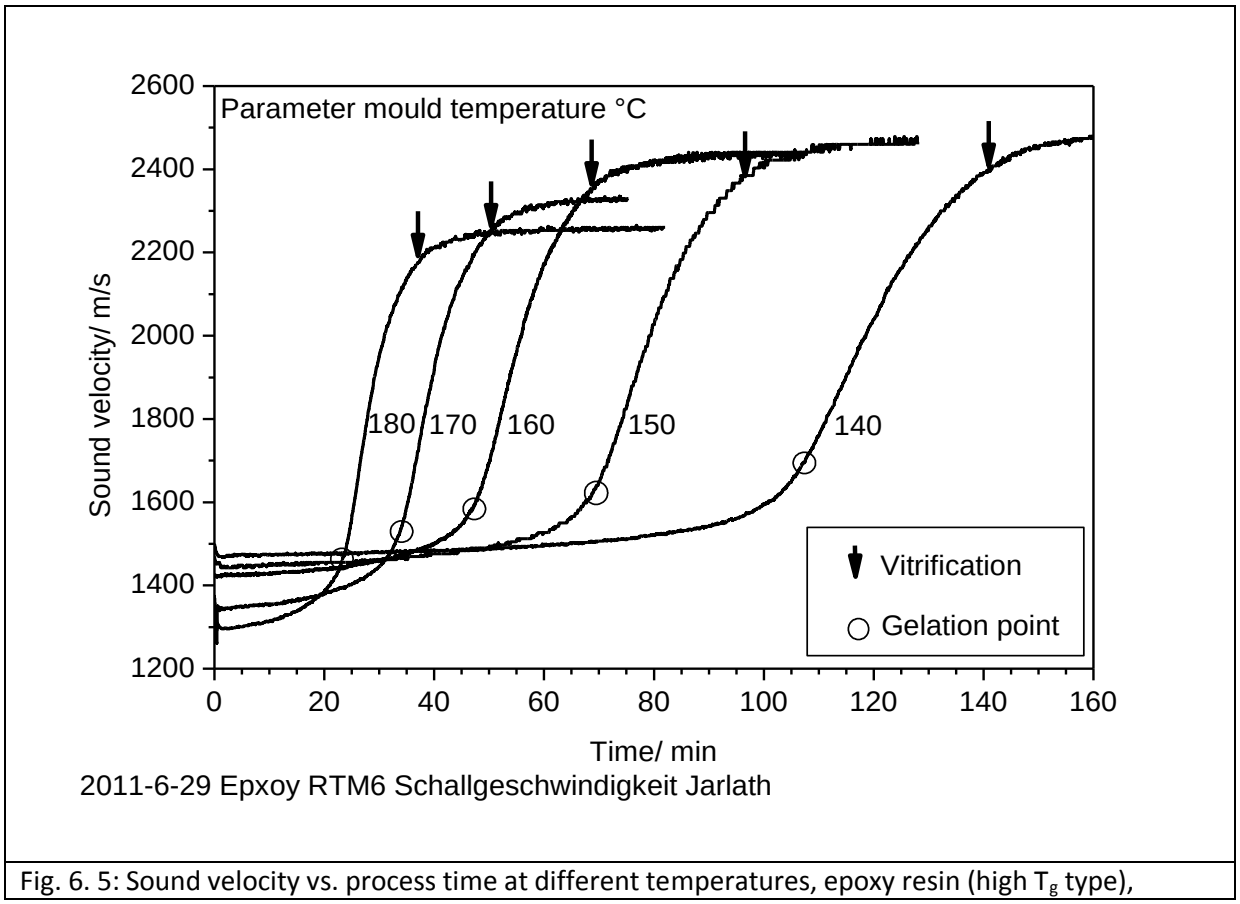

Fig. 6. 5: Sound velocity vs. process time at different temperatures, epoxy resin (high T_g type),

additional the times for gelation and vitrification from rheology are marked

In the next example in Fig. 6.6 the curing of unsaturated polyester resin for manufacturing of wind blades is described. Curing was performed at 60, 70 and 80 °C. The problem was to look for the known effect of a substantial heat release by the exothermic crosslinking reaction. Therefore into the resin an additional thermocouple was incorporated.

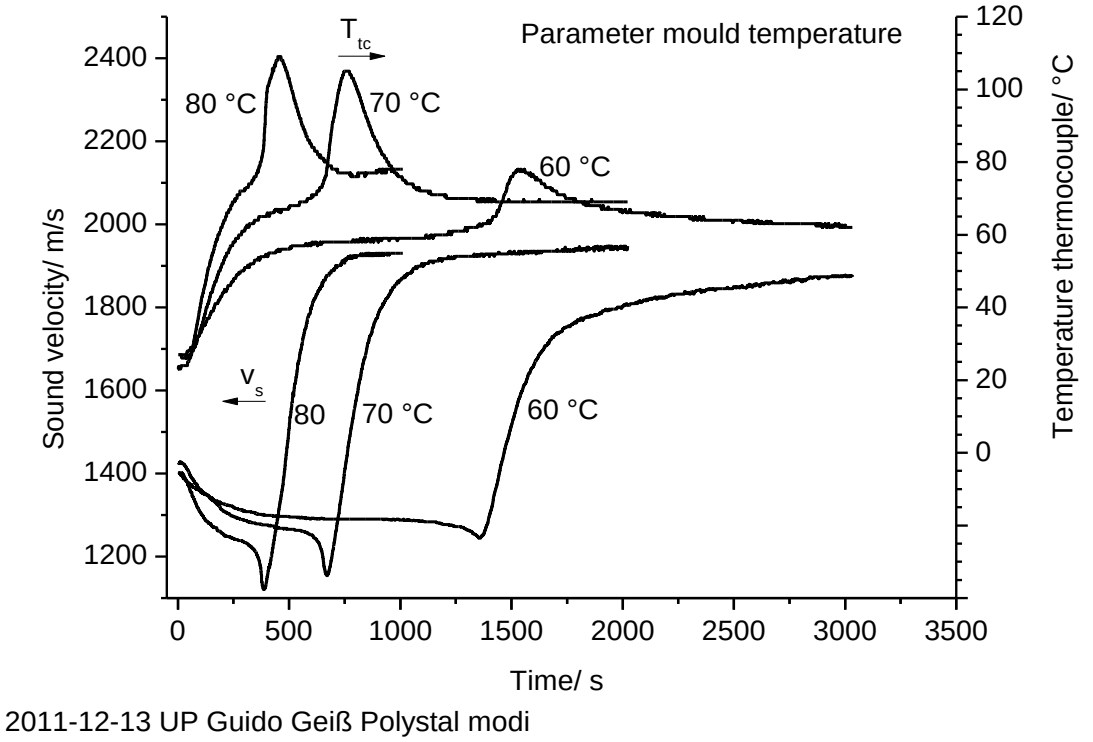

Fig. 6. 6: Sound velocity and thermocouple resin temperature vs. process time at three mould temperatures, unsaturated polyester resin

At the beginning the resin warming to the mould temperature emerges. In this phase the sound velocity decreases by reduction of resin viscosity. At all manufacturing temperatures a temperature raise appears when the reaction starts. At 70 and 80 °C this is considerably. The sound velocity gives the nice information that in the early state of the reaction the reduction of viscosity is substantially reduced by this effect before it increases. Such information can little be gained by rheological measurements because the heat flow to the measuring plates is too high. Also at monitoring of component manufacturing process where it is impossible to incorporate thermocouples into the resin ultrasound curves give this important additional information on strong temperature rise.

For additional flow front detection it is necessary to dispose a number of sensors in the tool. Therefore the measuring unit was extended by a multiplexer set-up with up eight or sixteen measuring lines.

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7. Examples for practical use of the ultrasound online process monitoring in the automotive field

7.1 Belt pulley from phenolic moulding compound PF

In recent times belt pulleys in the powertrain had nearly totally changed from transformed sheet steel to injection moulded mineral filled phenolic resin [33, 34]

An example is shown in Fig. 7.1.

Fig. 7.1: Belt pulley made from phenolic moulding compound, sensor position is marked

For this aim a special injection-compression moulding process with mould temperatures in the range of 160 °C was developed in industry [34]. In the process the not fully closed mould (preset gap thickness 1 … 10 mm) is filled by an injection moulding machine before it is closed by high pressure. This causes a very homogeneous mould filling and high compaction. The closed mould is hold for sufficient time to reach a high degree of curing.

During development of the technology the ultrasound measuring system was used to gain information on the process course [35]. Therefore two ultrasound sensors were incorporated into the mould. Fig. 7.2 gives a schematic view of the mould.

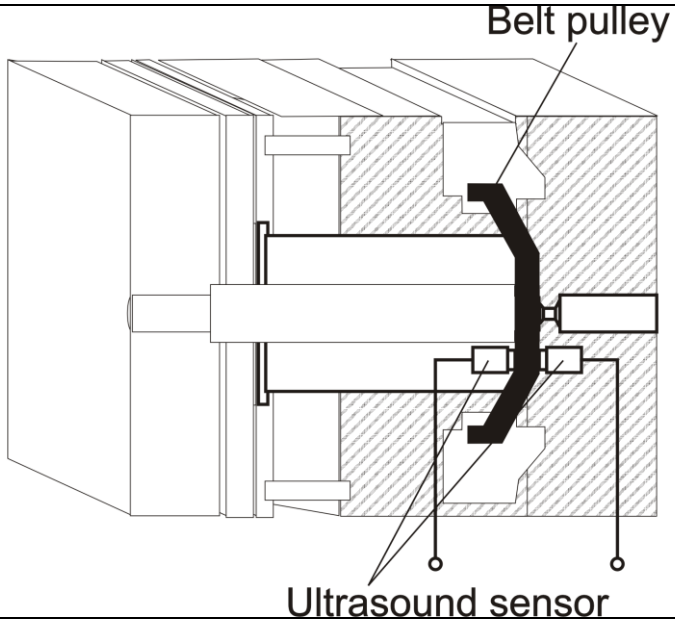

Fig. 7.2: Schematic view, mould for injection compression moulding with incorporated ultrasonic measuring line

Typical records of the change of ultrasound velocity during the manufacturing process of phenolic moulding compound are given in Fig. 7.3 [36]. During injection phase the first sensor signal arises from filling the gap between the sensors. The temperature increase of the compound leads to lowering of viscosity of the melt which is accompanied by a reduced sound velocity. After about 12 s the cross linking process dominates. The main part of the reaction takes 30 to 40 s. After that the reaction speed is distinctly reduced but does not come to an end during the 75 s cycle time. A sloped rise of sound velocity is a clear advice on a reaction being slowed down by beginning vitrification. The shift of glass transition temperature by crosslinking brings the glass transition temperature close to the mould temperature. The material solidifies, the viscosity is dramatically reduced and for the reacting agents resin and hardener it becomes difficult to meet each other. That this process is to be expected here is clear having a look on $T_{g\infty}$ of phenolic moulding compound being >250 °C and the mould temperature here of 160 °C, that means considerably below this final glass transition temperature. The reproducibility of the ultrasound curve shape is amazing good. So it is easy to notice automatically by the computer system deviations in the manufacturing process for example in mould temperature or compound composition very early.

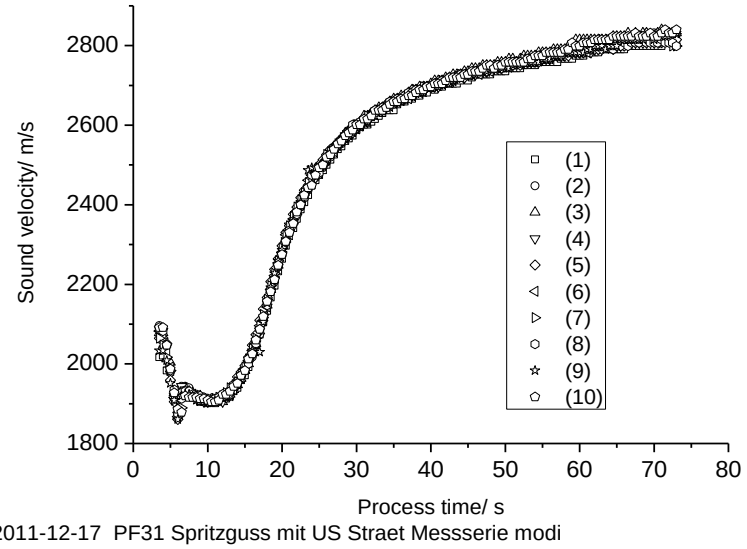

Fig. 7.3: Sound velocity vs. process time, injection moulding process of phenolic moulding compound, test of reproducibility

In Fig. 7.3 a superposition of 10 cycles is illustrated. The aim was to prove the reproducibility of the process. The curves demonstrate a high precision of the measuring and manufacturing technology. At injection moulding for specific process adjustments the influence of the crosslinking caused shrinkage of the resin emerged. An example is given in Fig. 7.4 for a change of the time to hold the post-stress from 10 s to 15 s in the phase of intensive curing.

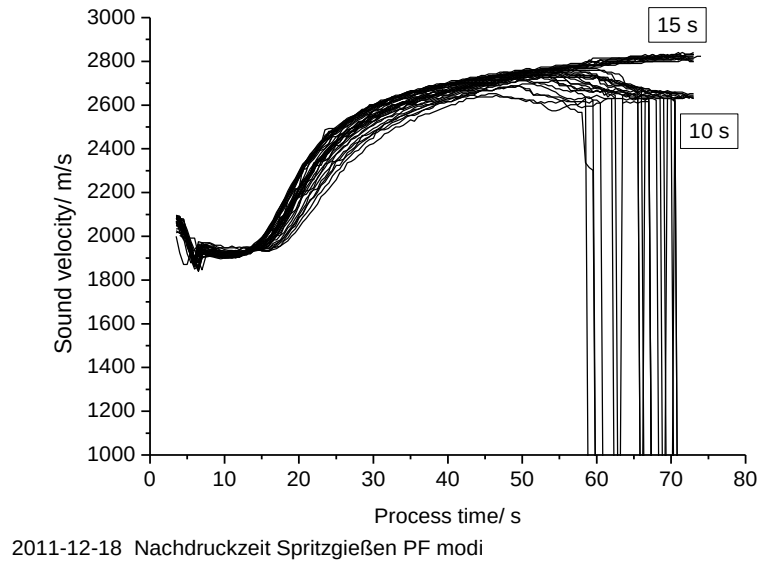

Fig. 7.4: Sound velocity vs. process time, injection moulding process of phenolic moulding compound, influence of switching time from injection pressure to hold pressure

In the consequence of a reduction switching time of post-pressure by 5 s a lowered sound velocity appeared in the flat part of the curve. In some cases the signal was interrupted before the process end. The reduced sound velocity or the signal interrupt are indications for the influence of shrinkage. Obviously at first only the pressure in the compound is reduced without a detachment from the mould wall.

Beside optimization and permanent documentation of manufacturing process online process monitoring offers the profitable control of incoming moulding compound. This can be dislocated from the laboratory into the production process. Deviations from stored master curves of sound velocity can be detected immediately by the measuring system and trigger an alarm.
An unexpected additional result was the correlation between the final value of sound velocity and the test of belt pulley strength – see Fig. 7.5 [35].

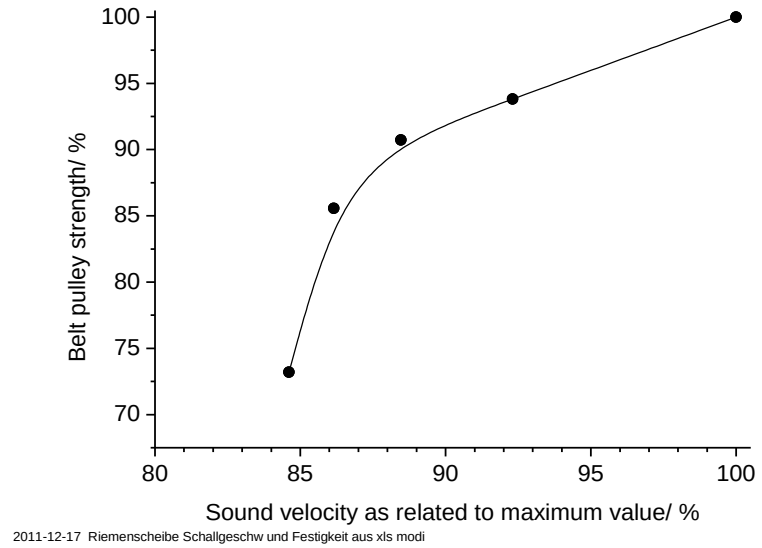

Fig. 7.5: Correlation between sound velocity and belt pulley strength

The higher the sound velocity level the better the strength values. A sound velocity less than about 90 % of the maximal value is an indication on mistake in the technological process. So by the ultrasound measuring system a control of end sound velocity is possible for every produced part and parts reaching not the predefined sound velocity level can be automatically rejected.

7.2 Automotive head lights from bulk moulding compound BMC

Modern automotive head lights with clear glass panels realize the form of the light output by concave mirrors. A technology to produce such mirrors is injection moulding of BMC. BMC is a composite material of unsaturated polyester resin (UP) and short glass fibres [37-39].

An example of a BMC-head light is given in Fig. 7.6

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Fig. 7.6: Head light from BMC produced by injection moulding process, product by automotive lighting, Reutlingen

To improve the production stability, especially to realize an incoming goods control, the ultrasound measuring system was installed in a BMC test compression mould – see Fig. 7.7 [40]. The mould was developed by ISK [41].

Fig. 7.7: Compression mould with incorporated ultrasound sensors for incoming goods control, photo: ISK Iserlohn

One main point in the first tests of the method was to find out if there are differences in curing behaviour between two BMC-suppliers – named material A and B – see Fig. 7.8

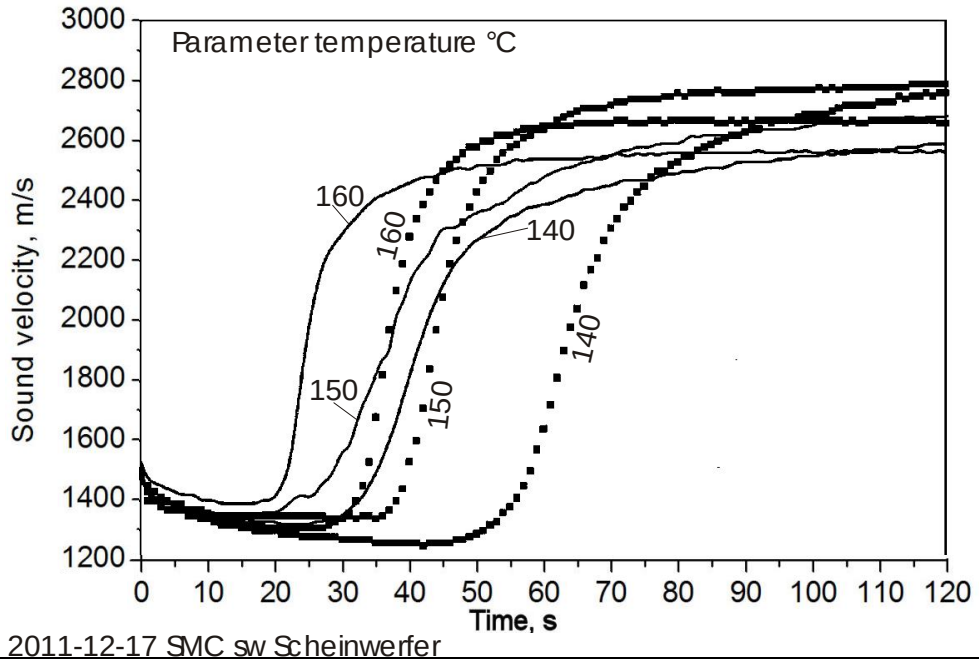

Fig. 7.8: sound velocity vs. process time, curing behaviour of two BMC materials (material A solid curves, material B dotted curves) at three typical manufacturing temperatures 140, 150 and 160 °C

By variation of the temperature between 140 and 160 °C an overlapping region of similar reaction speed could be found for both materials. On the basis of this insight a quick shift between both suppliers seemed possible without voluminous tests in the production line. Also a process optimization was possible. For every temperature an optimal process time could be determined and finally a cycle time reduction could be initialized. The reserves in reduction of curing time seemed to be up to 20 %.

7.3 Lorry cabin from glass fibre reinforced epoxy resin by resin transfer moulding (RTM) process

RTM is among the most present-day methods for composite manufacturing [42-46]. The ultrasound measuring system was applied in the process for fabrication of large-volume cabin parts for lorries. The problems to solve were to detect the resin flow front propagation and the uniformity of curing process in a large-volume tool. An RTM mould is given schematically in Fig. 7.9. The bifid mould establishes a gap. The gap is filled with inlayed fibre mat. A medium filling state is exemplified. The two components – resin and hardener – are pumped with a special equipment realizing the accurate mixing ratio into a preheated mixing chamber and from here via a runner direct into the mould. The reactive resin spreads in the gap and reaches finally the

rising gates. Here the displaced air passes off together with the resin. For flow front detection and cure monitoring an arrangement of ultrasound sensors can be realized at critical or interesting positions. This is suggested in Fig. 7.9 also.

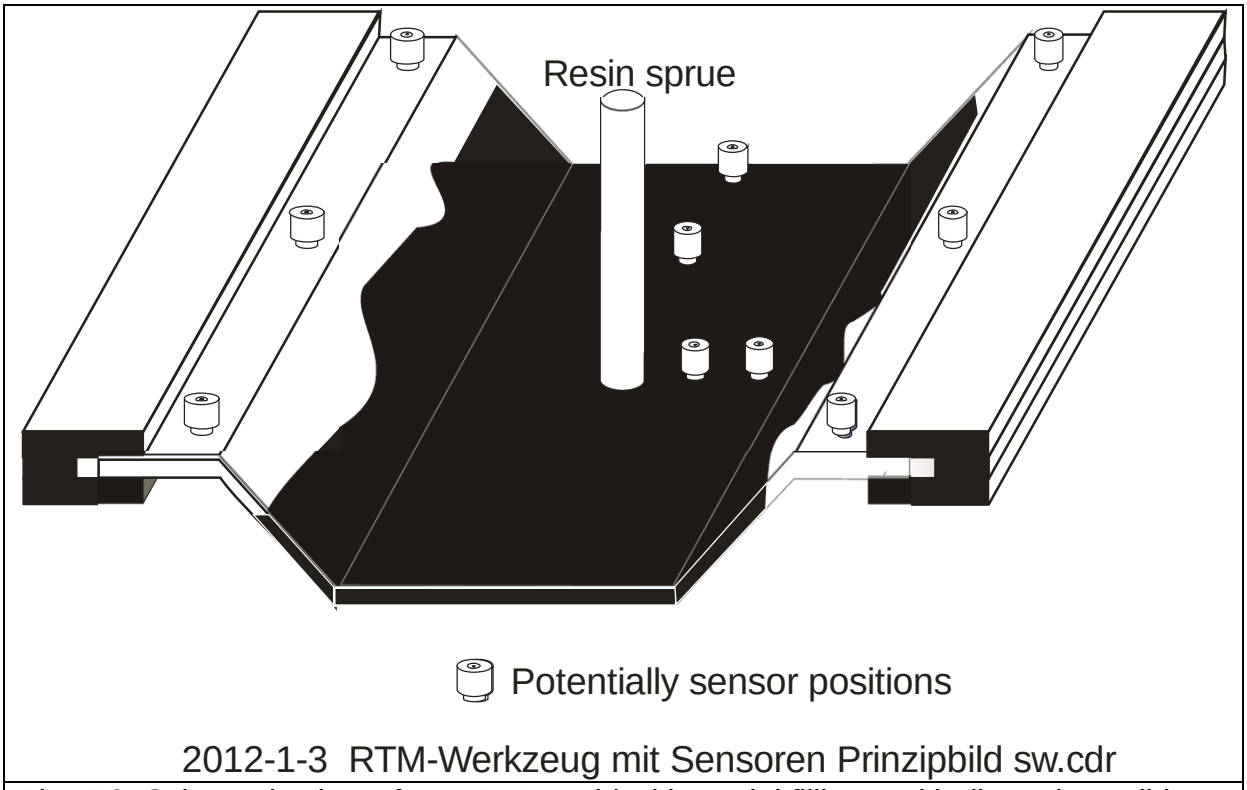

Fig. 7.9: Schematic view of an RTM mould with partial filling and indicated possible sensor positions

In a research project together with an second research institute IKV Aachen (http://www.ikv-aachen.de/en/) and partners from industry Bakelite (today Momentive http://ww2.momentive.com/home.aspx), Fritzmeier http://www.fritzmeier.de/dt/Sitemap/map_home.html) and BAM the ultrasound method was adapted to the RTM process for production of lorry cabin roofs – see Fig. 7.10.

Fig. 7.10: Photograph of the RTM part for lorry cabin produced by Fritzmeier

In the RTM-mould five ultrasound measuring lines were installed. Fig. 7.11 shows a photograph of the upper part of the mould and marks for the sensor positions.

Fig. 7.11: Upper part of the RTM-mould with signs showing the position of the sensors:
1 in vicinity to the inlet nozzle (arrow), 2, 3, 4 and 5 close to the outlet risers

The sensors were inserted from the back side in blind holes as hidden sensors behind the wall of the mould – Fig. 7.12

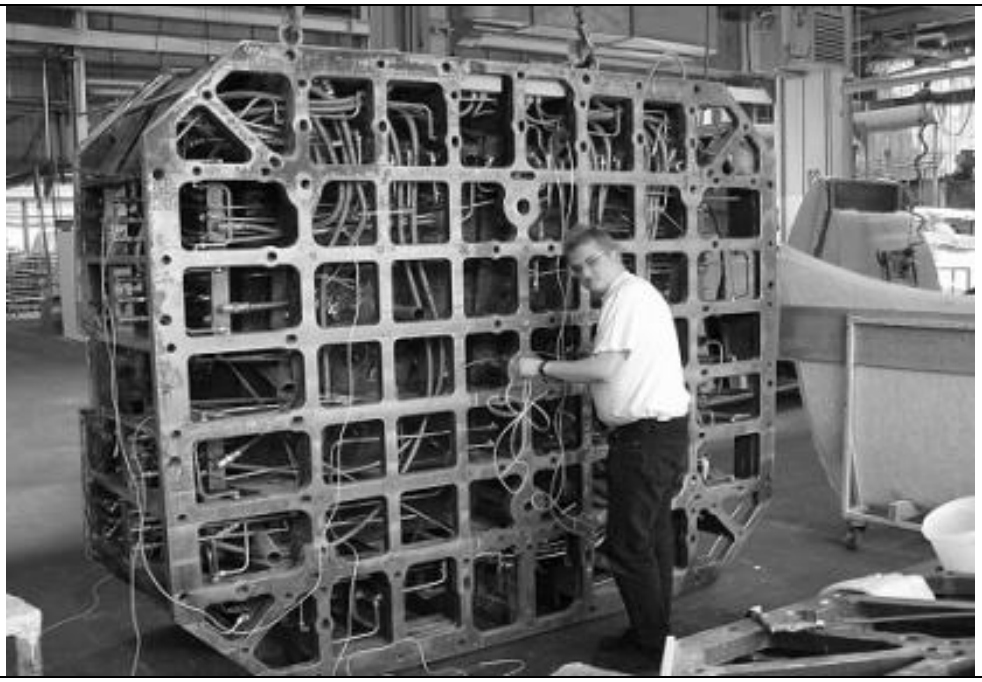

Fig. 7.12: Insertion of the sensors into the mould from the back side

Typical measurement results are given for the first four minutes showing the mould filling in Fig. 7.13.

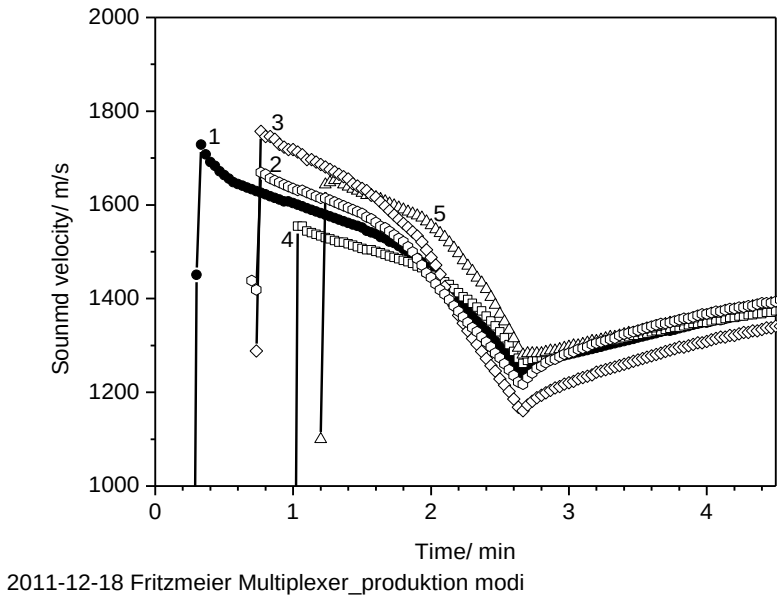

Fig. 7.13: Sound velocity vs. process time, flow front detection by signal onset at five measuring lines

As expected from the assembly of the ultrasound measuring lines the resin reaches line 1 at first since it is closest to the sprue, 2 and 3 are achieved at the same time, 4 and 5 later but not at the same time as expected from the geometry.
Fig. 7.14 shows the signal progress for the complete manufacturing process.

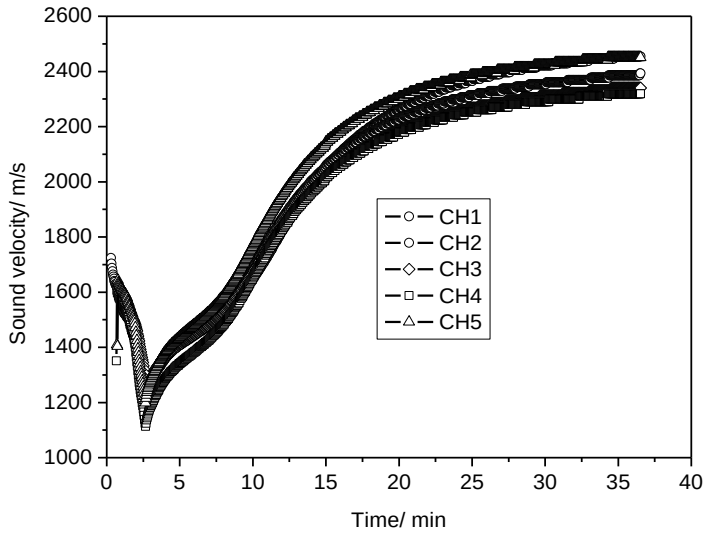

Fig. 7.14: Sound velocity vs. process time, the complete RTM-Process

After having reached the measuring line the resin viscosity decreases by warming up indicated by the decrease of sound velocity. The resin is injected with a temperature of 80 °C, the mould temperature is 160 °C. So the resin temperature increases substantially when it has reached the measuring line. This is accompanied by a reduction of sound velocity caused by viscosity decrease of the resin. After about 2.5 min the temperature has reached a value that curing reaction begins to dominate.

The curing process at all five sensor positions is rather similar. Characteristic for all ultrasonic curves is a kind of a two step process. After slowing the rise starting from about eight minutes the sound velocity change increases again. A possible explanation can be the exothermic character of the crosslinking. In thick components the thermal conduction is too low. So an increase of temperature may lead to an acceleration of reaction speed. The final continuous small rise of the sound velocity is an indication for a slow down of reaction speed influenced by vitrification. The sound velocity data for the five measuring lines show that the curing run is rather even. That

means that the temperature distribution in the mould is nearly perfect. Differences in the end value can be explained by different glass fibre contents of the composite in the measuring line and inexactnesses of the determination of the gap thickness. The RTM process with ultrasound process monitoring is described in more detail in [44] and [47].

7.4 CFK high pressure vessels for hydrogen storage – prepreg characterization

Fuel cell drive systems need a low weight tank for hydrogen. For gas storage 700 bar pressure vessels are under development. An example is shown in the BAM climate test chamber in Fig. 7.15 [48].

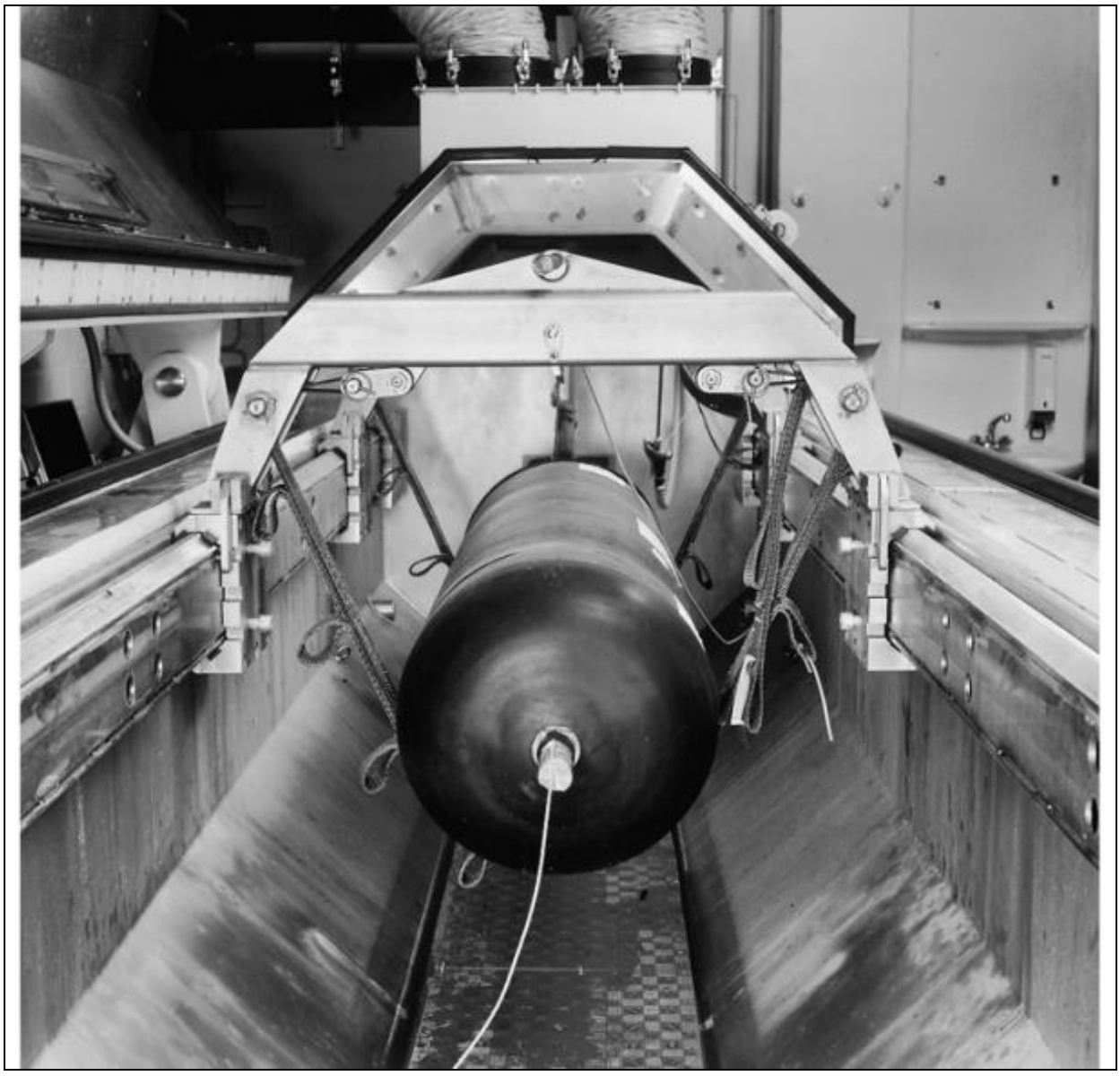

Fig. 7.15: CFK- hydrogen cylinders under test in a temperature-controlled high pressure test apparatus in the BAM, photo: BAM Federal Institute for Materials Research and Testing

An inliner, for example a polyethylene flask, is encapsulated by an epoxy impregnated carbon fibre prepreg wrapping. The prepreg is cured at high temperatures for example in an autoclave. The maximum curing temperature is limited by the inner polyethylene flask. To give the construction engineers a method for process optimization and to define standards for quality control of the production process a measuring cell for investigation of prepreg curing was developed by SLT – see photograph in Fig. 7.16.

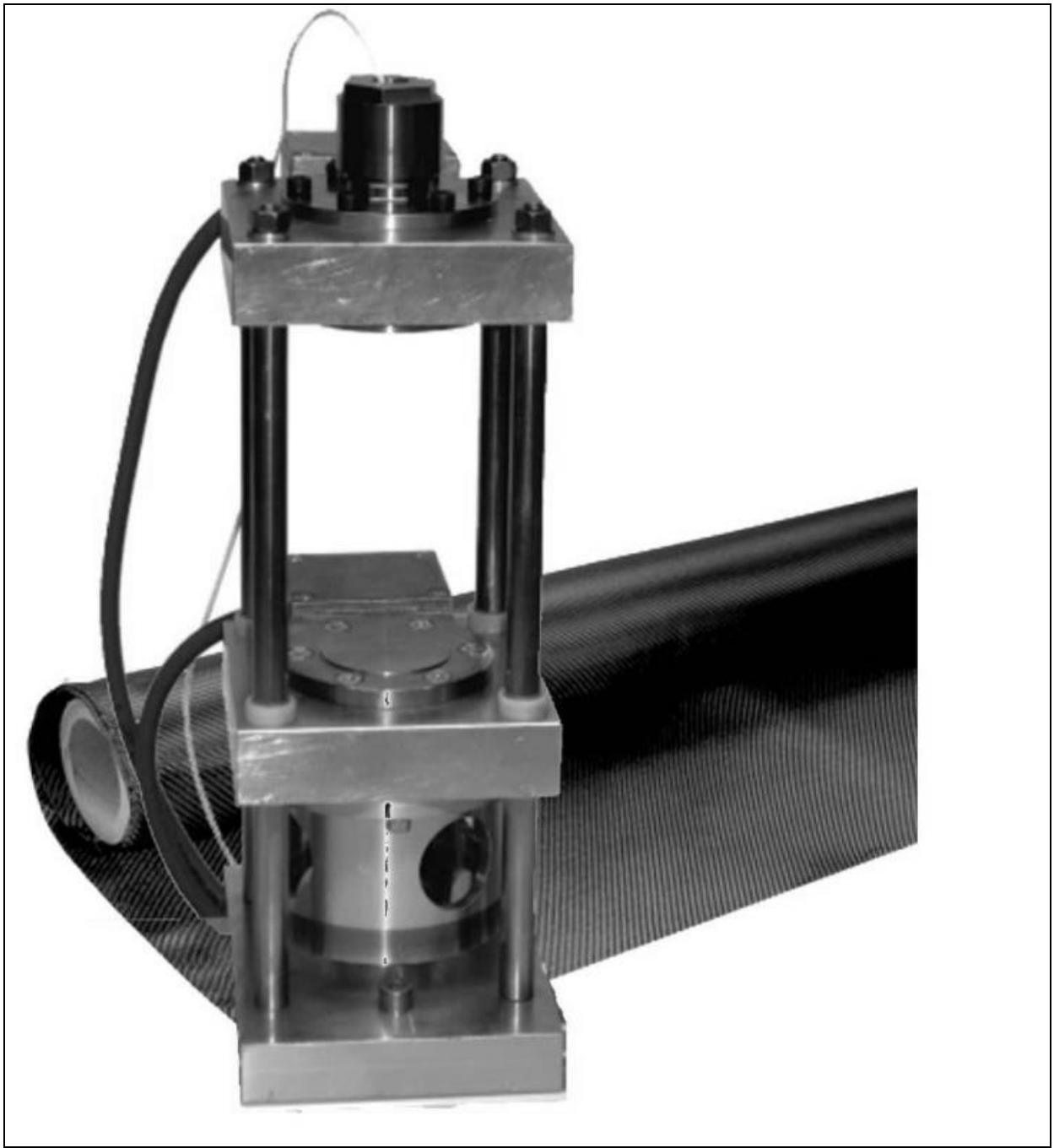

Fig. 7.16: Mini compression gadget with two heat regulated plates and incorporated ultrasound sensors for process monitoring in laboratory scale

The test gadget is based on a small compression mould consisting of a fixed upper plate and a lower plate moved by a pneumatic punch. Both plates have heating elements and separate sensors for controlling the temperature. By careful design and use of a thermocouple and a control circuit per plate a very homogenous temperature distribution is realized. The diameter of the plates is 50 mm. Additionally to isothermal

measurements temperature courses for example ramps can be programmed. So the complete manufacturing process can be simulated.

In Fig. 7.17 as an example the change of sound velocity and DMA storage modulus E' of a prepreg with a temperature program are given in one picture. The temperature program was adapted to the manufacturing process: first linear heating with 1 K/min to 110 °C and to hold this temperature for long time.

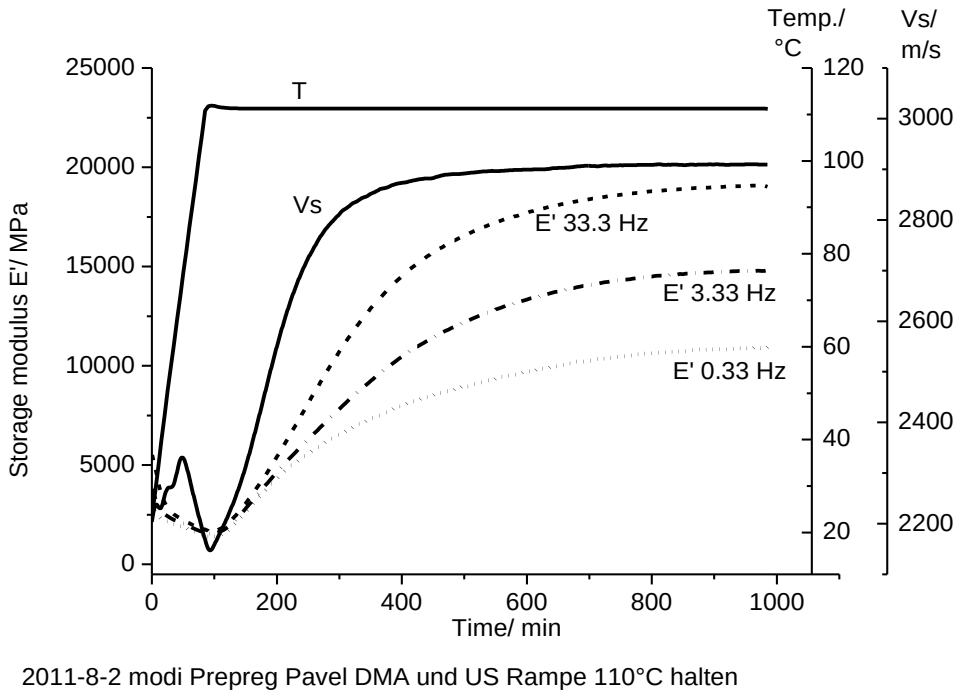

Fig. 7.17: Storage modulus, sound velocity and temperature vs. process time, epoxy prepreg linear heating and isothermal curing at 110 °C

At the beginning the reduction of viscosity with rising temperature leads to a decrease of the E' and v_s - curves before the crosslinking reaction setting in at 110 °C leads to a distinct rise. Ultrasound and DMA results are in a very good coincidence. The higher the frequency the steeper is the rise of the curves at curing. This is a consequence of frequency dependence of the glass transition temperature. For higher frequencies the vitrification impact is earlier and more clearly seen.

At room temperature where the resin is liquid the prepreg has the higher sound velocity what is caused by the high amount of stiff carbon fibre fillers. The changes

with increasing temperature are very similar for both kinds of samples. Always the prepreg shows the higher value of sound velocity. There is only a kind of parallel shift in the curves. The critical temperatures are very similar, also at cooling the knee in the curves appears at a similar temperature.

A linear heating experiment with a 1 K/min ramp for prepreg is shown in Fig. 7.18.

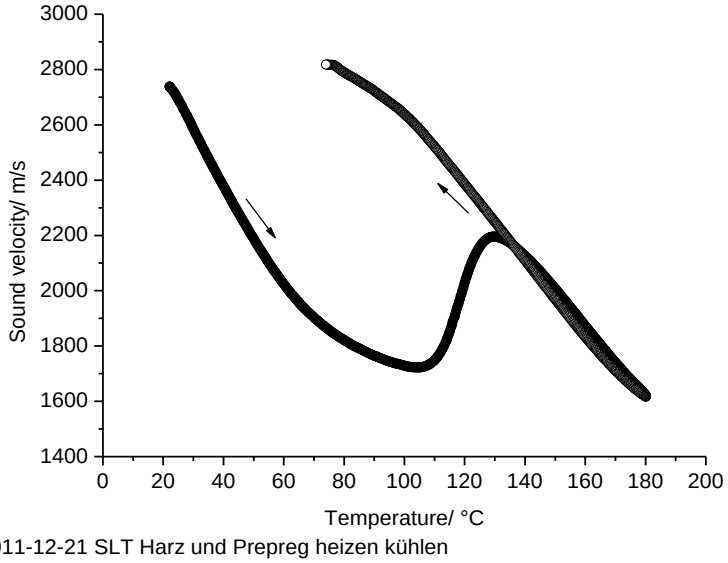

Fig. 7.18: Sound velocity vs. temperature at linear heating and cooling of prepreg, temperature rate 1 K/min

In the heating run the softening of the resin with increasing temperature is at first dominant. Near 105 °C the crosslinking caused increase of the modulus and thus of the sound velocity begins to dominate. With depletion of the reactants the increase of sound velocity comes to an end (about 130 °C) and from here it decreases continuously. This is an indication, that the glass transition temperature of the fully cured material was exceeded. An additional support for this interpretation is the identical temperature dependence in the cooling run, where both curves are nearly identical. Below about 100 °C the slope changes, the temperature dependence is reduced. This seems to be caused by passing the rubber to glass transition.
To prove this more in detail with a fully cured prepreg sample DMA for five frequencies was measured. The result is given in Fig. 7.19.

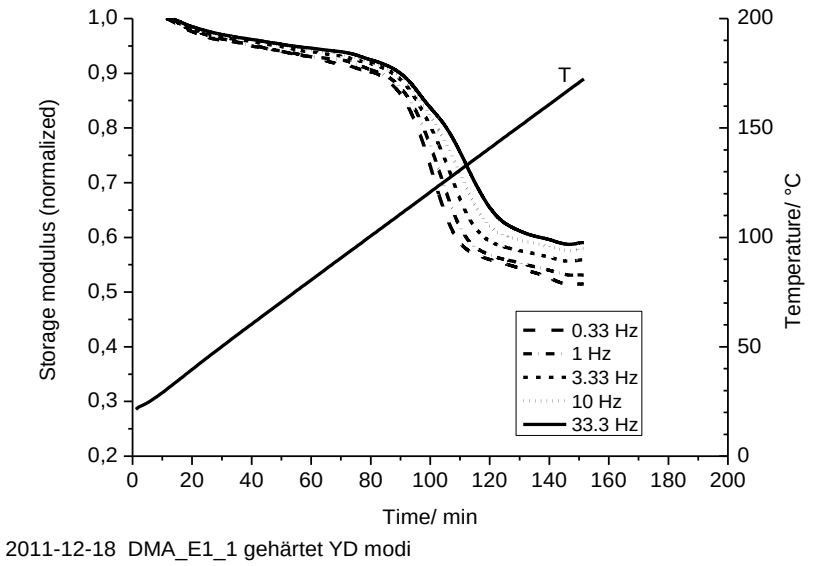

Fig. 7.19: Storage modulus E' of fully cured epoxy prepreg vs. time, sample from Fig. 7.17, heating rate 1 K/min

At circa 100 °C at the onset temperature a stepped decrease of E' which is typical for a transition from the glass to the rubber state appears. The frequency dependence shows the characteristic behaviour. A similar experiment with the fully cured prepreg was carried out with the ultrasound measuring system, too – Fig. 7.20. A change of sound velocity temperature function at about 115 °C is seen. This decrease is also a hint on passing the glass-rubber transition. The higher temperature for ultrasound (4 MHz) in comparison to DMA has its reason in the frequency dependence of T_g.

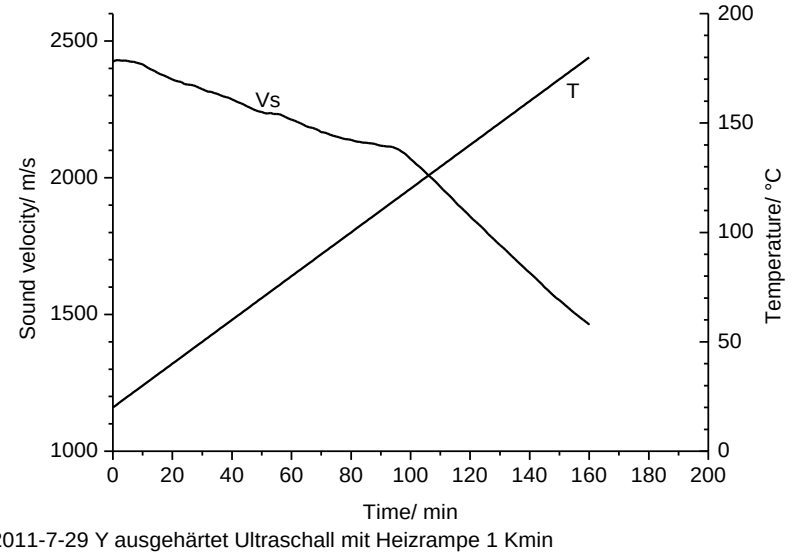

Fig. 7.20: Sound velocity of fully cured epoxy resin vs. time, sample from Fig. 7.17 at linear temperature rise, heating rate 1 K/min

The similar linear heating experiment with a 1 K/min ramp was carried out at the basic resin of the prepreg material to compare the behaviour of prepreg and the pure epoxy resin crosslinking. The results are given in Fig. 7.21

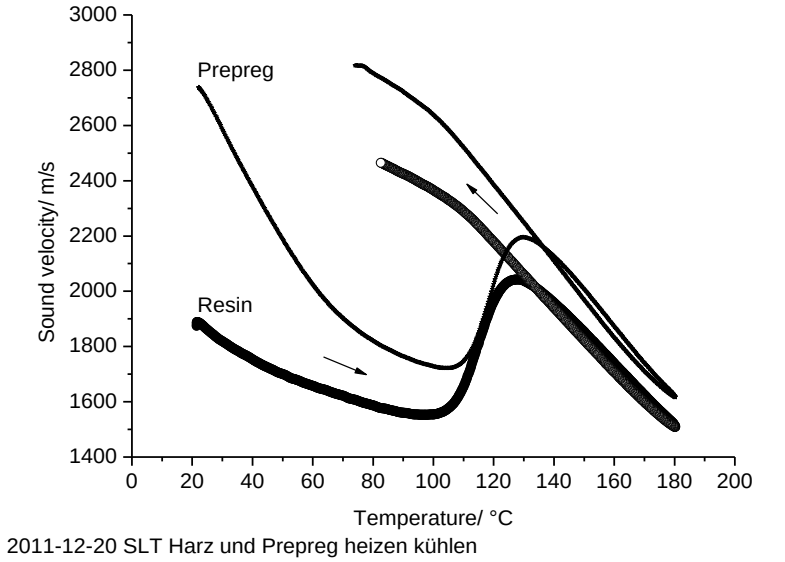

Fig. 7.21: Change of sound velocity at linear heating and cooling of prepreg and merge resin, temperature rate 1 K/min

At room temperature where the resin is liquid the prepreg has the higher sound velocity what is caused by the high amount of stiff carbon fibre fillers. The changes

with increasing temperature are very similar for both kinds of samples. Always the prepreg shows the higher value of sound velocity. There is only a kind of parallel shift in the curves. The critical temperatures are very similar, also at cooling the knee in the curves appears at a similar temperature.

To simulate the manufacturing process for three temperatures the isothermal curing process was recorded in Fig. 7.22.

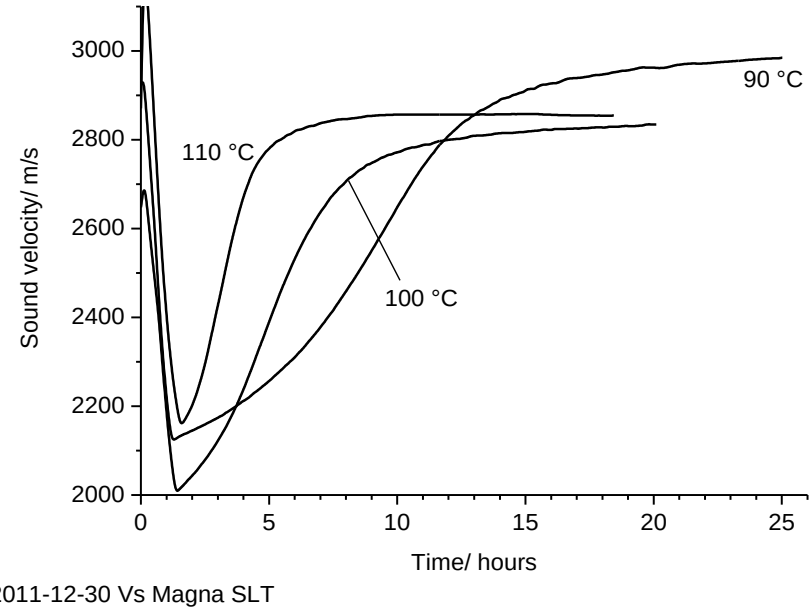

Fig. 7.22: Change of sound velocity by prepreg crosslinking for three temperatures

The mould was preheated to the selected temperature. The room temperature stored prepreg was deposited on the lower plate and the mould closed. The sharp decrease of sound velocity at the beginning is a consequence of viscosity reduction by heating up of the resin. The higher the temperature the earlier curing comes to the fore. At 110 °C a flat curve is reached. This is an indication for full curing. At 90 °C the appearance of vitrification reduces the reaction speed and causes a long lasting rise. For better illustration in Fig. 7.23 the is depicted the 1st derivative, i.e. the reaction rate, for the sound velocity curves was exemplified.

For these data also the first deviation was calculated. This is an expression of the reaction rate. The results are presented in Fig. 7.23.

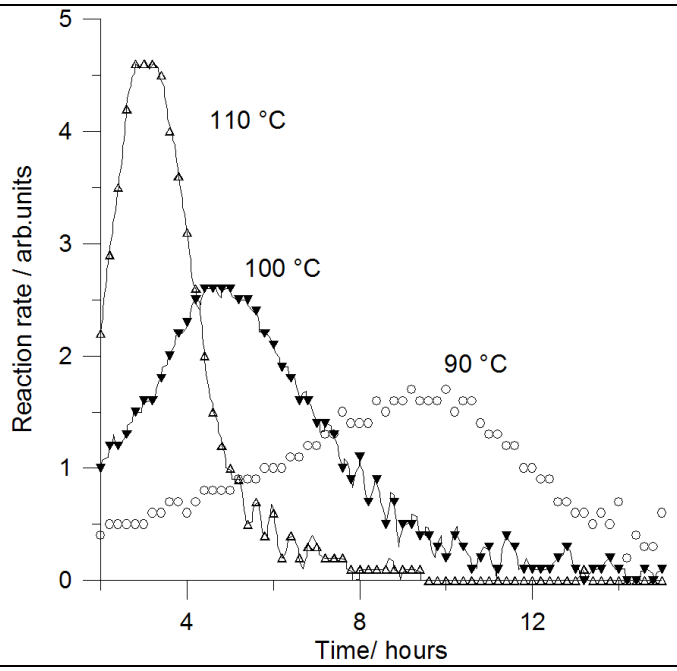

Fig. 7.23: Reaction rate vs. process time concerning results in Fig. 7.22 , prepreg crosslinking for three temperatures

The picture is very clear. The reaction rate and the time for the reaction maximum are distinct functions of the temperature.

For an another kind of prepreg (quick curing resin) by costumer's order the reproducibility of the ultrasound method has been tested. The results are shown for 120 °C mould temperature in Fig. 7.24 for seven measurements.

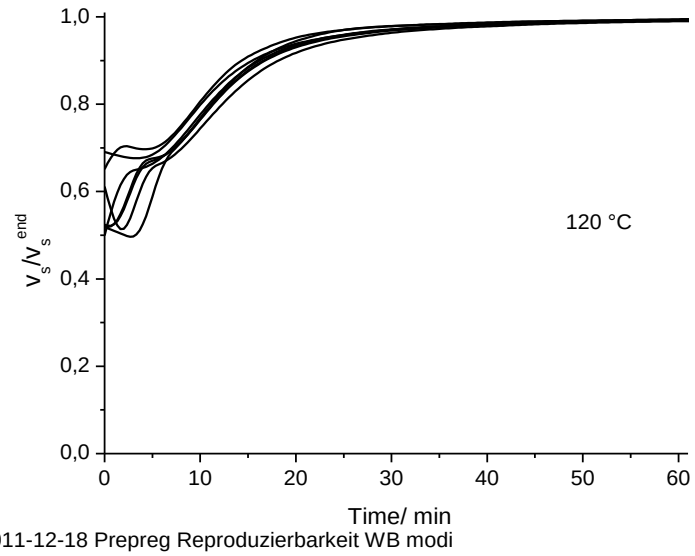

Fig. 7.24: Comparison of the change of sound velocity of glass fibre prepreg material – normalisation on the end value

The distinctions in the curves at the beginning have their reason in a different thickness change of the sample in the softening period. The curing process being seen behind circa ten minutes is very similar; especially the end of crosslinking process does not differ remarkably.

7.5 Test in autoclave curing process

After pre-investigations with the small laboratory mould also manufacturing of prepreg parts in an autoclave were performed. A photograph of the measuring assembly is given in Fig. 7.25. The sensors were incorporated into the mould inside the autoclave. The coaxial measuring cables were connected with coaxial feed through in a measuring flange – seen in the picture on the left side in vicinity to the door. The results were analogous to the pre-investigations in the laboratory mould.

Fig. 7.25: Ultrasound measuring assembly in front of an autoclave for prepreg curing, photograph from J. Döring, BAM

7.6 Control of vulcanisation process of tire rubber

After having collected experience with ultrasonic cure monitoring at thermosetting reactive materials the investigations were extended to the vulcanisation of rubber [49-53]. Here an example for a tire mixture is given.

At automobile tire production every new mixed rubber compound is controlled by a measurement of vulcanisation process for production release. The standard instruments in tire rubber industry are specially adapted plate-plate rheometers also named curometer or MDR – moving die rheometer. The rubber compound is placed between two heated plates which are pressed together until the sample is formed. The lower plate is fixed; the upper plate oscillates with a small angle. The torque to hold the oscillation angle constant is registered as function of time. The main information from such measurements comes from the time to start the reaction named scorch time at two or five percent increase of torque and the course of real

part of the complex torque. The critical times to reach 10, 50 and 90 % of the total change of torque by vulcanisation are defined by such measurements. Details are regimented in a standard [54].

To demonstrate the capabilities of the ultrasound cure monitoring method it is convenient to compare it with the well established curemeter measurements. In Fig. 7.26 the real part of the torque from the curemeter S' is depicted together with the sound velocity at isothermal vulcanisation of a tire rubber mixture at 160 °C. The data for the first 200 s are separately shown for more details in Fig. 7.27

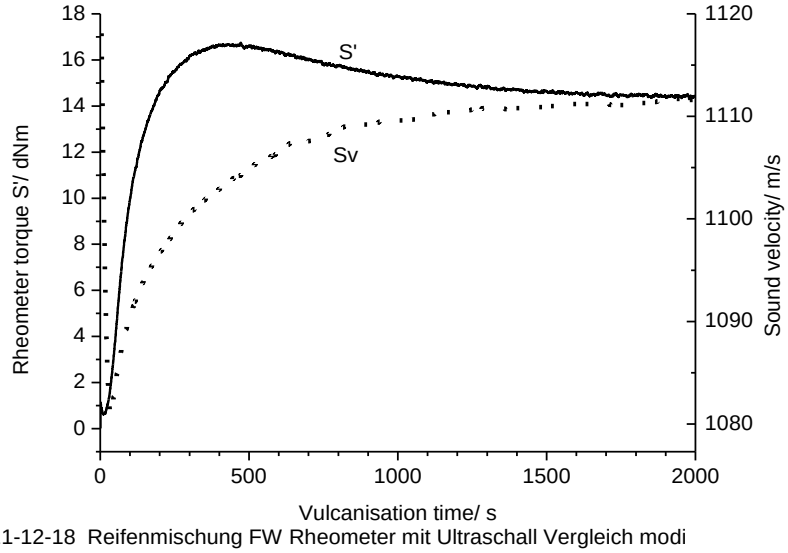

Fig. 7.26: Real part of torque S' from curemeter and sound velocity vs. process time, vulcanisation of a rubber compound at 160 °C

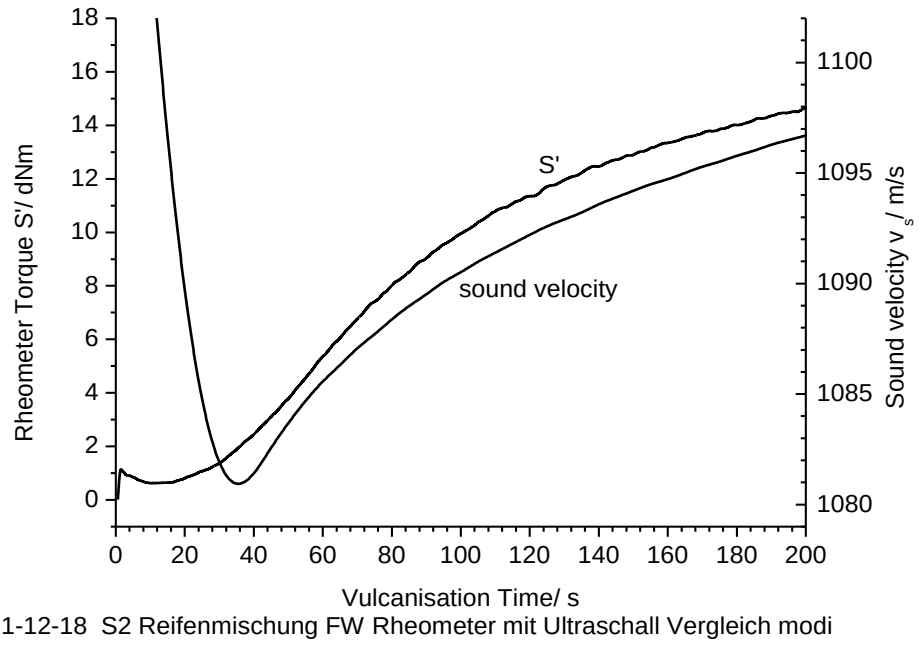

Fig. 7.27: Real part of torque S' from curemeter and sound velocity vs. process time, vulcanisation of a rubber compound at 160 °C, illustration of the begin of reaction in Fig. 7.25

In the starting phase both measurements give good comparable results. The ultrasound data could also be used for determination of a scorch time. The small difference between both methods can be understood by differences in time for warming up of the compound. The curemeter curve in Fig. 7.25 shows a maximum in torque S' and for longer times a reduction. This phenomenon is typical for sulfur cross linked rubber and named reversion. The reason is the thermal degradation of sulfur bonds. Surprisingly reversion is not detected by ultrasound. We assume the cause of this difference is the difference in the amplitude of mechanical excitation. We have found a pronounced influence of the angel of deflection in curemeter – the higher the angle the higher reversion.

Summarizing the rubber tests it can be stated that ultrasound can be used like a curemeter as vulcanisation monitoring system which can be applied in the mould. Beside that it gives direct information on reaction process not being covered by reversion.

Chapter 7: Non-destructive evaluation (NDE) of polymer matrix composites:
Using ultrasound to monitor the curing of composites
in: Non-destructive evaluation (NDE) of polymer matrix composites, Edited by Vistasp M. Karbhari,
Woodhead Publishing Limited, 80 High Street, Sawston, Cambridge, CB22 3HJ, UK

Legends

Fig. 2.1: Epoxy bisphenol A diglycidyl ether and diamine hardener

Fig. 2.2: Illustration of the crosslinked network structure of bisphenol A diglycidyl ether and diamine hardener

Fig. 3.1: Storage and loss modulus and calculated complex viscosity vs. curing time from rheological measurements, isothermal epoxy resin curing at 100 °C, logarithmic y-axis; insert: measuring principle of a rheometer

Fig. 3.2: Storage modulus vs. curing time from rheological measurements, epoxy resin curing, influence of process temperature, logarithmic y-axis

Fig. 3.3: DSC heat flow vs. temperature, epoxy resin, starting from the frozen state to a temperature of full crosslinking; insert: measuring principle of DSC

Fig. 3.4: DMA, storage and loss modulus vs. temperature, sample epoxy resin, heating rate 1 K/min, (E' – logarithmic axis); insert: measuring principle of DMA

Fig. 4.1: Epoxy resin, glass transition temperature vs. degree of curing, DSC

Fig. 4.2: PF-part (Bakelite) taken from the mould in an incomplete state of crosslinking. Such manufacturing defects can easily be avoided by utilisation of online process monitoring.

Fig. 4.3: Incorrect bicycle part, storage and loss modulus vs. temperature, detection of wrong glass transition temperature by DMA

Fig. 4.4: Impact strength vs. process time, parts from UF-moulding compound

Fig. 5.1: Scheme of an ultrasonic measuring arrangement - through transmission

Fig. 5.2: Illustration of the propagation of longitudinal waves (compression waves) between the sensors

Fig. 5.3: Photo of an ultrasonic transmitter (product of GE company)

Fig. 5.4: Technical drawing of an ultrasonic sensor

Fig. 5.5: Typical measuring set up for hidden ultrasonic sensors in the wall of the mould

Fig. 5.6: Output signal for different numbers of excitation pulses. One burst pulse consists of a rectangular pulse having duration time of 125 ns, 3 burst pulses means a group of 3 pulses with alternating polarity each pulse 125 ns (1/250 ns=4 MHz).

Fig. 5.7: Sound velocity, damping and mould temperature vs. process time, curing process for a T-ramp of 1 K/ min up to 180 °C followed by a constant temperature. Illustrated is the strong attenuation during softening (up to 75 dB/mm). The velocity increase at the end of the process is clear information about the crosslinking process.

Fig. 5.8: Opened measuring cell: the arrow depicts on the sensor in the lower part

Fig. 5.9: Schematic drawing of the complete computer controlled measuring system consisting of temperature controlled mould, distance measurement gauge, pulse generation and data acquisition unit.

Fig. 5.10 Main item of the US-plus® system designed for use in the production process. For application it has to be completed with a PC.

Fig. 5.11: Complete laboratory device for the registration of the curing process, based on the computer controlled ultrasound system US-plus®.

Fig. 6.1: Sound velocity vs. process time, compression moulding of phenolic moulding compound for the commercial mixture and a mixture without hardener

Fig. 6.2: Sound velocity, degree of curing and heat deflection temperature vs. process time, compression moulding of phenolic moulding compound

Fig. 6.3: Sound velocity, flexural strength and flexural modulus vs. process time, compression moulding of phenolic moulding compound

Fig. 6.4: Sound velocity vs. process time at different temperatures, epoxy resin (low Tg type) curing

Fig. 6.5: Sound velocity vs. process time at different temperatures, epoxy resin (high Tg type), additional the times for gelation and vitrification from rheology are marked

Fig. 6.6: Sound velocity and thermocouple resin temperature vs. process time at three mould temperatures, unsaturated polyester resin

Fig. 7.1: Belt pulley made from phenolic moulding compound, sensor position is marked

Fig. 7.2: Schematic view, mould for injection compression moulding with incorporated ultrasonic measuring line

Fig. 7.3: Sound velocity vs. process time, injection moulding process of phenolic moulding compound, test of reproducibility

Fig. 7.4: Sound velocity vs. process time, injection moulding process of phenolic moulding compound, influence of switching time from injection pressure to hold pressure

Fig. 7.5: Correlation between sound velocity and belt pulley strength

Fig. 7.6: Head light from BMC produced by injection moulding process, product by automotive lighting, Reutlingen

Fig. 7.7: Compression mould with incorporated ultrasound sensors for incoming goods control, photo: ISK Iserlohn

Fig. 7.8: sound velocity vs. process time, curing behaviour of two BMC materials (material A solid curves, material B dotted curves) at three typical manufacturing temperatures 140, 150 and 160 °C

Fig. 7.9: Schematic view of an RTM mould with partial filling and indicated possible sensor positions

Fig. 7.10: Photograph of the RTM part for lorry cabin produced by Fritzmeier

Fig. 7.11: Upper part of the RTM-mould with signs showing the position of the sensors: 1 in vicinity to the inlet nozzle (arrow), 2, 3, 4 and 5 close to the outlet risers

Fig. 7.12: Insertion of the sensors into the mould from the back side

Fig. 7.13: Sound velocity vs. process time, flow front detection by signal onset at five measuring lines

Fig. 7.14: Sound velocity vs. process time for the complete RTM-Process

Fig. 7.15: CFK- hydrogen cylinders under test in a temperature-controlled high pressure test apparatus in the BAM, photo: BAM Federal Institute for Materials Research and Testing

Fig. 7.16: Mini compression gadget with two heat regulated plates and incorporated ultrasound sensors for process monitoring in laboratory scale

Fig. 7.17: Storage modulus, sound velocity and temperature vs. process time, epoxy prepreg, linear heating and isothermal curing at 110 °C

Fig. 7.18: Sound velocity vs. temperature at linear heating and cooling of prepreg, temperature rate 1 K/min

Fig. 7.19: Storage modulus E' of fully cured epoxy prepreg vs. time, sample from Fig. 7.17, heating rate 1 K/min

Fig. 7.20: Sound velocity of fully cured epoxy resin vs. time, sample from Fig. 7.17 at linear temperature rise, heating rate 1 K/min

Fig. 7.21: Change of sound velocity at linear heating and cooling of prepreg and merge resin, temperature rate 1 K/min

Fig. 7.22: Change of sound velocity by prepreg crosslinking for three temperatures

Fig. 7.23: Reaction rate vs. process time concerning results in Fig. 7.22, prepreg crosslinking for three temperatures

Fig. 7.24: Comparison of the change of sound velocity of glass fiber prepreg material – normalization on the end value

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Fig. 7.26: Real part of torque S' from curemeter and sound velocity vs. process time, vulcanisation of a rubber compound at 160 °C

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