Making cure visible: monitoring the cross-linking process using integrated ultrasound sensors

A special ultrasonic measuring system was developed to monitor the cross-linking process, enabling interaction with the manufacturing process in order to optimise part quality and reduce cycle times.

By Wolfgang Stark, Juergen Bartusch, Joachim Doering, Jarlath McHugh
Federal Institute of Materials Research and Testing (BAM), Berlin

Casting resins such as epoxy or unsaturated polyester resins are essential matrix materials without which reinforcements such as glass or carbon fibres could not impart their special mechanical and physical properties to composite materials. The final outstanding properties of the composite are reached by chemical cross-linking of the reactive resin. Cross-linking is a chemical reaction. The effect of the extent of reaction or degree of cure of such resins quite often goes unnoticed during the processing or manufacturing process as it does not necessarily lead to visual defects. However, an under-cured part may have considerable influence on the mechanical properties of the composite component, particularly if it is exposed to large temperature variations during its working life.

Cross-linking of thermosetting materials

Thermosetting materials have been used for more than a hundred years – for example phenolic resins, known as bakelite. Epoxy and unsaturated polyester resins are becoming increasingly popular for applications in the aerospace, shipbuilding, wind energy and automotive industries, where the combination of lightweight and high-strength composite materials provides many advantages. Rubber vulcanisation is also a typical cross-linking process that has a wide market. The Federal Institute of Materials Research and Testing (BAM) in Berlin has a long history of active involvement with industrial partners on themes such as characterising reactive polymers or improving quality control. There was a voiced need to accurately monitor and control processing of thermosetting materials. Process monitoring has a significant advantage because changes in either material or processing parameters, which are difficult to simulate in the laboratory, can be directly observed and followed during manufacture. Monitoring and recording the cure process for individual components is possible even in multiple-cavity moulds. Based on our experience in non-destructive testing, a special ultra-sound technology was developed for such applications. Ultrasound parameters such as sound velocity and amplitude are sensitive to even small changes in the viscoelastic properties of plastic materials and their characteristic change during cross-linking reactions. This ultrasound technology and a variety of industrial applications are briefly presented below.

Ultrasound measuring technique

The measuring equipment consists in a computer-based electronic device (pulse generator, amplifier) and piezoelectric sensors [1,2]. The measured parameters are sound velocity and damping or attenuation of the acoustic pulses transmitted through the material. Two sensors are used, illustrated in the schematic drawing in Figure 1.

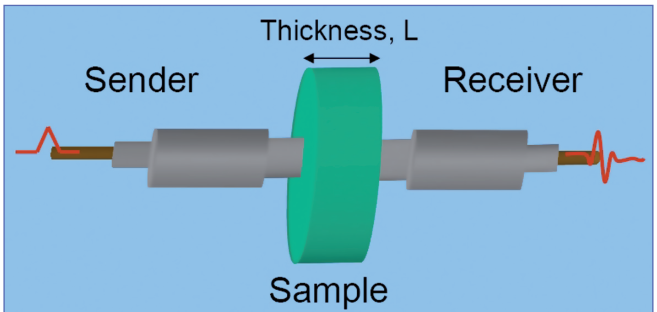

Fig.1: Illustration of ultrasound measurement principle

The through-transmission arrangement proved simpler to handle in industrial conditions than the reflection technique and does not require any special operator training. A photo of a sensor is shown in Figure 2.

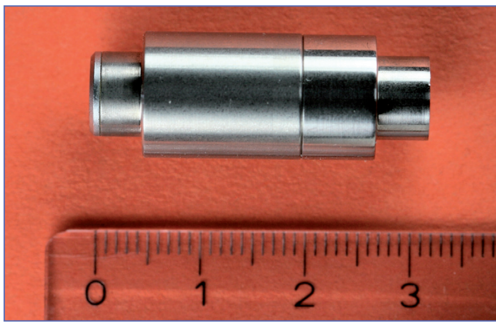

Fig.2: Ultrasound sensor developed for applications up to 180 °C

The sensors operate at an intermediate frequency of 4 MHz and can withstand temperatures up to 180°C. Adaptation of sensors means they can be mounted behind the mould surface using a dry coupling technique and therefore leave no marks on the manufactured parts [3]. A photo of the measuring device is shown in Figure 3.

Fig.3: Ultrasound measuring device US-Plus®, here the model with 8 measurement channels

Qualification of US technique

Research work based on a strong analytical background and a combination of techniques enables accurate interpretation of the results. Some common polymer physical analytical techniques are used to characterise the cross-linking reaction – differential scanning calorimetry (DSC), rheometry and dynamic mechanical analysis (DMA) [4]. Figure 4 illustrates typical cure curves using sound velocity as the measured parameter for an epoxy resin (in this case RTM6 from Hexcel).

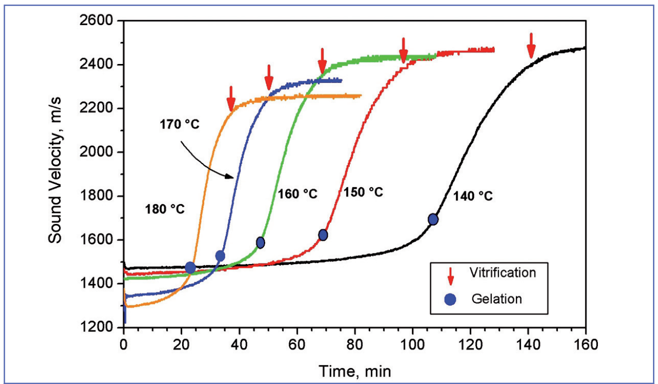

Fig.4: Ultrasound cure curves for RTM6 epoxy resin

The cross-linking process can be easily visualised by a typical increase in sound velocity [5]. Additionally, process times until gelation and vitrification (determined using the aforementioned techniques) are marked on the curves. A good correlation between these characteristic points and the shape of the sound velocity curves was established for this and other resin systems [6].

Implementation of ultrasound cure monitoring into the manufacturing process

At present, the main application of this ultrasound technique is process control in manufacturing processes involving moulding compounds [7]. In cooperation with the IKV Aachen, the ultrasound technique was also successfully tested in a large industrial mould for the production of fibre-reinforced housings (sleeping modules) for lorries manufactured using the resin transfer moulding (RTM) technology [8,9]. The company Fritzmeier mounted five measurement channels using hidden sensors incorporated behind the mould wall. The sensor positions are marked (1 to 5) on the male mould half illustrated in Figure 5.

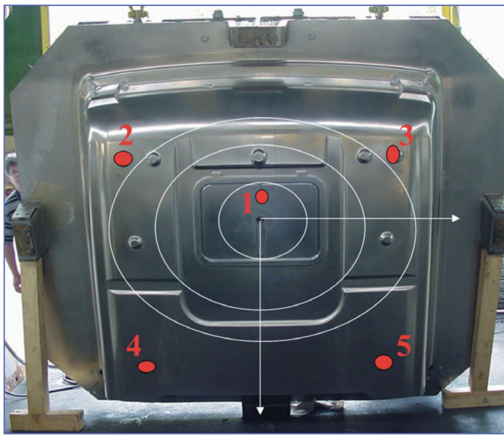

Fig.5: Upper mould half used in the production of lorry sleeping modules from glass fibre composites

Using an arrangement of sensors and a specially developed multiplexer, it is possible to simultaneously monitor the flow front and the progression of cure at each marked position. A typical result showing sound velocity curves for each of the five measuring channels is shown in Figure 6.

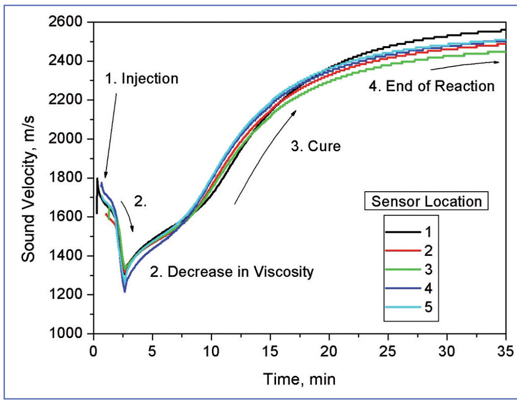

Fig.6: Simultaneous monitoring of cure at 5 different positions in the mould from Fig.5

Mould filling is seen by a gradual appearance and increase in amplitude of the sound signal when the resin has reached the location of the sensors (due to the large 35-minute time scale used on the axis, it is not well resolved in this figure). The decrease in sound velocity indicates that the resin temperature increases until the set mould temperature is reached, resulting in a reduction of viscosity. This process is interrupted by the cross-linking reaction and resin viscosity increases, correlating with an increase in sound velocity. Variations in resin properties (e.g. viscosity or reactivity) as a result of batch quality or variations in process parameters such as mould temperatures will be detected almost immediately and cycle times or parameters may be varied accordingly to optimise component properties. Similar results were obtained for an epoxy resin used in the manufacture of gliders (see Figure 7).

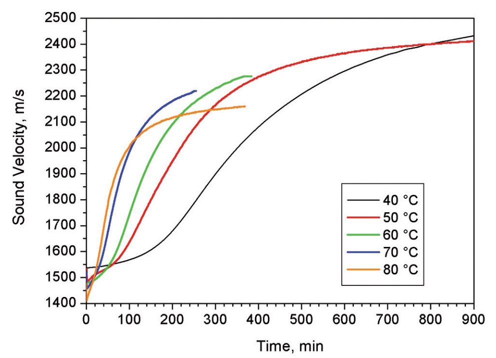

Fig.7: Ultrasound cure curves for epoxy resin employed in the manufacture of glider planes

This resin is processed at much lower curing temperatures than the RTM6 resin system and a lower final glass transition temperature is achieved in the cured state leading to lower absolute sound velocity values (compare Figure 4 and 7).

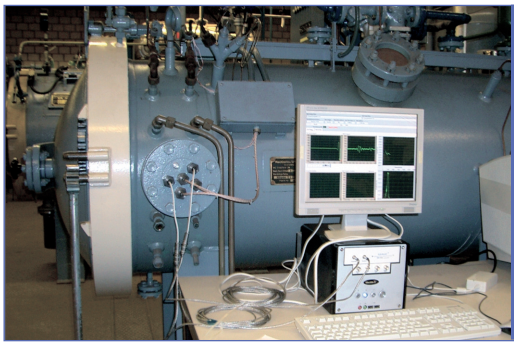

Fig.8: Cure monitoring of composite components in an autoclave (background)

The last figure (Figure 8) shows that the ultrasound equipment can easily be used in industrial environments. In this case, it was combined in a research project involving integration into the autoclave process, where 10-metre long coaxial cables were led into the oven through coaxial plugs in the barrel wall. ■

Contacts: Wolfgang.Stark@bam.de
Joachim.Doering@bam.de

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