Ultrasonic Measurements for Cure Monitoring in Polymeric Material Systems

There is a significant prospective industrial market for real time, on-line cure monitoring in the processing of polymer-based materials; such as composites, adhesives and plastic coatings. Ultrasonics, in particular, has shown potential for application within this field by establishing relationships between changes in the characteristics of propagating ultrasound and the real-time mechanical properties of a component.

This Measurement Note provides an evaluation of the performance of several ultrasonic methods used to assess the stage and state of cure of thermosetting polymers. Particular emphasis is placed on detailing the experimental techniques, requisite equipment, benefits and limitations and the requirements for extending the method into an industrial manufacturing environment.

Four methods were examined: ultrasonic time of flight measurement, both in through-transmission and pulse-echo modes, natural frequency determination using impact excitation and laser-induced surface acoustic wave velocity measurement. The most successful of these for on-line process monitoring were the ultrasonic time of flight techniques. The natural frequency method proved useful for real-time, in-situ measurements but was unlikely to find application in the majority of large scale polymer processing routes.

M J Lodeiro and C Hobbs

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INTRODUCTION

Cure monitoring is a means of tracking the changes in physical state or progress of reaction that occurs during the processing of many polymeric materials.

The “cure” of thermoset polymers is a process that converts a liquid resin mixture into a solid by means of chemical reactions, often activated by heating. As cure progresses, there is a growth in molecular weight and an accompanying increase in viscosity until eventually the system “gels” (no longer able to flow) and finally “vitrifies” (material Tg rises above the cure temperature) [1].

There is a significant prospective industrial market for real time, on-line cure monitoring in the processing of thermosetting polymer-based materials; such as composites, adhesives and coatings.

Acoustics and ultrasonics, in particular, have shown potential for application within this field by establishing relationships between changes in the characteristics of sound waves/vibrations propagating through a component and its real-time mechanical properties. In addition, these methods are non-intrusive, such that the probes required for measurements can be incorporated into mould walls, remaining in intimate contact with the component, but not embedded.

The aim of the study presented here was to evaluate the performance of several ultrasonic methods for their ability to assess the stage and state of cure of thermosetting polymers and investigate their relevance to industrial manufacturing processes.

The monitoring methods investigated include:

- ultrasonic time of flight (through-transmission),
- ultrasonic time of flight (pulse-echo),
- natural frequency determination using impact excitation, and
- surface acoustic wave velocity determination.

Laser-Induced Surface Acoustic Wave Measurements

This method is generally suitable for the non-destructive testing of thin coatings, being sensitive to elastic properties and density. This is especially useful as the properties and behaviour of thin coatings is often different to the bulk material equivalent.

The technique involves firing a short burst of laser light onto the surface to be investigated. This generates rapid localised heating and thermo-elastic expansion which induces broad bandwidth surface acoustic waves.
waves (SAWs) [2].

The vertical displacement of the surface due to the passage of these waves is monitored by a piezoelectric transducer some distance away. This is recorded by a high sample rate oscilloscope and a fast Fourier transform (FFT) analysis is performed on the collected signal. The phase velocity dispersion curve thus produced is then used to calculate the material stiffness. The higher frequency components of the SAWs produced have little penetration depth and are thus more strongly affected by the coating properties.

The equipment used in these trials was an LaWave unit (Alotec, GmbH). The equipment is shown in Figure 1. A two part room temperature curing epoxy was coated onto a substrate. It was expected that there would be no measurable signal until the resin had cured sufficiently to propagate surface waves (i.e. after gelation when it no longer behaves as a fluid).

**Results**

It was found that there was no measurable disturbance of the surface even when the epoxy coating was fully cured. This may be due to a number of causes:

- polymer modulus too low to propagate surface waves, and/or
- polymer attenuation too high to propagate surface waves.

It was also noted that the accuracy of the technique is very sensitive to the coating thickness uniformity which is infrequently tightly controlled in most manufacturing processes. The rise in temperature caused by the pulse of laser energy caused the surface of the coating to char as a result of the low thermal conductivity of the polymer.

**Recommendations**

This method is inherently unsuitable for low modulus polymeric material systems.

**Natural Frequency Measurements**

The principle of this non-destructive method is to induce a vibration in a sample by a mechanical impulse. The vibration is detected by a transducer and the signal produced is analysed [3].

The frequency spectrum of this vibration depends on the resonant frequencies which are affected by:

- elastic properties of material,
- sample geometry,
- material density.

In this investigation, a Resonant Frequency and Damping Analyser (IMCE n.v.) was used to perform the measurements. A typical set-up is shown in Figure 2.
A variety of room temperature curing resins were studied, including:

- 3M Scotch-Weld DP 460 epoxy,
- 3M structural adhesive 5027 epoxy,
- Crystic 196 polyester.

The resins were contained within glass petri dishes supported on taut wires to allow free vibrations. The changes due to cure were monitored using an automated mechanical impulse device impacting the rim of the disc (to induce flexural and torsional modes of vibration), repeatedly sampling the resonant frequencies of the glass/resin assembly at regular intervals.

The resulting vibration was detected by a closely positioned microphone. The captured signal was analysed using FFTs giving reproducible frequency “fingerprints” at each stage of cure for this complex object.

A two part room temperature curing epoxy adhesive (RS) was also investigated (in flexural vibration mode) as a coating on a thick rectangular aluminium substrate and as a bond between two similar aluminium plates.

![Figure 3 - Vibration signal after impact excitation.](image)

**Results**

A typical vibration signal is shown in Figure 3. FFT analysis produces frequency spectra similar to those shown in Figure 4.

The changes in the frequency “fingerprint” as the material viscosity and stiffness changes throughout cure can be seen in Figures 5 and 6.

![Figure 4 - Typical frequency “fingerprints”, in this case from DP460 before and after cure.](image)

These graphs show an initial frequency plateau region correlating to the period during which the resin was liquid, followed by an increase in frequency as the conversion to solid proceeded. This was again followed by a gently upward sloping plateau region once the conversion to solid...
was essentially completed and further cure was limited.

The point at which the frequencies began to increase was observed to coincide with the point of gelation. The levelling off after the rapid increase in natural frequency was similarly observed to coincide with hardening of the polymer.

This same effect was seen with the other resin systems; although less clearly for the viscous, rubber-filled 5027, as shown in Figure 7.

The same trend was again seen for the epoxy coated and bonded substrates shown in Figure 8, with the frequency changing in line with the degree of cure.

Notes

- For certain geometrically shaped cured samples, this method can be used for post-production QA calculation of elastic properties.
- The test can be extended to elevated temperatures by using a waveguide to transmit the vibrations from the material to the receiving transducer.
- Higher frequency components in the “fingerprint” show greater changes due to differences in state or viscosity or stiffness and are more effective for cure monitoring.

Recommendations

The method works well for materials with a distinctive change in stiffness from uncured to cured state, such as was seen for the polyester. The change was less marked for the rubbery polymer 5027 which is very viscous when uncured and remains pliable even when fully cured.

This method is unlikely to be successful in an industrial processing environment due to the requirement for small samples which are freely supported, naturally resonating with relatively high frequencies, well above that of interference from background or environmental noise. Thus it is likely to be most useful for QA type post cure examination or small scale laboratory assessments of industrial processes.

It also requires the material to be contained within or carried on a rigid substrate which rings with a distinctive “fingerprint”, such that changes due to cure could be easily seen.

A modified version of the same method, using low frequency transducers with solid rod waveguides to transmit resonance generating ultrasound directly through to the curing material and receive the amplified natural vibrations from the material, could overcome some of these problems and be more flexible for application at high temperatures and on large scale structures.
Ultrasonic Velocity Measurements

The speed of sound in a material is dependent on its density and modulus. This fact is exploited in the use of ultrasound velocity measurements in cure monitoring applications. Hence, the time of flight can reflect the state of cure directly where thickness and density variations are negligible.

Through-transmission

For the through-transmission technique, two transducers are required, aligned collinearly. An electronic excitation unit produces a voltage spike which triggers a pulse of ultrasound from the transmitting transducer. The pulse travels through the material and is received by the second transducer, as shown in Figure 9.

Figure 9 - Ultrasonic through-transmission set-up, with (inset) typical received signal.

The received signal, which may be amplified, is then captured and displayed on a PC. A distinctive feature of the pulse, e.g. a baseline crossover, is then used to time the passage of the ultrasound from one probe to another. The timings need to be resolved down to approximately 1 ns to ensure the required sensitivity for cure monitoring.

These measurements are repeated at regular intervals during processing to produce a trace directly related to the material properties throughout cure. This procedure can be automated using software control and analysis. Typical signals are shown in Figures 10 and 11.

The availability of robust high temperature ultrasonic transducers and coupling media enables this method to be used for high temperature processes.

Notes

- The system needs to be calibrated for variations in the transducer response with temperature.
- The frequency, power and transducer diameter determine the maximum thickness/attenuation of material which can be investigated.

Recommendations

The inclusion of transducers into tool walls, within a few mm of the material, enables this method to be employed in enclosed processing environments.

The ability of this technique to effectively assess the degree of conversion even within the confines of a mould is well-documented [4, 5], but it may not be suitable for all manufacturing methods e.g. liquid polymer coating lines, open mouldings or for situations where spot measurements on a high speed line are preferred.

Figure 10 - Typical received signal.

Figure 11 - Typical time of flight trace showing changes during elevated temperature cure: I - heating stage, II - curing, III - over - curing.
Pulse-echo

Pulse-echo is based on the same principles of ultrasonic time of flight, but here only a single transducer is used, as shown in Figure 12. A pulse is sent through the material and at the boundary between the material and air or mould wall the pulse is partially reflected due to the acoustic impedance mismatch. This reflected signal is then captured by the same transducer and the transit time determined.

![Figure 12 - Ultrasonic pulse-echo set-up, with (inset) typical received signal showing additional reflected signals from mould walls.](image)

Initial checks were made using a traditional ultrasonic system to check for suitable adaptation to pulse-echo mode operation. A simple trial using a container filled with varying depths of water was conducted. The results are shown in Figure 13. This confirmed the capability of the system to detect and analyse pulse echo signals effectively.

![Figure 13 - Pulse echo transit times for varying water depths.](image)

Subsequently, a sample of DP 460 epoxy was allowed to cure within a container at room temperature, whilst monitored with a single transducer, as shown in Figure 14. The results from this are presented in Figure 15 showing the familiar changes in transit time during cure.

![Figure 14 - Experimental set-up for pulse-echo measurements on DP 460 epoxy.](image)

![Figure 15 - Pulse-echo ultrasonic transit times with degree of conversion for DP 460 resin.](image)

**Recommendations**

Pulse-echo has limited use for very thick or high attenuation material, as the pulse travels through the sample twice and experiences twice the signal loss. It is also limited by complex reflected signal received from multiple interfaces (especially filled polymers such as fibre–reinforced composites) and interference between transmitted and received signals. Some restrictions would exist for thin coatings where the sample signal would be masked by the ringing triggered by the excitation pulse.

However this method is ideal where only one-sided access is available, it is also more sensitive than through-transmission (twice the transit time therefore twice the difference in the measured time of flight) and has lower equipment costs.
CONCLUDING REMARKS

The most suitable method for on-line monitoring is ultrasonic time of flight measurement. In through-transmission mode it is suitable even for enclosed processes and the complementary pulse echo mode extends application to open processes or production lines. The correlation with mechanical properties means the time of flight data can be used as a quantitative guide to state of cure and eventually to the degree of cure of the final product.

References


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For further information contact:

Maria J. Lodeiro
NPL Materials Centre
National Physical Laboratory
Queens Road
Teddington
Middlesex
TW11 0LW
Telephone: 020-8977 3222 (switchboard)
Direct Line: 020-8943 6034
Facsimile: 020-8943 6177
E-mail: maria.lodeiro@npl.co.uk
Website: http://www.npl.co.uk/npl/cmmt/cure/

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