ATTENUATION OF ULTRASOUND BY HOLLOW CERAMIC SPHERES EMBEDDED WITHIN A CURING RESIN

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INTRODUCTION

The basic technology of using embedded acoustic waveguides (AWG) for cure and NDE monitoring of resins and composite materials has evolved[1-11] over the last forty years. A recent paper[11] describes new applications of AWG in which acoustic wave transmissions between two embedded waveguides allows cure monitoring of large areas of a composite panel and also, in principle, the sensing of voids occurring during curing (simulated by burying hollow ceramic spheres within a composite panel). A surprising result was the system sensitivity, as the presence of only 0.16% by volume of hollow ceramic spheres could be detected. This result prompted the more detailed study reported here of ultrasound attenuation by voids (hollow ceramic spheres) embedded within a curing resin.

In this latest work, experiments were performed in which the acoustic properties of a fast (10 to 15 minutes for 50% bond strength) curing epoxy resin were monitored during curing, both with and without embedded hollow ceramic spheres, and also with an embedded AWG, for time periods up to 10^4 minutes (167 hours). Analysis of the experimental results demonstrates that these voids are acoustically lossy within a non-rigid curing structure, but are not lossy after the resin presumably reaches a glassy state.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic of the experimental apparatus, Figure 1, illustrates a pulsed signal generator feeding pulsed ~60 kHz electrical wavetrains to an acoustic transmitter. This acoustic transmitter is glued to a semi-circular section, 1.25 cm I.D. x 3 mm wall thickness, 10 cm long rubber channel which is glued at its termination to a ~60 kHz acoustic receiver, Figure 2. With the transmitter and receiver resting on a felt pad, the rubber channel effectively acoustically isolates the transmitter from the

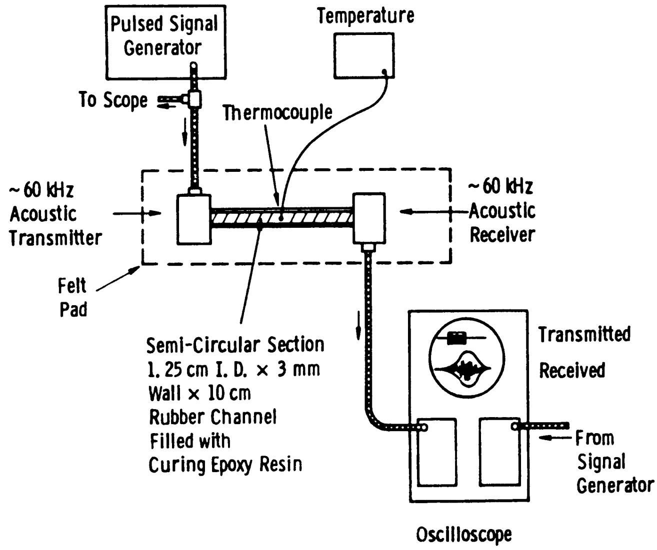
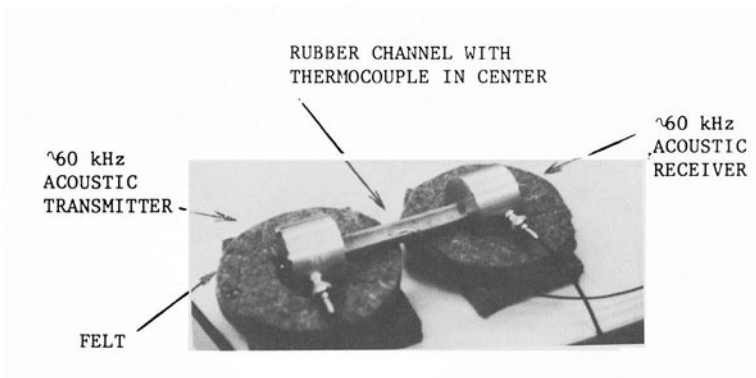
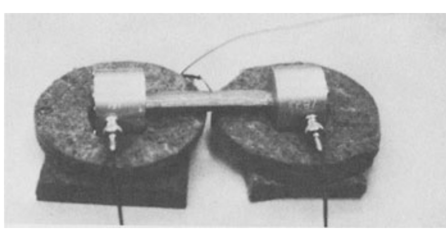


Figure 1. Schematic of experimental apparatus for determining the acoustical properties of curing resin filled with hollow spheres.



EMPTY RUBBER CHANNEL CONNECTED BETWEEN ACOUSTIC TRANSMITTER AND RECEIVER.



RUBBER CHANNEL FILLED WITH CURING RESIN TO FORM ACOUSTIC WAVEGUIDE BETWEEN ACOUSTIC TRANSMITTER AND RECEIVER.

Figure 2. Pictures of acoustic transmitter and receiver with curing resin forming acoustic waveguide between them.

receiver. However, when curing epoxy resin is poured into the rubber channel, the resin gradually forms an acoustic waveguide and consequently, acoustic signals are transmitted to the acoustic receiver where they are converted to electrical signals and oscillographically displayed, Figure 1. Records can then be made versus cure time of the variations in magnitude of the received acoustic signal, and also the acoustic wave transit time from which the acoustic wave velocity within the resin can be calculated. A thermocouple buried within the resin allows the measurement of resin temperature during cure.

The test procedure as described was performed several times with curing epoxy resin alone within the rubber channel for time periods up to $\sim 10^4$ minutes, and also with ~100 (~0.5% of total resin volume) hollow ceramic spheres buried and fairly evenly distributed within the resin.

EXPERIMENTAL RESULTS

In Figure 3, oscilloscope pictures of acoustic signals are shown which are typical of those received after transmission through the curing epoxy resin. The top traces in the pictures show the one volt peak value pulse wavetrain used to activate the acoustic transmitter throughout a complete cure cycle, while the bottom traces illustrate the acoustic signal levels received at various times during cure. Measurement of the time delay of the received acoustic signal yields the acoustic wave transit time along the 10 cm length of curing epoxy waveguide, and the acoustic wave velocity can be calculated using this value. The varying peak values of the received acoustic signal envelope throughout the complete cure cycle are used for curve plotting.

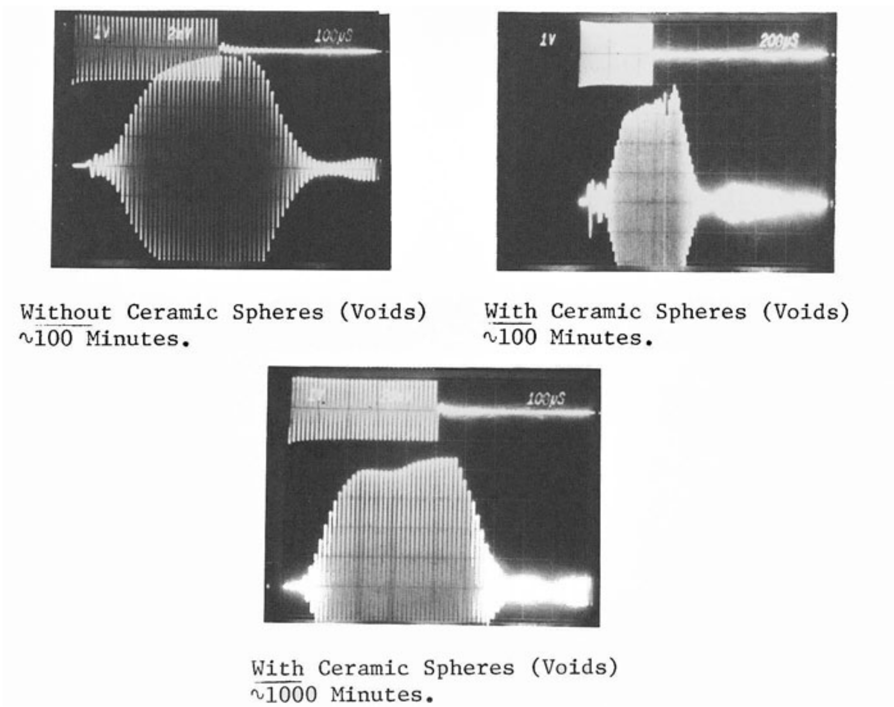


Figure 3. Representative acoustic signals received after transmission through curing resin with and without embedded ceramic spheres (voids).

The results of the first two cure monitoring experiments, one with embedded "voids" within the curing epoxy, and one without, are given in Figure 4. It can be seen that at or near gelation (the transition of the resin from a liquid state to that of a rubbery gel), which occurs about 15 minutes after pouring the resin, acoustic signals can now be measured after transmission through the curing resin which is beginning to form an efficient acoustic waveguide. Over the complete cure cycle, which lasts about 10^4 minutes, the level of the transmitted acoustic signal increases by over two orders of magnitude. Most significant is the difference in the value of the transmitted signal levels for curing epoxy with and without embedded artificial voids (hollow ceramic spheres). Although in both cases at approximately 20 minutes after pouring the resin the transmitted signals are of the same magnitude, throughout most of the cure cycle the resin with embedded voids exhibits up to an order of magnitude less signal transmission. Although at the end of cure, ~10^4 minutes, the signal transmitted reaches a similar value to that of the "non-void" resin. Also plotted in Figure 4 is the resin internal temperature versus time. It is interesting to note that the temperature peaks at close to 80°C about 4 minutes after pouring the resin and returns to around 20°C soon after gelation. As might be expected, due to the hollow ceramic spheres absorbing heat, the temperature of the resin with embedded spheres peaks earlier (at 3 minutes instead of 4 minutes) and at a lower temperature, 70°C, instead of 80°C.

As the first two experiments were performed with different acoustic transmitters and receivers, and at different frequencies, 61 kHz without voids and 74.5 kHz with voids, for improved accuracy it was decided to repeat the experiment using the same transmitter and receiver for both tests and the same transmitting frequency. The results, Figure 5, both at 60 kHz, are similar to the previous ones, except the difference in transmitted signal between no voids, and voids, is only 2 to 1, rather than 10 to 1. Unfortunately, for various reasons these tests could not be continued for 10^4 minutes and were not extended beyond 10^3 minutes, so the experiments were repeated once more.

The results of the third experimental series, Figure 6, clearly confirm the difference between the levels of acoustic waves transmitted within curing epoxy resin with and without embedded voids (hollow ceramic spheres). The presence of 0.5% by volume of embedded voids within this curing resin specimen reduces the transmitted acoustic signal by an order of magnitude over most of the cure cycle, except when approaching the end of cure at 3 x 10^3 to 10^4 minutes. At this stage the transmitted signal is close to that measured for the resin specimen without voids. One difference for this test series was the measured epoxy maximum temperature of 60°C rather than 80°C, which may have been a result of too long of a mixing time before pouring the resin. Another difference is seen near the end of the tests, where the specimen with voids exhibits higher readings than the void free specimen. This is interesting, but there is not sufficient data for any conclusions to be drawn.

In order to gather more information about this epoxy resin, another experiment was performed without embedded voids, but with a 0.5 mm diameter Nichrome acoustic waveguide embedded within the curing resin and bonded to both the transmitter and receiver, Figure 7. The major difference between this experiment and the previous ones is that at the start of the experiment, a very large value acoustic signal is

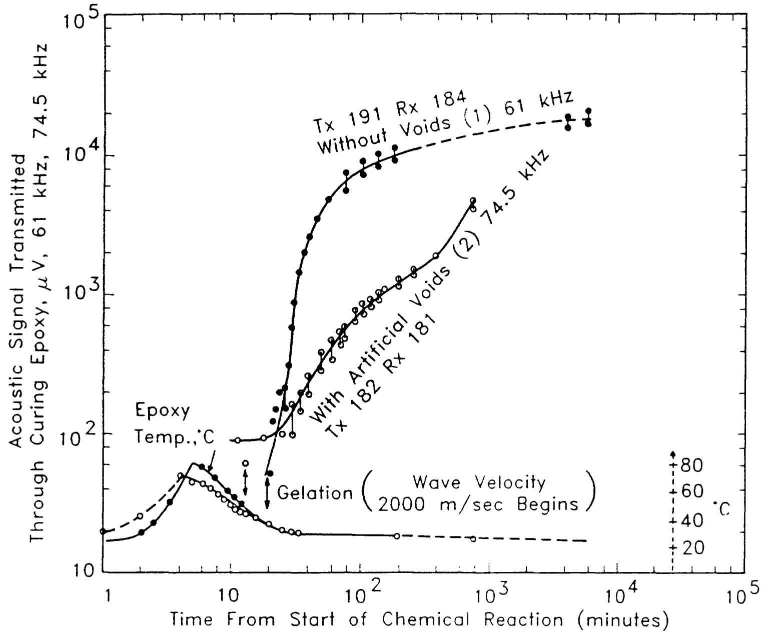


Figure 4. Changes in the acoustic signals transmitted through curing epoxy with and without artificial voids.

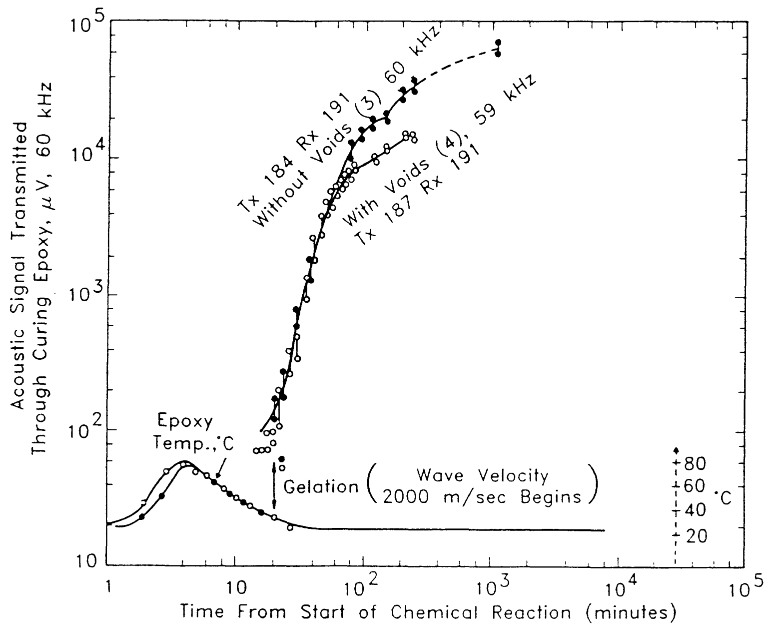


Figure 5. Changes in acoustic signals transmitted through curing epoxy with and without artificial voids.

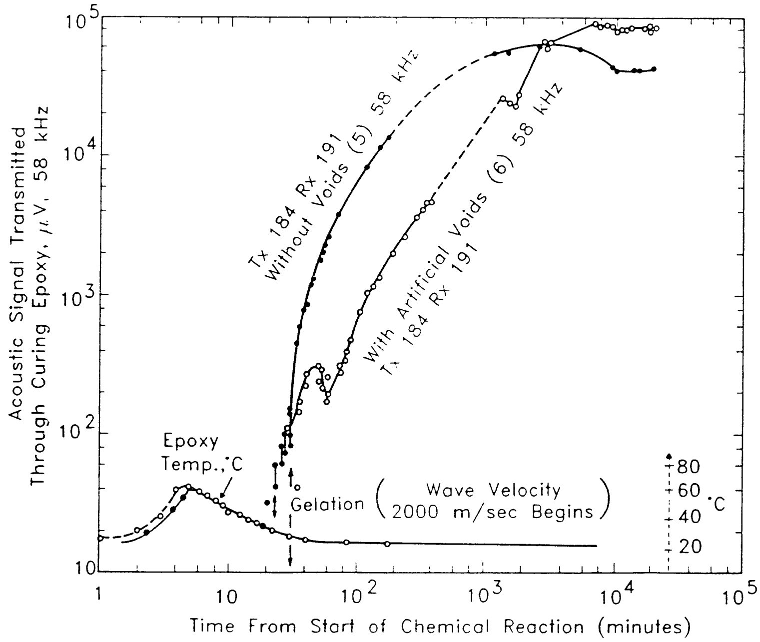


Figure 6. Changes in the acoustic signals transmitted through curing epoxy with and without artificial voids.

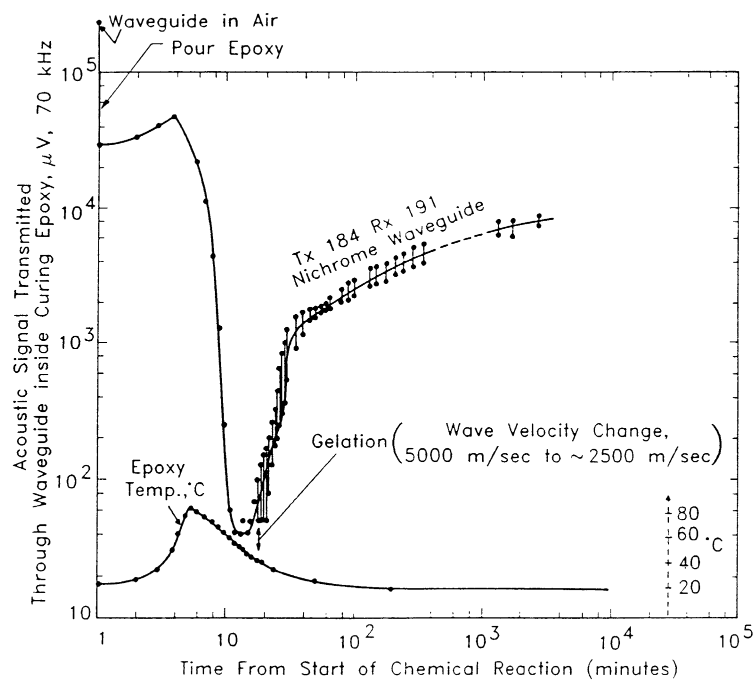


Figure 7. Changes in acoustic signals transmitted through Nichrome waveguide inside curing epoxy.

transmitted via the Nichrome waveguide. As the resin is poured the transmitted acoustic signal reduces rapidly to reach a minimum at gelation, and thereafter increases toward a maximum at the end of cure near 10^4 minutes. In contrast, the previous experiments without an embedded waveguide did not exhibit acoustic wave transmission until after gelation when the curing resin formed an acoustic waveguide.

Dynamic Mechanical Analysis (DMA) and loss tangent measurements were also carried out on resin samples, and these confirmed that resin curing is still occurring ~10^4 minutes after mixing of the resin.

DISCUSSION

Analysis of the experimental results reveals important features of the curing process in the fast cure epoxy resin, and also gives an insight into the acoustic wave losses associated with hollow ceramic voids embedded within the resin during cure. Although the resin should reach 50% of its bond strength after only 10 to 15 minutes, the measurements performed with the resin acting as an acoustic waveguide indicate that up to 10^4 minutes are actually required for complete cure. As can be seen in Figures 4 through 7 the transmitted acoustic signal increases rapidly after gelation (about 20 minutes after pouring the resin) and still increases at a substantial rate up to 10^3 minutes, and finally is of constant value at ~10^4 minutes. This means that during this long time period the resin is becoming more solid and molecular bonding is still continuing and the resin is becoming a more efficient acoustic waveguide. It is assumed that after ~10^4 minutes when no further change occurs in the level of the transmitted acoustic signal, the resin is completely solid and has reached a glassy state. It should be noted that the acoustic wave velocity of ~2000 m/sec in the resin as measured just after gelation (the change from a liquid to a rubbery gel) does not change throughout the cure cycle, although the transmitted acoustic signal increases by over two orders of magnitude.

The experiments with hollow ceramic spheres embedded within the curing resin clearly demonstrate that when a resin is not solid, large (20 dB or 10 to 1) ultrasonic frequency losses are caused by small (0.5% by resin volume) quantities of the spheres (artificial voids). After final cure, or complete bonding of all the resin molecules, or when a glassy rate is reached, the artificial voids no longer cause losses in ultrasonic frequency tranmission within the resin. This is presumably because the hollow ceramic spheres are only free to vibrate and introduce losses when the resin is not completely solid.

The results of the experiments reported here also help to explain the characteristics of acoustic waveguide cure monitoring as observed by us previously.[4-10] Initially, when the resin surrounding the waveguide is in a liquid state all of the acoustic wave transmission occurs within the Nichrome waveguide at a velocity of ~5000 m/sec. As a first order chemical reaction proceeds within the resin, the waveguide transmitted signal falls rapidly because of the increasing viscosity of the resin which results in a change in acoustic impedance (resin density x acoustic wave velocity in the resin). This change in the resin acoustic impedance causes the rapid attenuation of signals within the waveguide due to an improving acoustic impedance match with the Nichrome waveguide. When the waveguide transmitted signal reaches a minimum value, gelation, or a change from a liquid to a rubbery gel, occurs within the resin. This can also be identified by a sudden change in acoustic wave velocity, from 5000 m/sec to ~2500 m/sec. As can be noted from the experimental results reported here, the actual acoustic wave velocity in curing epoxy is 2000 m/sec, so it is likely that the measured value of 2500 m/sec is due to a transmission condition in which most of the acoustic wave is travelling within the curing resin close to the waveguide surface. After gelation, the transmitted acoustic signal increases in value as the resin hardens and cures and forms into a glassy state.

CONCLUSIONS

It has been clearly demonstrated that for a fast (10 to 15 minutes for 50% bond strength) curing epoxy resin, molecular bonding or curing, actually continues for up to 10^4 minutes (167 hours) after mixing the resin (start of the chemical reaction).

The presence of 0.5% by total resin volume of hollow ceramic spheres within a curing epoxy resin can reduce the transmission of 60 kHz ultrasound within the resin by an order of magnitude during curing. However, by the end of the curing process, the hollow ceramic spheres do not cause any loss in ultrasound transmission. This demonstrates that "voids" within a non-rigid curing resin structure are acoustically lossy as they are free to vibrate, but are not lossy after complete solidification or the change of the resin to a glassy state.

REFERENCES

1. G. A. Sofer and E. A. Hauser, Journal of Polymer Science, Vol. 8, No. 6, pp. 611-620 (1952).
2. W. Roth and S. R. Rich, Journal of Applied Physics, Vol. 24, No. 7, pp. 940-950 (1953).
3. E. P. Papadakis, Journal of Applied Physics, Vol. 45, No. 3, pp. 1218-1222 (1974).
4. R. T. Harrold, U.S. Patent No. 4,590,803, May 27, 1986, "Acoustic Waveguide Monitoring".
5. R. T. Harrold and Z. N. Sanjana, Polym. Eng. & Sci. 26, 5 (1986).
6. R. T. Harrold and Z. N. Sanjana, Proc. 31st Intn'l. SAMPE Symp., p. 1313 (1986).
7. R. T. Harrold and Z. N. Sanjana, Proc. 1986 Intn'l. Congress on Technology and Technology Exchange, Pgh., PA, October 6-8, 1986, Paper AM-2-3.
8. R. T. Harrold and Z. N. Sanjana, "Review of Progress in Quantitative Non-Destructive Evaluation", Vol. 6B, pp. 1277-1285 (1987).
9. R. T. Harrold and Z. N. Sanjana, "Review of Progress in Quantitative Non-Destructive Evaluation", Vol. 7B, pp. 1549-1553 (1988).
10. R. T. Harrold and Z. N. Sanjana, Int. Soc. for Optical Eng. (SPIE) Symposium, Boston, MA, Sept. 1989.
11. R. T. Harrold and Z. N. Sanjana, "Review of Progress in Quantitative Non-Destructive Evaluation", Vol. 10B, pp. 1267-1272 (1990).