ACOUSTO-ULTRASONIC MONITORING OF GLUELINE CURING

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ABSTRACT

Hard maple electrodes were bonded with three types of epoxies in a lap joint and acousto-ultrasonic transmission monitored during curing. The electrodes, 3.2 × 25 × 115 mm, were lapped for a 25- × 25-mm bond area. Standard acoustic emission sensors, 175 kHz transmitter and 75 kHz receiver, were used to provide an RMS voltage output, which increased as the adhesive cured. The transmission increase was quantified using a halftime to cure. The increase in transmission is comparable to the predicted increase in longitudinal modulus. Increasing glueline thickness from 0.05 to 0.5 mm caused an increase in apparent cure time as measured by the halftime. By controlling glueline temperature, an activation energy was determined from the halftime to cure.

Keywords: Acousto-ultrasonics, ultrasonics, glueline curing, epoxy, glueline thickness.

INTRODUCTION

In a review paper on adhesion to wood substrates, Wellons (1977) proposed two frontier areas: analysis of chemical composition of wood surfaces and a nondestructive technique to monitor the development of an adhesive bond in place. The needed chemical instrumentation and techniques have advanced rapidly since this review, but little has been accomplished in the latter area. Bolton and Humphrey (1977) have discussed the difficulty in direct assessment of bond curing and bond strength for wood-based composites. In general, there appears to be no means of simultaneously measuring adhesive curing and adhesive strength. An overall objective of this study is to attempt to develop such capability.

Lindrose (1978) conducted an ultrasonic analysis of epoxy curing that typifies subsequent work. He used a pulse/echo technique with a 1 MHz system and measured wave attenuation and velocity. Figure 1 shows the longitudinal wave results. The shear wave curves were similar to those of the longitudinal, except for the absence of transmission prior to the gel point (about 25 h). Note that attenuation is very sensitive to the gelling of the resin, whereas the velocity changed smoothly through the entire curing. Yew (1984) was the first to report monitoring of glueline curing using ultrasonic techniques. He passed horizontal shear (SH) waves through an aluminum plate that was bonded with epoxy resin to an aluminum block. The second mode SH wave showed a steady decrease in amplitude, disappearing at final cure.

Vary and Bowles (1979) have shown that ultrasonic transmission with resonant sensors, "acousto-ultrasonics" (AU), is very sensitive to the quality of material in which the energy is dissipated. AU is a combination of ultrasonic and acoustic emission (AE) technologies, in that the system is actively pulsed (as in ultrasonics) and AE resonant sensors are used for signal generation. The AE sensors provide a very sensitive response to changes in the transmitted pulse. Two approaches to AU are ultrasonic transmission and stress-wave factor (SWF). Ultrasonic transmission involves amplification and detection of the sensor signal, providing an

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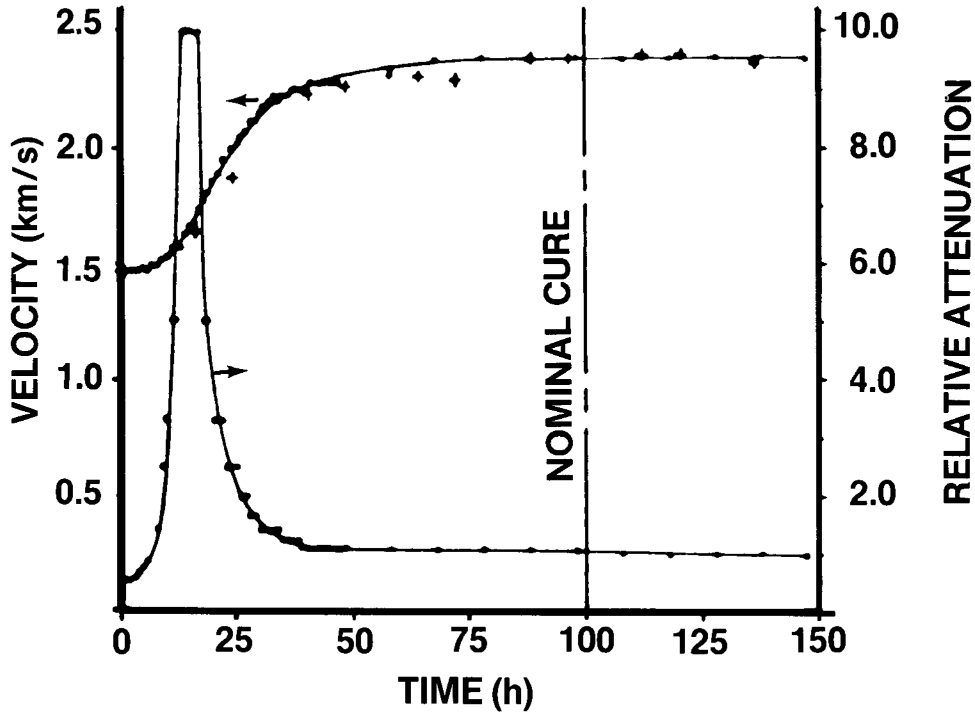

FIG. 1. Longitudinal wave velocity and attenuation for room temperature curing epoxy (after Lindrose 1978).

RMS output. Stress-wave factor uses AE signal processing technology to count threshold crossings of the sensor signal. An application of ultrasonic transmission monitoring of curing of fiber-reinforced composites has been reported by Hinrichs and Thuen (1984). They have shown that AU transmission is proportional to the dynamic viscosity in the final curing of fiber-reinforced composites. Since viscosity is the key material variable, AU transmission is used to control pressure and temperature of an autoclave to optimize the cure.

Preliminary studies using standard AU equipment had shown that ultrasonic transmission correlated with the apparent curing of gluelines for various types of adhesives and produced curves very similar to those of Lindrose (1978) for wave velocity. The present study was designed to improve the ultrasonic technique and extend the variables to ultimately simulate commercial practices. This paper reports the ultrasonic technique and some preliminary data from curing of several types of commercially-available epoxies.

The long-term objectives of this study are:

1. Select the appropriate ultrasonic technique to monitor glueline curing.
2. Measure the ultrasonic attenuation characteristics of representative gluelines during curing.
3. Clarify effects of wood species, surface condition, moisture content, adhesive spread conditions, and process variables on ultrasonic attenuation.
4. Determine the relationship of glueline strength to ultrasonic attenuation during the curing process.

The specific objectives of the work reported in this paper were: (1) to find a suitable configuration for reproducible results, and (2) develop a quantitative measure of cure time. Epoxy adhesives were used because of their "ideal" nature in curing at room temperature, curing without evolution of volatiles, and ease of preparation.

MATERIALS AND EQUIPMENT

Resins

Three epoxies were used for different portions of the study, with the following characteristics reported by the manufacturer. A 5-min epoxy (Devcon S208) had a 5-min set time, could be handled in 15 min, and developed full strength in 1 h (all at room temperature). Devcon S31 had a 30-min set time, could be handled in 2 h, and developed full strength in 8 h. Reichhold 37-140 resin and 95-445 hardener (60/40 mix) cures in 24 h at 25 C, followed by 2 h at 100 C.

Adherends

The configuration selected for monitoring glueline curing is shown in Fig. 2. The lapped specimens are 3.2 × 25 × 115 mm, with a lap length of 25 mm,

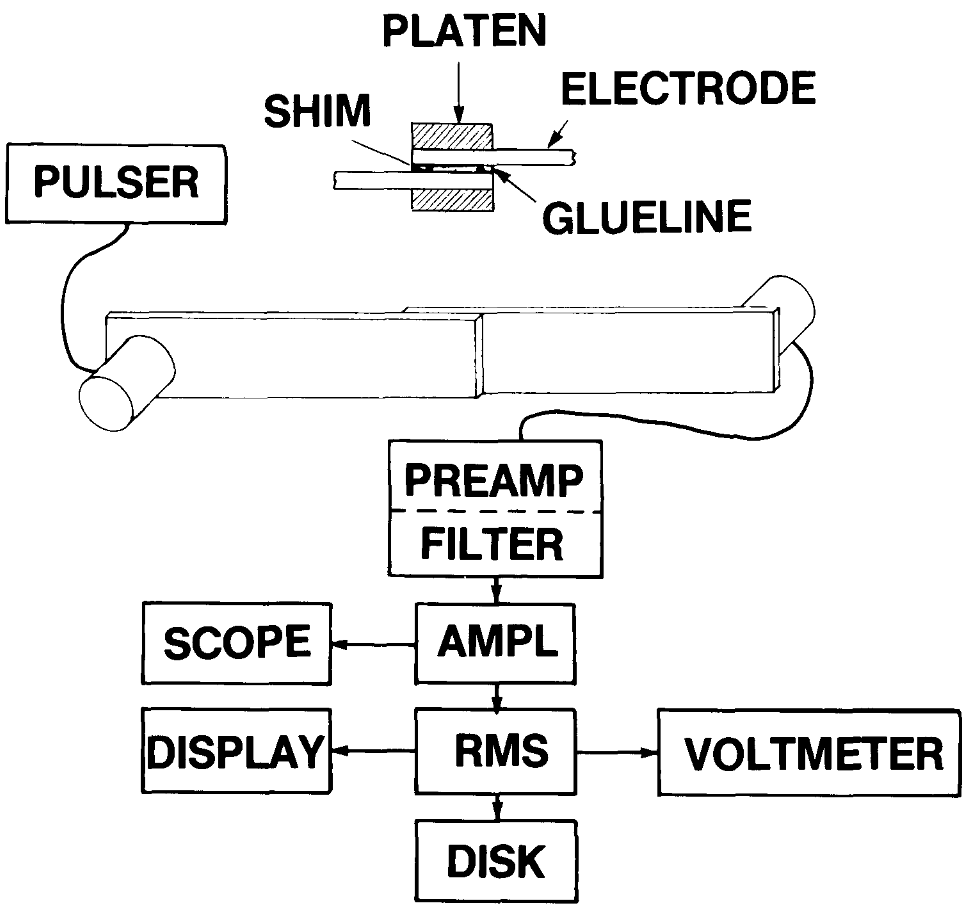

FIG. 2. Specimen configuration and block diagram of acousto-ultrasonics system.

corresponding to BS 1204, synthetic resin adhesives (phenolic and aminoplastic) for wood. This bonding arrangement was selected primarily because of the ease of ultrasonic monitoring, since each lap-half functions as an ultrasonic electrode and waveguide. Also, the glueline is easily prepared and clamped. The electrodes were hard maple (*Acer saccharum* Marsh.) with flat-grain faces and grain angle along the length. The side in contact with the glueline had been planed. The electrodes had been stored under 10% EMC conditions.

Bonding fixture

The fixture was designed to properly orient the electrodes and maintain the 25-mm lap length. The system includes 25- × 25-mm aluminum platens, heated by an inserted element, and thermocouples to monitor temperature for the control units. Pressure control was maintained using constant-force clamps. Transducers were bonded to electrodes with a low temperature hot-melt adhesive, using a separate bonding fixture to obtain consistent sensor positioning. For these experiments, the hot melt coupling gave more consistent results than a typical grease couplant.

Acousto-ultrasonic (AU) system

The AU system consisted of a Metrotek pulser operating at 700 Hz repetition rate, delivering a single pulse of very short rise time and width, and about 30 volt peak-to-peak amplitude to the piezoelectric transmitter. The crystal resonates with a peak at 175 kHz, but actually provides a rather broad-band output. Ultrasonic energy moves through the waveguide, glueline, and receiving waveguide to a 75 kHz sensor. The lower frequency receiver "detunes" the system, improving the range of linear signal output. Output of the receiver was filtered (45 to 90 kHz), amplified, and a pseudo-RMS voltage generated from the envelope of the output. Both the amplifier and RMS outputs can be monitored during curing.

PROCEDURE

In a typical test, sensors were bonded to the waveguides, wire shims were attached to the lap area, adhesive was added, and the lap was clamped. The system gain was typically 200× (preamplifier, 100×; amplifier, 2×). The amplifier output was monitored with an oscilloscope to assure run-to-run consistency in pulse shape. The RMS output was displayed in real time to obtain the change in ultrasonic transmission; at the end of the run, this display was dumped to a printer. Repetition rate and system gain were selected to provide the highest gain without pulse interaction and amplifier saturation, respectively. The 175 kHz frequency was the highest of the commercial series (next highest is 375 kHz) that provided a reasonable output. At 375 kHz, material attenuation of the waveguides substantially reduced the system sensitivity. Major tests were made on the effect of glueline thickness on cure time and measurement of activation energy.

RESULTS AND DISCUSSION

Transmission curve

Figure 3 shows a typical glueline "curing" curve for the 5-min epoxy, having the lapped area lightly clamped with an 18-N (4-lbf) spring. The minimum value at time 0 corresponds to the level of energy that would be coupled through the

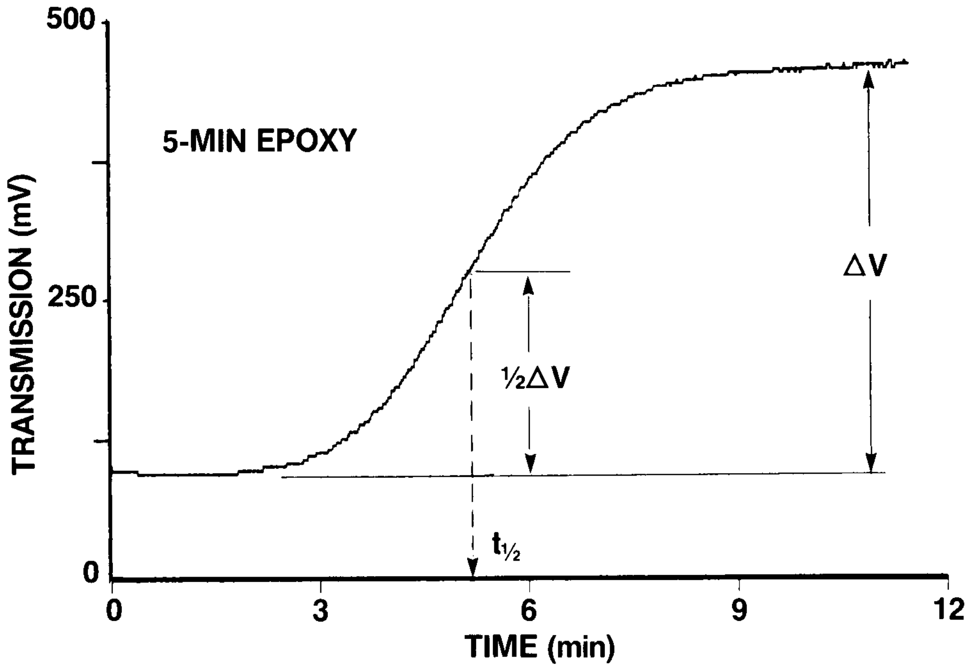

FIG. 3. Typical printed output of transmission during glueline curing of 5-min epoxy (Devcon S208). Halftime corresponds to manufacturer's "cure time."

lapped area if it were simply in intimate contact without adhesive. At this point the adhesive is acting as a typical acoustic emission couplant. The increase in transmission with time reflects the increase in bonding from polymerization of the epoxy. The curves were reduced to singular values by calculating a halftime as shown in the figure. The use of the halftime technique minimized the error in ending the run before complete curing. Alternatively, a time constant (TC) could be found (1 TC = 0.632 of the change; 1 TC = 1.26* halftime). As discussed earlier, the transmission curve in Fig. 3 is remarkably similar to the velocity curve of Lindrose (1978); however, the increase in velocity in his epoxy was only about 50%. Since elastic moduli are dependent on velocities through a material, it appeared reasonable to consider the relationship of ultrasonic transmission to the apparent moduli. The longitudinal wave in a three-dimensional solid has bulk and shear components of moduli (Cracknell 1980):

$$F = K + \frac{4}{3}G \tag{1}$$

where F = longitudinal modulus, K = bulk modulus, G = shear modulus.

For linear, homogeneous, isotropic elastic solids, K and G can be described in terms of velocities:

$$K = \rho\left(c_L^2 - \frac{4}{3}c_s^2\right) \tag{2}$$

$$G = \rho c_s^2 \tag{3}$$

where ρ = density, c_L = longitudinal velocity, c_s = shear velocity.

Lindrose (1978) applied Eq. 1 to curing of a room temperature epoxy. He also demonstrated that the linear relationship between K and G in Eqs. 2 and 3 was consistent with the experimental data:

$$K = a + bG \tag{4}$$

By defining a normalized reaction parameter, R(t), equal to 0 at time = 0 and 1 at time = ∞, he expressed each modulus in terms of R(t):

$$K(t) = a + hR(t) \tag{5}$$

$$G(t) = mR(t) \tag{6}$$

Giving

$$F(t) = a + pR(t) \tag{7}$$

Substituting for the constants and using a reasonable function for R(t) that accounts for the delay in moduli development,

$$R(t) = 1 - \exp\left[-k\left(t - \frac{1}{\gamma}(1 - \exp(-\gamma t))\right)\right] \tag{8}$$

where k and γ are arbitrary constants obtained through curve fitting.

Figure 4 shows the relationship of each apparent modulus with time for the epoxy curing. G(t), as expected, is initially at zero. K(t) increases about a factor of 0.8, whereas F(t) increases by 2.6. Typical changes in the ultrasonic transmission for 5-min epoxy were about 3 to 4, giving a reasonable fit to the F(t) curve.

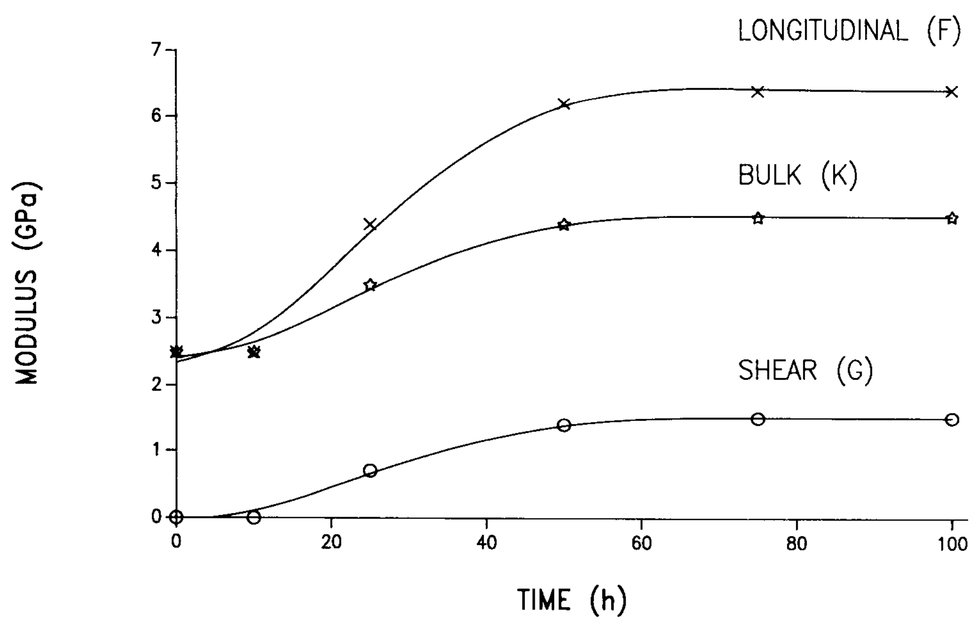

FIG. 4. Apparent moduli calculated from Eqs. 5, 6, and 7 for epoxy curing (after Lindrose 1978).

Output waveform

Figure 5 is a photograph of the amplifier output displayed on the oscilloscope during a typical run. This waveform is a mixed mode type, containing a leading longitudinal wave followed by a shear wave. Shear wave velocities are typically one-half of those of longitudinal waves. During runs, the waveshape changed little in form, indicating that the glueline did not affect the nature of the transmitted wave. Although the wave injected from the transmitting transducer is in the longitudinal mode, reflections from the boundaries of the electrode cause immediate mode conversion. However, the difference in acoustic impedance between wood and air causes the energy to be almost totally contained within the electrode, making it act as a waveguide to the glueline. The initial delay (about 40 μsec) to the leading edge of the wave is from the transit time in the wood electrodes. From the sensor spacing, this time corresponds to about 4 km/sec, consistent with that reported for wood parallel to the grain (Jung 1979). If a 175 kHz receiving transducer had been used, the pulse shape would have been exponentially decaying, greatly limiting the operating range.

Glueline thickness

Initial studies showed substantial variability in halftimes, despite careful control of sequence of events. In order to control the resin spread, pairs of copper wire

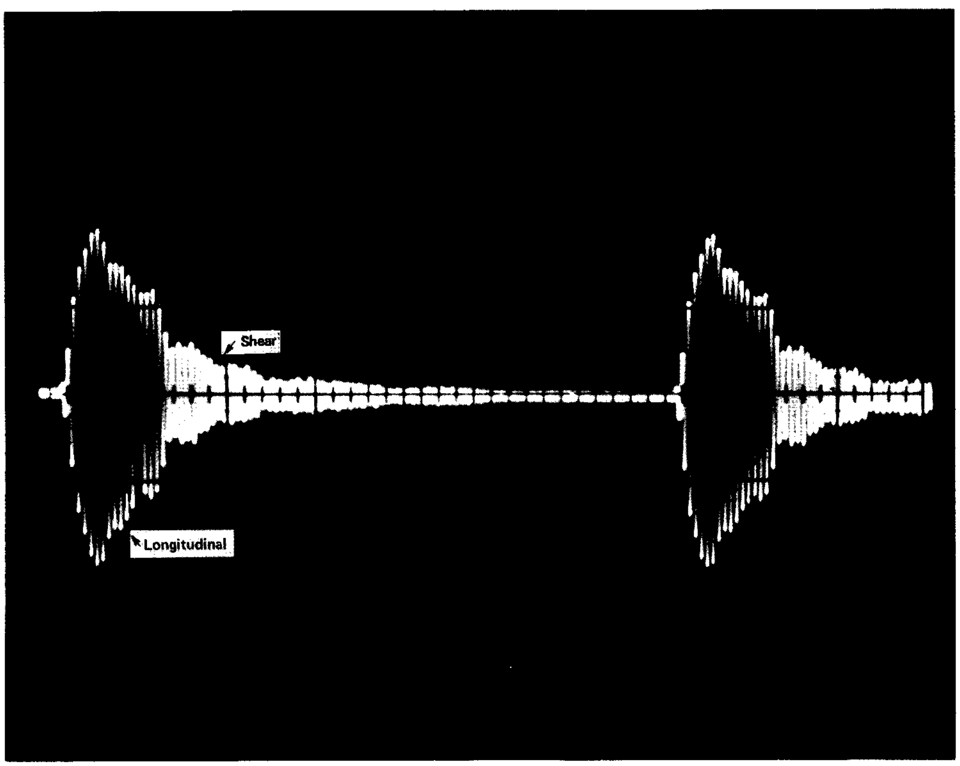

FIG. 5. Output waveform from amplifier for cured glueline. Oscilloscope sweep is 2,000 μsec. Repetition rate of pulses is 700 Hz. Vertical scale is 2 V/cm.

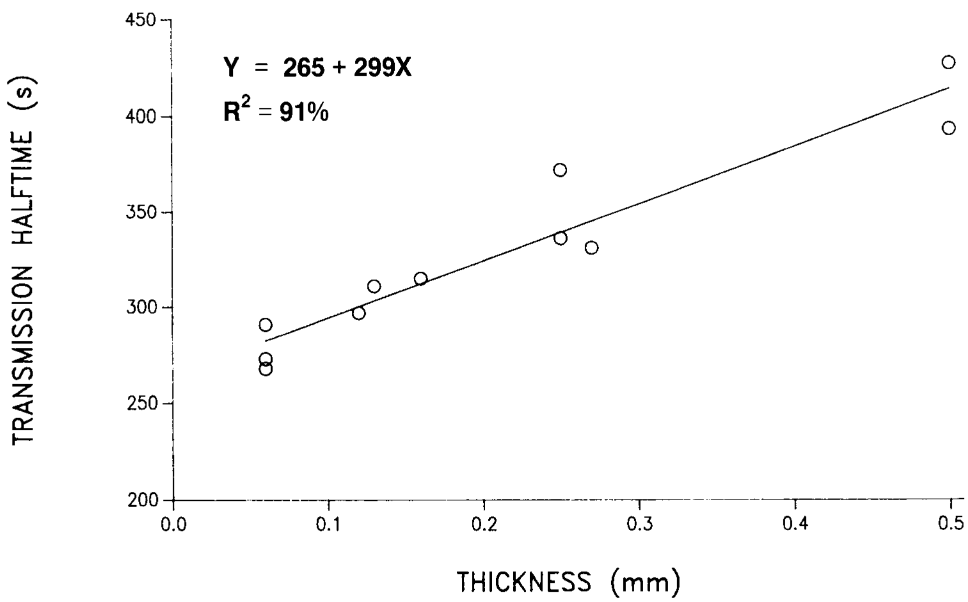

FIG. 6. Halftime of transmission vs. glueline thickness for 5-min epoxy (Devcon S208).

shims were placed on one electrode before the addition of adhesive. A series of tests were run with shims from 0.05 to 0.5 mm diam. to determine if glueline thickness affected transmission. Figure 6 shows the results of transmission vs. average thickness (measured microscopically at 12 points). Three additional tests were performed on 0.125-mm gluelines with the pulser operating with a 15% duty cycle (10 sec on; 60 sec off), which verified that the ultrasonic energy had no detectable effect on curing. Because of the variation of apparent cure time with glueline thickness, all further tests were run with 0.125-mm shims, the most consistent in halftime. Similar results were obtained with the 30-min epoxy, with a range of halftimes from about 20 to 40 min. The use of shims for controlling glueline thickness was necessary since the flow of resin under constant pressure caused nonreproducible changes in transmission during all stages of curing and precluded a meaningful analysis of the "curing" curve. At this point, the reason for the change in curing with glueline thickness is uncertain and tests are underway to clarify the effect. The possible effect of shims on transmission was discounted by testing with four shims vs. the standard two.

Material attenuation

The geometry of the electrodes and area of the lap were expected to have an effect on attenuation through the glueline. Several tests were run with increases in electrode width and thickness. In each case, attenuation increased because of the increase in volume of the electrodes, irrespective of changes in the glueline area. A further test was run by creating a 50-mm-long lap, which was cured and then removed in 10-mm increments to reduce the length of the lap. The resulting transmission curve vs. lap length (Fig. 7) shows that two offsetting factors affected transmission: an increase from increased lap length followed by a decrease caused

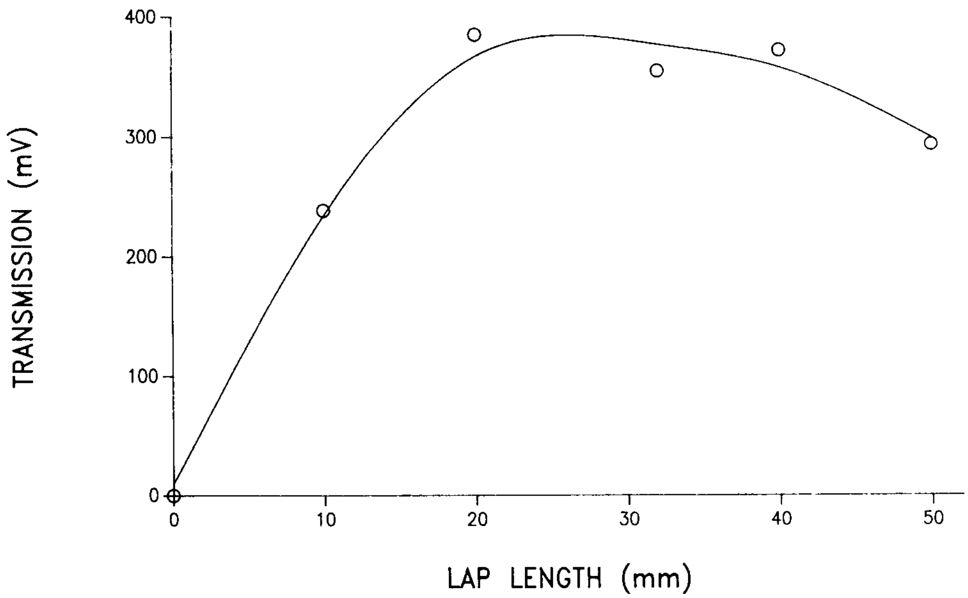

FIG. 7. Ultrasonic transmission vs. lap length for 5-min epoxy (Devcon S208). Initial length was 50 mm, which was reduced in nominal 10-mm increments.

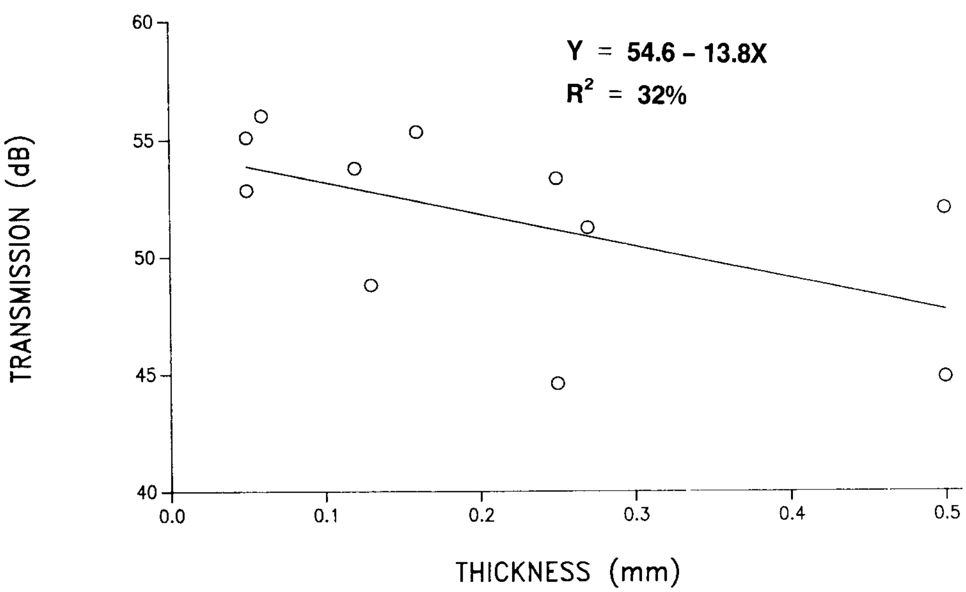

FIG. 8. Final transmission value (see Fig. 3) vs. average glueline thickness for 5-min epoxy (Devcon S208).

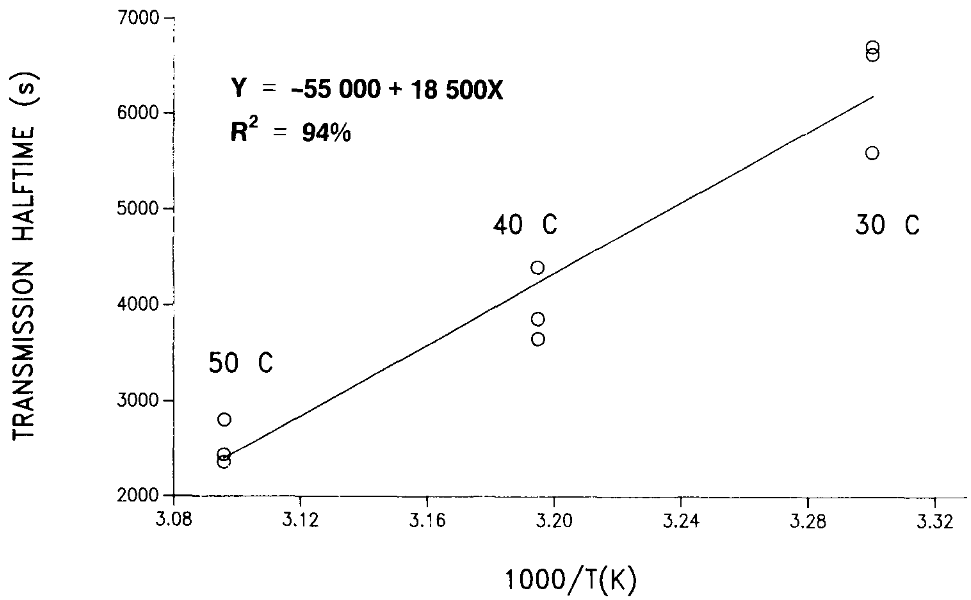

FIG. 9. Halftime of transmission vs. reciprocal of absolute temperature for Reichhold epoxy (37-140 resin; 95-445 hardener; 60/40 mix).

by material attenuation of the waveguide. The insensitivity in the range of 25 mm indicated that small errors in lap length should not affect the magnitude of transmission. Attenuation of the glueline itself was determined from obtaining the final transmission value and plotting against glueline thickness (Fig. 8). Although there is considerable scatter, this relationship is typical for attenuation of ultrasound in materials.

Activation energy

Figure 9 shows the halftime to cure for Reichhold epoxy, with the gluelines maintained at the indicated temperatures. Glueline thickness was maintained at a constant value using the 0.125-mm shims. Preliminary runs had provided the temperature drop across the maple electrodes, permitting an adjustment to reach the indicated temperature within ±1 C. The time constant for the temperature change was measured as about 60 sec, about 1% of the halftime for 30 C, and therefore was considered insignificant compared with run-to-run variability in halftime. For the more rapidly curing epoxies, the heat-up time would have been significant. If first-order kinetics is assumed, then an activation energy of 8.9 kcal/mol is obtained. Above 50 C, halftimes were inconsistent; however, this is substantially above the recommended range for initial curing.

CONCLUSIONS

The preliminary portion of this study provided several specific findings:

1. Curing of an epoxy glueline can be monitored by acousto-ultrasonic transmission, which appears related to longitudinal modulus. The halftime (or time constant) obtained from the curve corresponds to the manufacturers' specifications.

2. The halftime for transmission increased with glueline thickness from 0.05 to 0.5 mm. The cause for this time difference is uncertain.
3. By controlling glueline temperature, and assuming a known kinetic order, the activation energy for curing can be obtained for epoxy adhesives.

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