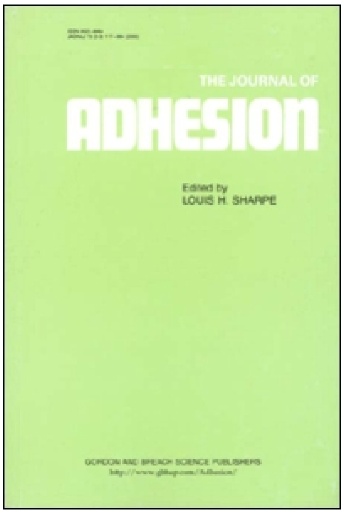

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# Residual Stress in the Interfacial Bond Zone of Curing Adhesives by a Sensitive Strain Measurement Technique

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Highly sensitive electrical resistance measurements are used as the basis for development of a technique to measure simultaneously the residual stresses developed in the interfacial bond and the bulk regions of a curing, initially liquid adhesive. Constantan wires of 0.025 mm diameter are immersed in the adhesive, and the resistance during cure is tracked on a six-digit ohmmeter. Stress values are calculated from the gage factor and the modulus of elasticity of the wire. The technique is applied to an Epoxylite 810—aluminum system. Significant differences in residual stress between the interfacial and the bulk zone in the cured adhesive are demonstrated.

## INTRODUCTION

The analysis of adhesive bond strength and an understanding of the mechanism of bond failure require information on the physical condition of the adhesive in the most local sense. While this requirement is broadly recognized by truisms such as the prediction that failure will occur at the "weakest link in the chain", the availability of such information is often nil. As a result, the investigator resorts to the assumption that properties are uniform throughout the interfacial area of the adhesive and substrate.

Techniques for studying the properties of the interfacial accommodation zone (IAZ) clearly are required. A significant advance in this area has been the application of ultrasonic Rayleigh waves to the determination of shear modulus in the IAZ.[1,2] The variation of shear modulus in the adhesive region extending from the interface out to about 0.25 mm has been definitely demonstrated.

The purpose of this paper is to describe a technique for measuring strains in an initially liquid adhesive layer as they develop during the curing process. The locale of measurement is a matter of choice and ability to position the equipment. However, in the work reported here the objective has been to compare strains developed in the IAZ with those developed concurrently in the bulk of the adhesive. To do this, strain gage methods have been refined to achieve a high degree of sensitivity.

## EXPERIMENTAL APPROACH

Since the interfacial zone of interest in an adhesive is only about 0.25 mm thick, the size of any intrusive measuring device should be limited to ten percent of this value or less. This condition is fulfilled by the one-mil (0.025-mm diameter) wires frequently used in strain gages.

The ideal strain gage wire should have high resistance, a large change in resistance as the strain develops, a high elastic limit, and be insensitive to temperature.[3] The copper-nickel alloy Constantan has a uniquely low temperature coefficient of electrical resistance, estimated to be $\pm 2 \times 10^{-6}$ ohms per ohm per degree centigrade. This coefficient remains small over a relatively wide temperature range encompassing ambient temperatures.[4] The resistance of a 0.025-mm diameter wire is not particularly high, about 1 ohm/mm, but high enough to provide for our purposes the desired resistance in a practical length. The strain sensitivity of the wire is expressed by the gage factor F, the dimensionless ratio of the fractional change in resistance to the fractional change in length.

$$F = \frac{\Delta R/R}{\Delta L/L} \tag{1}$$

At a value of 2.1 the gage factor of Constantan is adequate for the measurements reported here.

In order to obtain significant changes in electrical resistance as the curing action of an interfacial adhesive proceeds, a proper choice of wire length must be made. The magnitude of tensile or compressive strains will depend of course on the materials involved in the adhesive bond. However, to design experimental equipment, an order of magnitude must be chosen. Based on measurements by other techniques of stresses developed in the bulk of various plastics,[5-7] a stress value of $6.89 \times 10^6$ Pa (1000 psi) was selected arbitrarily.

The published value for the modulus of elasticity E of Constantan is $E = 1.65 \times 10^{11}$ Pa. Since the definition of this modulus is the ratio of stress to strain, a stress of $6.89 \times 10^6$ Pa in Constantan corresponds to a strain of $4.2 \times 10^{-5}$. With this value as the denominator in Eq. (1), the fractional change in resistance is $8.8 \times 10^{-5}$. While small, this sensitivity is within the measurement capability of the Data Precision Digital Multimeter Model 3500, particularly when all six digits of the ohmmeter are used. The latter condition arises if the measured resistance is in the range 100.000 to 119.999 ohms, whereat a variation is produced of 9–11 milliohms per $6.89 \times 10^6$ Pa of stress.

From the foregoing considerations, the optimum length of 0.025 mm diameter Constantan wire would be slightly over 10 cm. With allowance for clearance of the coupon, all tests have been conducted with span lengths slightly larger.

## LABORATORY APPARATUS

It is essential that the resistance wire be fastened firmly to the meter leads and that the junction points be rigidly fixed so that strains are not introduced inadvertently. At the outset 25-mm square copper pieces were used for resistance wire attachment. Initially, bonding of the Constantan to the copper with small electronic soldering irons failed, due to the heat-sink property of the copper pieces. A spot-welder was also unsuccessful in producing a satisfactory bond. Ultrasonic joining was attempted with a West-Bond Wire Bonder, but this procedure failed, apparently due to dissimilarities in the hardness of Constantan and copper. Laser bonding also failed. The only successful method has been soft soldering with a relatively large-wattage soldering iron.

While preliminary measurements were made with a single wire, the ultimate objective was to observe the behavior of adhesives in the IAZ relative to the bulk of the adhesive. This required two electrically isolated wires separated by about 0.7 mm when immersed in the adhesive. To monitor the effect of accidental fluctuations in ambient temperature or voltage supply, we employed a third Constantan wire of approximately the same length as a reference. All three resistance wires were monitored by Data Precision 3500 digital ohmmeters connected to the same Sola 60-va constant voltage transformer. Each was used in four-wire mode.

Both the upper wire of the pair and the reference wire were attached to Lucite® fixtures designed as shown in Figure 1a. The lower wire was attached to copper plates on a Lucite® square as depicted in Figure 1b. In assembly, spacers and film insulators were laid on top of the copper plates on the square, the upper wire fixture was inverted, carefully positioned on top of the square, and the two fixtures were then clamped together as indicated in Figure 2.

The test coupon containing the adhesive resides on a platform which fits within the opening of the square. Liquid adhesive is added to the coupon prior to immersion of the resistance wires. Sufficient adhesive is added to cover the coupon over its 10-cm width, although surface tension will normally contain the liquid at the edges. The platform is raised into position by a laboratory jack until the lowest wire contacts

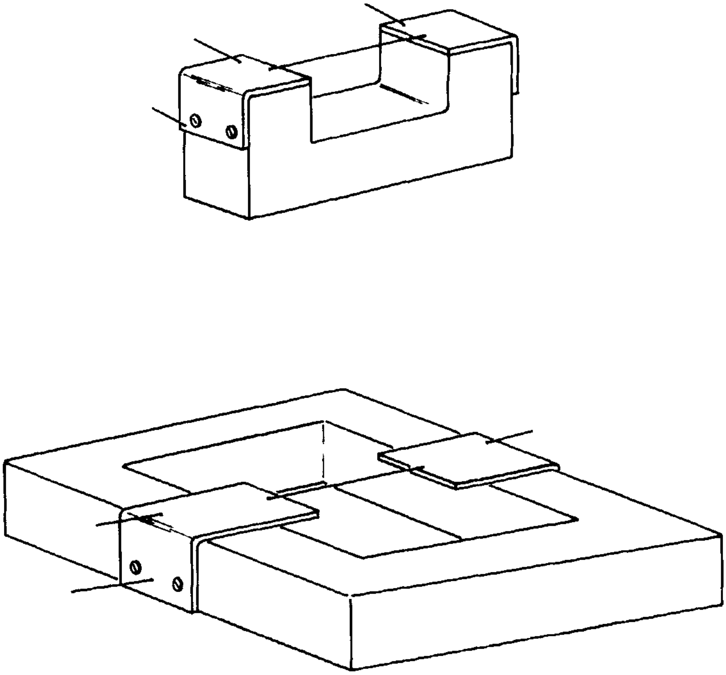

FIGURE 1 Configuration of Lucite® and copper plates used to immobilize the Constantan wires.

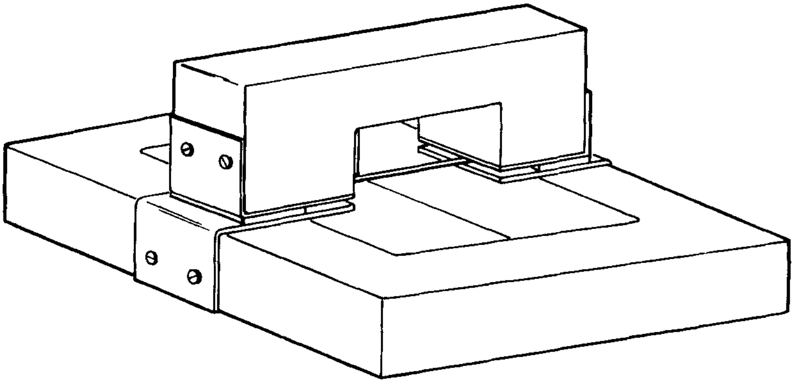

FIGURE 2 Assemblage of upper and lower wire supports to provide parallel closely-spaced fine wire spans with insulation from each other.

the adhesive. The jack is then raised further until both wires are immersed and at the desired elevation above the coupon. In the present work, an intense light was used to locate the positon at the edges of the coupon of the lower wire. If close proximity to the coupon (say, less than 0.1 mm) is desired, considerable care must be exercised to avoid raising the coupon too far and thus severing the wire. Contact of the wire with the coupon can be observed as an increase in resistance as the wire is strained, but the increase may prove irreversible.

The ultimate position of the wires is determined by metallographic sectioning after completion of the experiment. A typical section showing the two wires in a cured sample of Epoxylite 810 adhesive is presented in Figure 3.

## EXPERIMENTAL RESULTS

The adhesive system which has been investigated most thoroughly has been that of Epoxylite 810 (without filler) on aluminum substrates. The aluminum coupons were pretreated by a phosphoric acid etch. Curing of the Epoxylite resin was accomplished at ambient temperature by adding curing agent in 1 : 4 ratio to the resin and mixing intimately. The curing strains were monitored in a controlled temperature environment with temperature held to ±0.5°C within the periods shown on the accompanying diagrams.

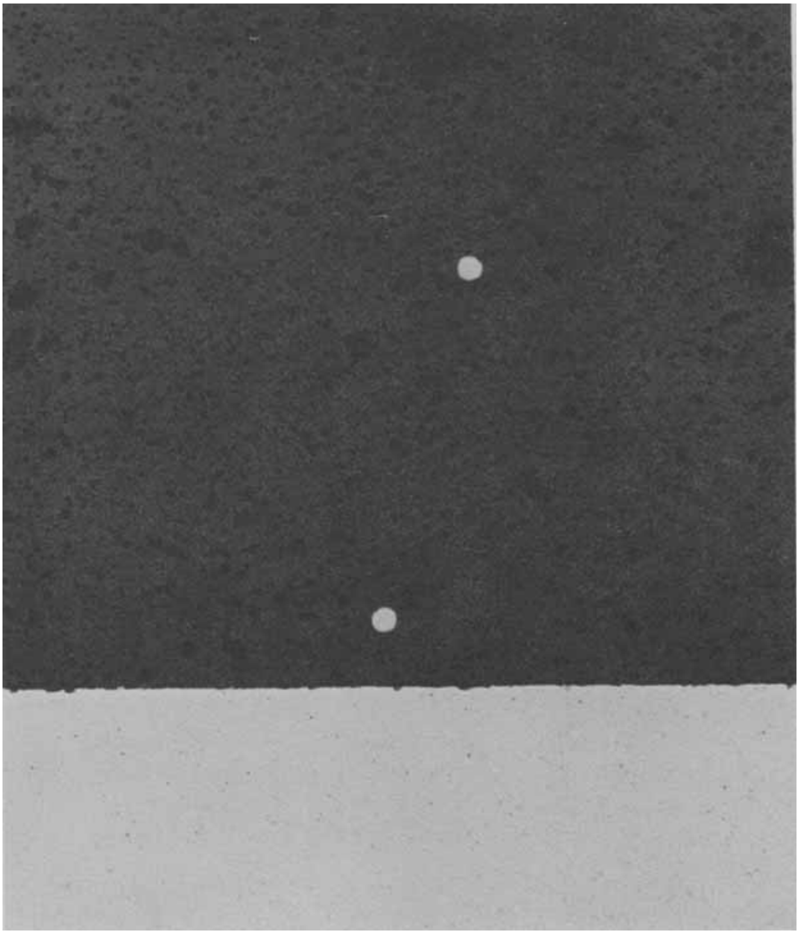

FIGURE 3 Metallographic section showing 0.025 mm wires embedded in Epoxylite 810 on aluminum substrate.

Several experiments have been completed, each with the resistance wires at different elevations above the substrate. Since each test was performed on a different day and since the objective was only to compare behavior in the IAZ versus the bulk adhesive, it was deemed inappropriate to combine the results.

In Figure 4 resistance readings obtained during the curing of Epoxylite 810 at 25.5°C are plotted *versus* cure time. The average elevation

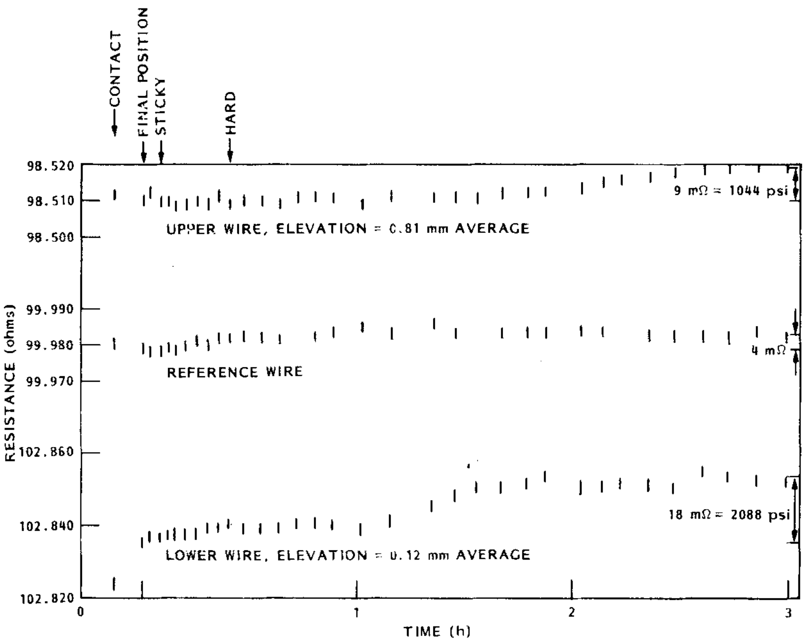

FIGURE 4 Constantan wire resistances in Epoxylite 810 on aluminum substrate at 25.5°C as a function of cure time.

of the upper wire was 0.81 mm (32 mils) in an adhesive layer which averaged 2.26 mm in thickness. No significant change in reading was noted for 110 minutes in this layer, after which a tensile stress of about $6.89 \times 10^6$ Pa developed. The lower wire was at an average elevation of 0.12 mm (4.8 mils). In this layer, which should have been within the IAZ, a significant tensile stress was observed after only 80 minutes, and the stress reached a value about twice that of the upper wire. It should be noted that the changes in resistance of both embedded wires were significantly greater than the resistance variation of the reference wire.

Although a study of the curing behavior of Epoxylite 810 is beyond the scope of this paper, some differences in cure time and physical appearance have been noted in otherwise identical experiments. The results of an experiment in which both the upper and lower wires were closer to the aluminum surface are shown in Figure 5. In this test, the upper wire averaged 0.68 mm (26.7 mils) elevation while the lower

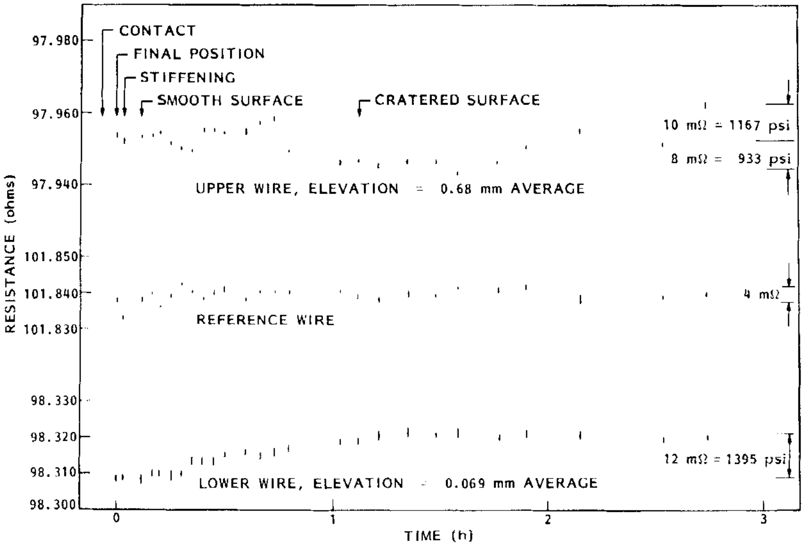

FIGURE 5 Constantan wire resistances in Epoxylite 810 on aluminum substrate at 25.0°C as a function of cure time.

wire was only 0.069 mm (2.7 mils) above the surface. The ambient temperature was 25.0°C during the experiment and the thickness of the cured adhesive layer was 2.07 mm. As before, a significant tensile stress developed in the lower wire, this time within 30 minutes. The upper wire appeared to be in tension initially, but then entered a compressive period, presumably resulting from a curing reaction (*vide infra*). Subsequently, this bulk adhesive wire also returned to tension. The stability of the reference wire resistance indicated that voltage supply and temperature control were excellent and that meter drift was unlikely in the relative short time periods involved.

In still another curing experiment with Epoxylite 810, in which the ambient temperature was 27.5°C and the resistance wires averaged 0.42 mm (16.5 mils) and 0.069 mm (2.7 mils) above the surface, increased resistances were observed to occur in both wires as the adhesive cured. Thus tensile stresses were evidenced again.

Although there is no obvious reason why, during curing, one of the wires could not be in tension while the other wire is in compression, experience with the Epoxylite 810 system has shown that the lower wire (elevations 0.046-0.122 mm) has developed tension in all experiments but one. The anomaly occurred in the experiment conducted at 29.5°C and has never been repeated. The upper wire (elevations 0.42–0.81 mm), on the other hand, may enter a compressive period lasting up to two hours, after which it passes into tension also. The compressive period appears to be related to the appearance of small craters in the epoxy surface.

With ambient temperature controlled to ±0.5°C and all three calibrated ohmmeters supplied by the same constant voltage transformer, this technique has followed successfully the stress developed in a curing liquid adhesive. The use of three (or more) highly sensitive, relatively expensive meters, however, may prove prohibitive to some. It was suggested by one of the referees that greater sensitivity could be achieved with a resistance bridge and greater confidence in the results with only one meter. However, the use of one meter to monitor the resistances of three wires would require the use of one or more switches. Because measurements on the order of micro-ohms are involved, there

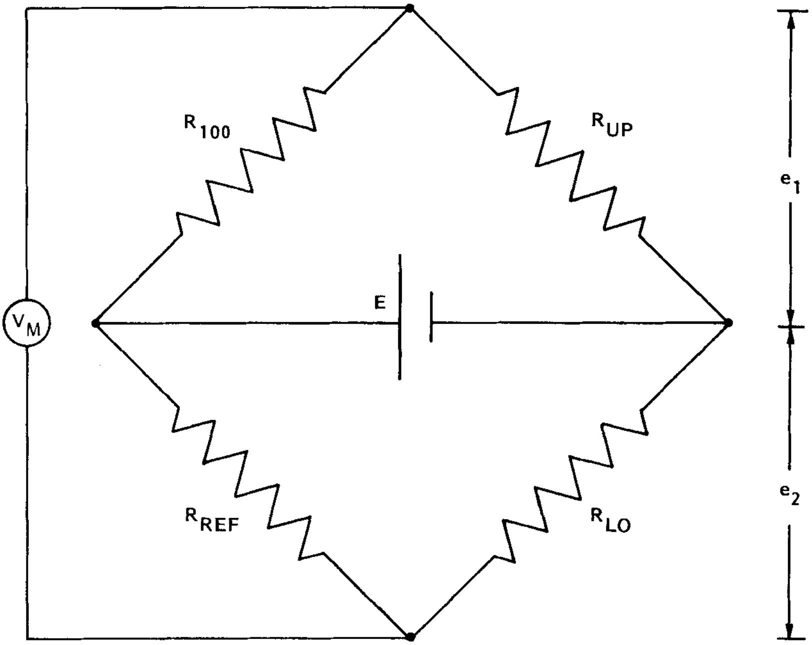

FIGURE 6 Resistance bridge used to follow differentials developed between upper and lower wires during curing.

is no assurance that the resistance reproducibility of available switches is adequate.

Since the original objective was to determine whether differences in resistance were developed at the two elevations, this problem was circumvented in the following way. The combination of a resistance bridge and one meter, without switches or an adjustable resistance, was used to measure differences in resistance between the two Constantan wires. The meter was used as a voltmeter instead of ohmmeter, and the bridge was employed in a standard arrangement as shown in Figure 6. The voltage source was a Datel-Intersil Voltage Calibrator Model DVC 8500 at 1.000 volt. In addition to the two strain measurement wires ($R_{up}$, $R_{lo}$), the reference wire (R *ref.*) and a standard 100-ohm resistor ($R_{100}$) completed the bridge.

From current balances the voltmeter reading ($e_1$-$e_2$) before a strain is introduced is given by:

$$e_1 - e_2 = \mathrm{E}\left[\frac{R_{up}}{R_{100} + R_{up}} - \frac{R_{lo}}{R_{ref} + R_{lo}}\right] \tag{2}$$

After the wires are immersed in the adhesive and strains produce the resistance changes $\Delta R_{up}$ in $R_{up}$ and $\Delta R_{lo}$ in $R_{lo}$, the meter reading becomes:

$$(e_1 + \Delta e_1) - (e_2 + \Delta e_2) = \mathrm{E}\left[\frac{R_{up} + \Delta R_{up}}{R_{100} + R_{up} + \Delta R_{up}} - \frac{R_{lo} + \Delta R_{lo}}{R_{ref} + R_{lo} + \Delta R_{lo}}\right] \tag{3}$$

If all the resistances were 100 ohms identically, the original reading ($e_1$-$e_2$) would be zero. Since no adjustable resistances were used, the values did differ somewhat and an original non-zero reading resulted. From Equation (3), the observed voltage will change little or not at all if $\Delta R_{up}$ and $\Delta R_{lo}$ change in the same amount and direction. Bridge resistances in the present work were such that the second term in Equation (3) exceeded the first term and the observed voltage was negative. When $\Delta R_{lo}$ exceeded $\Delta R_{up}$ the observed voltage became more negative, *i.e.*, the absolute value increased. When $\Delta R_{up}$ exceeded

$\Delta R_{l_0}$ the absolute value decreased. The calculated relationship was 25 micro-volts per 10 milliohm resistance net change. If the resistance of the wire just above the metal surface increased relative to the wire in the bulk of the adhesive, the absolute value of the potential would increase also, and *vice versa*.

Experimentally, the bridge potential was found to increase from $-0.002440 \pm 0.000002$ v., to peak at $-0.002479 \pm 0.0000002$v. This corresponds to a peak differential of 0.016 ohms in favor of the lower wire, with a subsequent decline to less than 0.013 ohms differential. From Figure 4 the corresponding experimental values are 0.016 ohms peak, retreating to 0.008 ohms. From Figure 5, the differential rose to 0.036 ohms and then also declined. The bridge potential measurements thus tend to corroborate the direct resistance measurements. However, the bridge results express only the relative conditions of the two wires, *e.g.*, that the surface wire is in greater tension than the bulk wire or that the surface wire is in tension while the bulk wire is in compression.

## DISCUSSION

The concept of varying elastic properties in an interfacial adhesive layer as the interface is approached has been introduced by Knollman and Hartog.[1] Their measurements of shear modulus through the IAZ supported this thesis. The present measurements of stress in the IAZ of Epoxylite 810 substantiate the existence of residual stress variations. Not enough experiments have been completed to confirm the inverse relationship between stress and shear modulus which is suggested by the findings of Knollman and Hartog.[2] However, the results obtained do confirm that during curing a difference in stress occurs between the IAZ and the bulk adhesive.

The technique which we have developed is limited to adhesives which are initially liquid at the temperature of measurement. Because of the low but finite temperature coefficient of resistance for the Constantan wire, accurate measurements can not be made in thermoplastic adhesives until this coefficient can be reproducibly measured to an accuracy concomitant with the high sensitivity of the measurement system. However, this does not preclude application of the technique to systems which cure at elevated temperature as long as the system has proper thermostatic control.

# CONCLUSION

A highly sensitive strain measurement technique has been developed for application to initially liquid adhesive systems. Measurements of stress in the interfacial bond region of the Epoxylite 810-aluminum systems have demonstrated that significant differences exist in residual stress between the interfacial and the bulk adhesive zones.

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