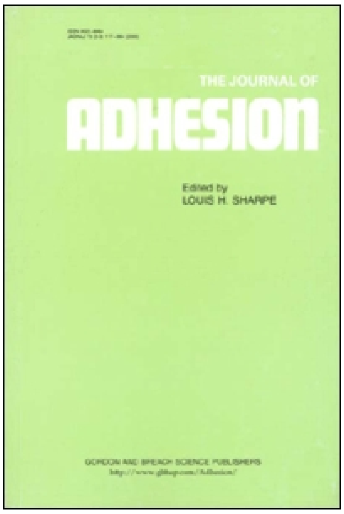

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Experimental Determination of the Variation in Shear Modulus Through the Interfacial Zone of an Adhesive

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Experimental Determination of the Variation in Shear Modulus Through the Interfacial Zone of an Adhesive

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A gradient in shear modulus occurs in the interfacial accommodation zone (IAZ) of FM 73, a commercial film adhesive, bonded to aluminum. Such determination has been made by means of ultrasonic Rayleigh waves (surface waves) generated on successively exposed layers of the adhesive throughout the bondline region. Experimental Rayleigh wave apparatus is described which has been used to obtain the shear-modulus gradient in FM 73. Various substrate surface treatments and adhesive cure times were considered, demonstrating that the variation of shear modulus in the IAZ of FM 73 is independent of substrate treatment or cure time. Preparing the aluminum substrate with BAC results in an IAZ of greater extent than occurs with the other two treatments. Cure time does not affect the range of the IAZ, but does influence somewhat the shear modulus of the adhesive beyond the IAZ.

1. INTRODUCTION

In the technical community, analytical models are being developed for studying the nature and behavior of interfacial adhesive bonds. Such models are intended, for example, to predict adhesive failure modes as well as crack propagation in the so-called interfacial accommodation zone or IAZ. The IAZ is regarded as a region very close to the adherend through which a crack propagates when significant stress/strain is present in a failing adhesive joint.

Adhesive bond strength and failure models involve the mechanical and elastic parameters of the interfacial adhesive material. For a given adhesive, these fundamental quantities have been taken in the past as constants throughout the thickness of the interfacial layer. Should the elastic moduli vary with distance from the adhesive-adherend interface through the IAZ, failure scenarios could be significantly affected. Modulus gradients are certainly conceivable and could arise from chemical diffusion, abnormal cure, material anisotropies, and/or residual strain.

Indeed, variations of the shear modulus throughout the IAZ of some typical adhesives have recently been quantitatively delineated by the authors[1,2] using ultrasonic Rayleigh wave (URW) techniques. These acoustic waves were generated on progressively exposed surfaces of an adhesive bond, from the bulk material down toward the adhesive-adherend interface. Determination of the Rayleigh wave speed at successive adhesive layers leads to a calculation of the shear modulus at various depths within the IAZ. A relationship between shear modulus and wave speed exists because the latter is established by the elastic properties of the adhesive material in the surface layer.

For the purpose of determining the shear modulus layer-by-layer through the IAZ of adhesives, the authors have utilized Rayleigh waves rather than Lamb or plate waves. The latter type wave would propagate along the adhesive layer as a whole and thus only provide a measure of the average shear modulus for the given thickness of adhesive. On the other hand, since Rayleigh waves are confined to a very thin surface layer of the adhesive, one can readily determine shear modulus on a layer-by-layer basis. After a URW measurement is made on a surface of adhesive bonded to a substrate, this layer simply is removed to expose a second surface for subsequent URW testing, etc.

In this paper, an in-depth study is presented concerning the shear modulus gradient in the IAZ of one particular adhesive, American Cyanamid's FM 73, as found from URW measurements. The adhesive was bonded to a metallic substrate. Variations in shear modulus were obtained throughout the interface layer for adhesive samples prepared with three different substrate surface treatments. In each case, the adhesive was subjected to two distinct cure times with the cure temperature taken as that recommended by the manufacturer.

2. BACKGROUND

Acoustic waves which propagate along a free, plane boundary of a homogeneous, isotropic solid half-space were first introduced by Rayleigh.[3] He showed that the amplitude of these waves decays rapidly with depth in the solid material. The properties and behavior of Rayleigh surface waves have since been discussed in various technical literature.[4-7]

Rayleigh waves with frequencies well into the ultrasonic range (above a megahertz) have emerged as a tool for the nondestructive evaluation of material surfaces and surface layers.[8,9] In particular, ultrasonic Rayleigh waves have found application in studies of surface layer phenomena in metals,[10-16] as well as for assessing residual stresses in the metallic surface layer.[17] The current utilization of acoustic surface waves for analyzing adhesive material is the first such application known.

In general, ultrasonic waves which are directed through a liquid onto an immersed planar solid surface are, in part, specularly reflected if the interface is flat and smooth. The sound energy which is reflected from the solid surface is a function of the angle of soundwave incidence. When the angle of incidence equals the so-called Rayleigh angle, a surface wave is generated at the solid surface and propagates along it. At this occurrence, some of the previous acoustic energy in the reflected wave becomes, instead, surface wave energy.

The approach in determining shear-modulus gradients for an interfacial adhesive has been that of measuring the Rayleigh angle for a very high frequency (small penetration depth) ultrasonic wave made to impinge on a flat, smooth adhesive surface. During the process, the adhesive sample is immersed in a special, inert liquid to provide the liquid-solid interface for URW generation and propagation.

3. THEORY

With a plane, longitudinal soundwave impinging on a planar liquid-adhesive boundary surface, the specularly reflected wave has amplitude and phase depending on the angle of soundwave incidence. When the angle of incidence equals the Rayleigh angle θ_r, an abrupt decline in amplitude and/or change in phase occurs, marking the generation of a Rayleigh surface wave. Much of the incident soundwave energy which had been reflected at the boundary now is contained instead in a soundwave propagating over the surface.

The Rayleigh wave speed v_R on the adhesive surface is obtained from Snell's Law of Refraction as[1]

$$v_R = v_L/\sin\theta_R \tag{1}$$

where v_L is the speed of the longitudinal acoustic wave in the immersion liquid. In the URW tests, this quantity is measured separately for the given liquid which is used.

The experimentally determined Rayleigh angle is a function of the frequency associated with the incident acoustic wave. In measuring the Rayleigh angle at various depths within the adhesive IAZ, a fixed acoustic frequency is used for all the measurements. The same frequency is employed to measure the soundwave speed in the immersion fluid. Thus, in Eq. (1), both the Rayleigh angle θ_R and the wave speed v_L are determined for the same frequency.

Rayleigh wave speed is a function of the speed v_S at which a transverse or shear acoustic wave would propagate in the adhesive surface layer. Having determined the Rayleigh speed from the measured Rayleigh angle in Eq. (1), one can calculate the corresponding shear speed[18]

$$v_S = Kv_R \tag{2}$$

where

$$K = \frac{1+\sigma}{0.87+1.12\sigma} \tag{3}$$

in terms of Poisson's ratio σ for the adhesive. In the URW analysis, this ratio is obtained by independent means. The quantity K in Eq. (3) is rather insensitive to σ, varying but from about 0.87 to 0.95 for the entire possible range 0 to 0.5 of Poisson's ratio.

Equation (3) is based on the assumption of an air-solid interface. The presence of a liquid at the boundary increases the surface wave speed in the solid over that occurring in the absence of the liquid. However, the increase in wave speed due to the presence of the liquid is rather small. From curves presented in Ref. 4, one finds that the increase for the adhesive material of interest here is a few percent at most. Since the present paper is basically qualitative in nature, the small effects of the external fluid have not been included.

Shear modulus G of the exposed surface material of adhesive is found from the relationship

$$G = \rho v_S^2 \tag{4}$$

where the layer material is assumed to be homogeneous and isotropic. In Eq. (4), ρ is the density of material in the surface layer.

Herein, the moduli obtained from Eq. (4) through the IAZ of an adhesive were all determined for a specific frequency. Of course, the Rayleigh angle measurement process could have been repeated at a number of different acoustic frequencies. Such a procedure would be valuable in identifying any viscoelastic characteristics of the adhesive in the IAZ. Such elaboration was not the purpose of the present investigation.

4. EXPERIMENT

A. Apparatus

The experimental Rayleigh apparatus devised for URW measurements on adhesives is shown in Figure 1. A sketch of the system is presented as Figure 2. A cylindrical Plexiglas vessel is mounted on a spectrometer table which rotates about its longitudinal axis (normal to the plane of the paper in Figure 2). This vessel is partially filled with Dow Corning 200 fluid (DC-200) of about 1cS viscosity. For the FM 73 adhesive, this liquid as an immersion fluid provides Rayleigh critical angles of appropriate magnitude to be readily measurable with the laboratory apparatus.

A sample of adhesive bonded to a substrate is positioned at the axial center of the Plexiglas vessel, as depicted in Figure 2. The exposed adhesive surface faces two identical acoustic transducers, one fixed in position and the other rotatable. Rotation of the sample about its longitudinal axis is accomplished by rotation of the spectrometer table (and consequently the attached Plexiglas vessel). Such rotation changes the angle of incidence for the soundwave originating at the fixed acoustic transducer. Short trains of longitudinal ultrasonic waves are generated by this transducer at a frequency of 25 MHz. These wave trains propagate from the transducer through the DC-200 fluid to the surface of the adhesive sample.

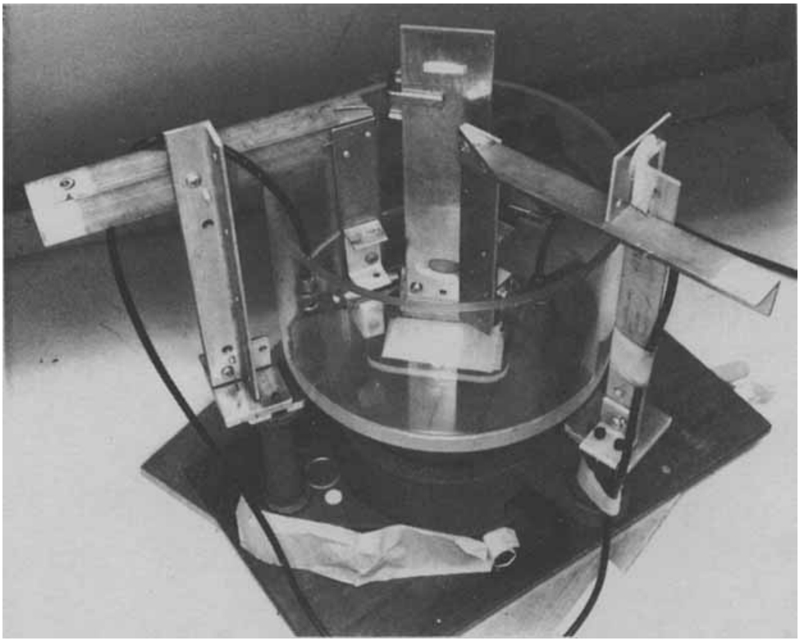

FIGURE 1 Photograph of laboratory URW apparatus used for measuring Rayleigh angles of FM 73 adhesive.

Soundwaves reflected from the adhesive surface are received by the movable transducer when it is properly aligned along the path of the reflected acoustic wave train. For any orientation of the adhesive sample relative to the stationary acoustic transducer, the receiver is correspondingly positioned such that the received signal is a relative maximum. Alignment of sample and transducers for this optimization to occur is aided by an optical system involving a laser (not shown in Figures 1 and 2).

As part of the Rayleigh apparatus calibration, the sound speed v_L is measured for a longitudinal, 25-MHz acoustic wave train propagating in DC-200 fluid. This quantity is determined as a function of fluid temperature. When a URW test is conducted on an adhesive sample, a simultaneous record is made of the temperature in the immersion fluid. The calibration curve is then utilized to obtain the appropriate sound speed v_L for calculating Rayleigh wave speed from Eq. (1).

Evaluation of the laboratory URW apparatus was performed utilizing

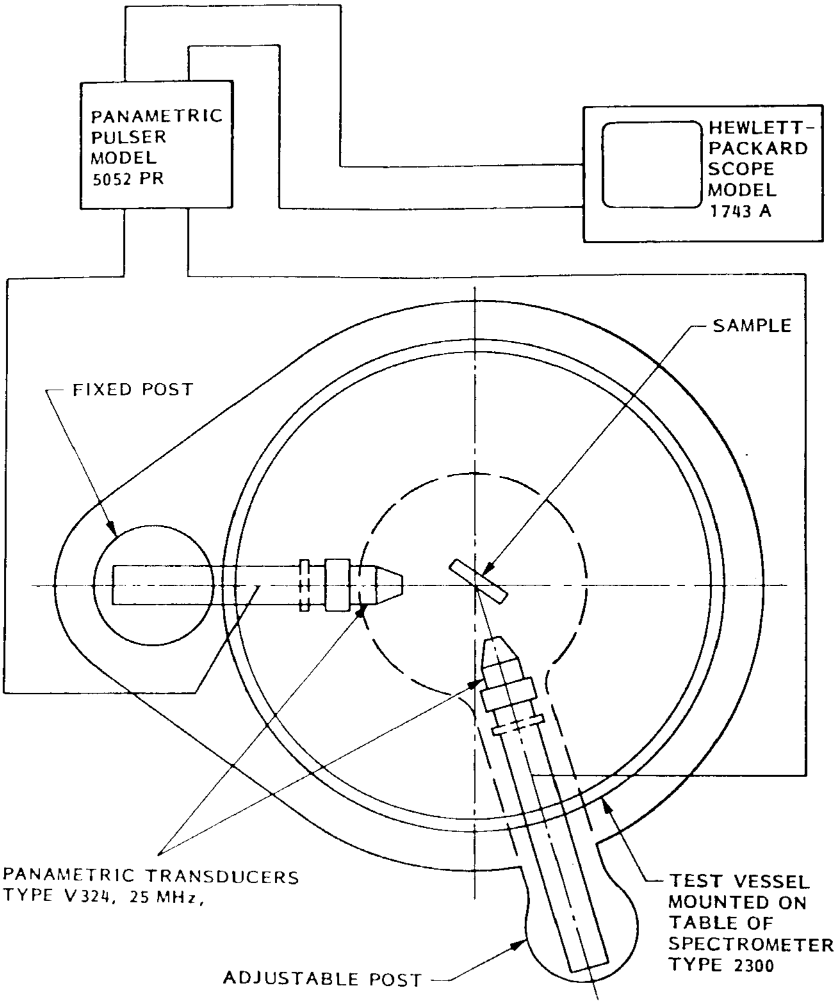

FIGURE 2 Sketch of laboratory URW apparatus including associated acoustic and electronic systems.

standard materials such as metals, glass, and plastics. Results of these measurements are presented elsewhere.[1] A slab of Plexiglas is used as a reference standard for the URW system. A series of URW measurements on adhesive samples is not undertaken until the Rayleigh equipment is validated by measuring the Rayleigh angle for the Plexiglas sample.

B. Test Procedure

An adhesive sample undergoing URW measurement is oriented sequentially in each of four planar orthogonal positions in place within the Rayleigh apparatus. For a given sample orientation, the sample is systematically rotated about its longitudinal axis and the acoustic receiver correspondingly aligned for maximum received signal. When the peak received signal suddenly undergoes a marked phase shift, one has found the Rayleigh angle, or the critical angle of soundwave incidence which abruptly causes a surface wave to arise and propagate on the exposed adhesive layer.

On the occurrence of a sudden phase shift in the reflected soundwave, the angle between the normal to the adhesive sample (in the plane of the paper in Figure 2) and the transmitter-to-sample line-of-sight is the Rayleigh angle θ_R. A URW now propagates in a thin layer (approximately 50 μm thick) along the adhesive interface at the Rayleigh wave speed given by Eq. (1). Some of the incident acoustic energy has been converted into surface wave energy and lost from the reflected soundwave. Equations (2), (3) and (4) are used to calculate the Rayleigh surface wave speed and the shear modulus of the thin surface layer on which the URW propagated.

For each of the four orientations of the adhesive sample in place, an independent measurement is made of the Rayleigh angle. An average of the four readings is taken as the particular Rayleigh angle for the sample under test. Removal of the exposed adhesive surface layer of the sample provides another adhesive surface for subsequent URW measurement. Repeated removal of surface material followed by URW testing is performed to obtain through-the-bond shear modulus as a function of adhesive thickness. However, by properly structuring the adhesive samples as discussed below, a less tedious procedure can be employed.

5. SAMPLE PREPARATION

Adhesive samples for URW measurement were obtained by first preparing a layup of FM 73 on an aluminum (Al 6061) substrate. Three different substrate surface treatments were variously utilized – FPL, STAB, and BAC. The FPL preparation is the industry standard surface treatment for aluminum and involves Forest Products Laboratory's acid etch procedure. Surface treatment for aluminum bonding, or STAB, is an alkaline treatment of high concentration sodium hydroxide solution which has recently been introduced.[19] The third substrate treatment is based on Boeing Aircraft Company's phosphoric acid anodize (BAC-5555) with primer (BR-127). Phosphoric acid anodize surface treatment for aluminum alloys has proven to yield strong, durable adhesive bonds.[20]

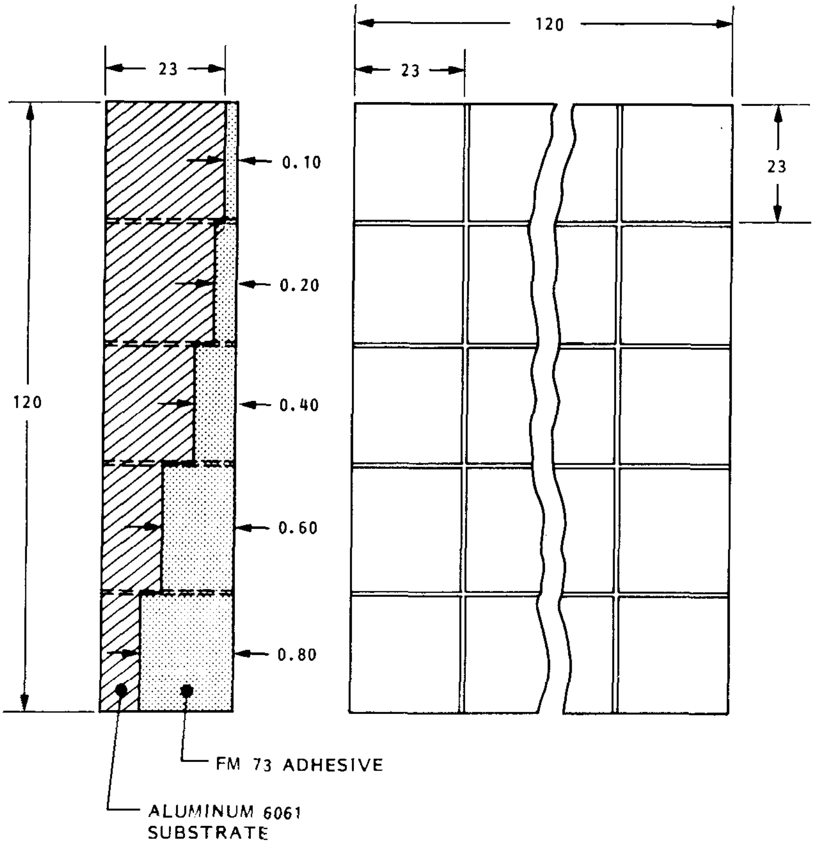

FIGURE 3 Layup configuration (not to scale) of FM 73 adhesive prior to removal of individual URW samples. All dimensions are approximate and are expressed in millimeters.

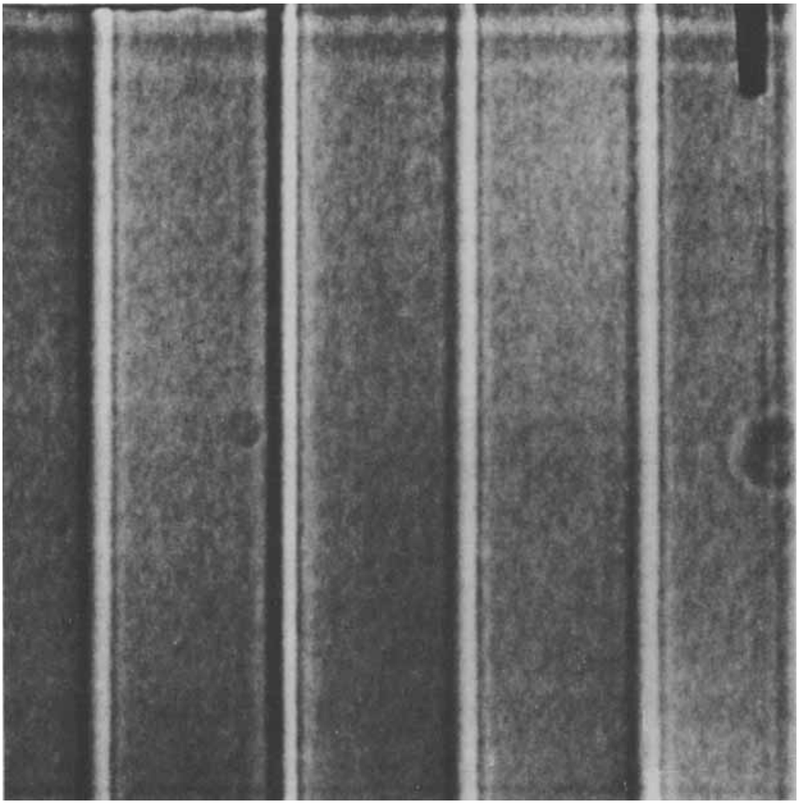

FIGURE 4 Acoustic image of an FM 73 layup block showing two anomalies (round dark spots) interior to the adhesive. Black tab at upper right is part of the block support structure. Horizontal striations are artifacts.

All adhesive layups were vacuum cast and cured for either 1 hour (manufacturer recommended) or 4 hours. In all cases, the cure temperature was 120°C as suggested by the adhesive supplier. After preparation, each FM 73 layup was machined to yield the step configuration shown in Figure 3. The adhesive surfaces were then polished smooth to remove all visible microcracks and crazes.

Thereupon, each sample block of adhesive was inspected nondestructively throughout its interior by means of acoustic imaging. The acoustic imaging system used for this screening operation is described elsewhere.[21] Unbonded areas, voids, porosity and impurities were exposed by the acoustic inspection. Figure 4 is an acoustic image of one FM 73 layup block which was involved in the URW test program. The image reveals the presence of two subsurface anomalies which were not visually observable. Needless to say, these anomalous regions were avoided in sample selection.

Final samples for URW analysis were obtained from the block configurations by first cutting away each strip and subsequently slicing each strip into five individual samples. Those individual samples which contained acoustic-image anomalies were discarded. All adhesive surfaces of the final samples were repolished with 10 μ grain paper. Following a URW test, the various samples were machined again to remove a small amount of the previously exposed surface layer. Each newly exposed adhesive surface was polished anew since accurate URW results require a smooth surface, as well as one parallel to that of the substrate.

Table I contains a summary of the samples which were prepared with FM 73 adhesive material on aluminum substrates.

TABLE I
Matrix of substrate treatments and cure times involved in URW tests of FM 73 adhesive

Number of samples	Substrate treatment	Cure time (hrs)
5	FPL	1
5	FPL	4
5	STAB	1
5	STAB	4
5	BAC-5555 (w/BR-127)	1
5	BAC-5555 (w/BR-127)	4

6. RESULTS

Figures 5 through 10 are plots showing the results of URW measurements conducted on FM 73 adhesive bonded to aluminum substrates. Plotted in the figures is the shear modulus G, calculated from Eq. (4) above, *versus* thickness of the adhesive as measured from the substrate surface.

Figures 5 and 6 are the data obtained in the IAZ for all samples which were prepared with FPL treatment of the adhesive-adherend surface, Similarly, Figures 7 and 8 are the results for STAB treatment

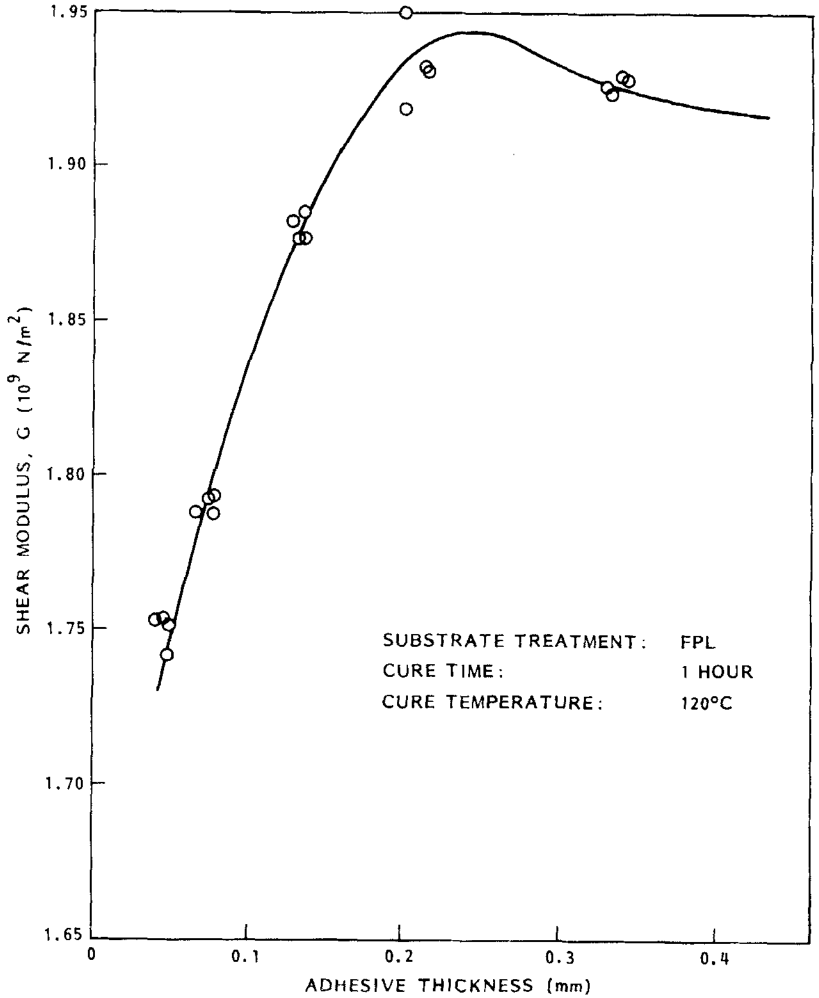

FIGURE 5 Shear modulus of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for FPL treatment of substrate surface and adhesive cure time of 1 hour.

of the substrate, and Figures 9 and 10 contain the findings for BAC surface treatment.

Adhesive cure times of 1 hour are represented in Figures 5, 7, and 9, whereas data for cure times of 4 hours are those in Figures 6, 8, and 10.

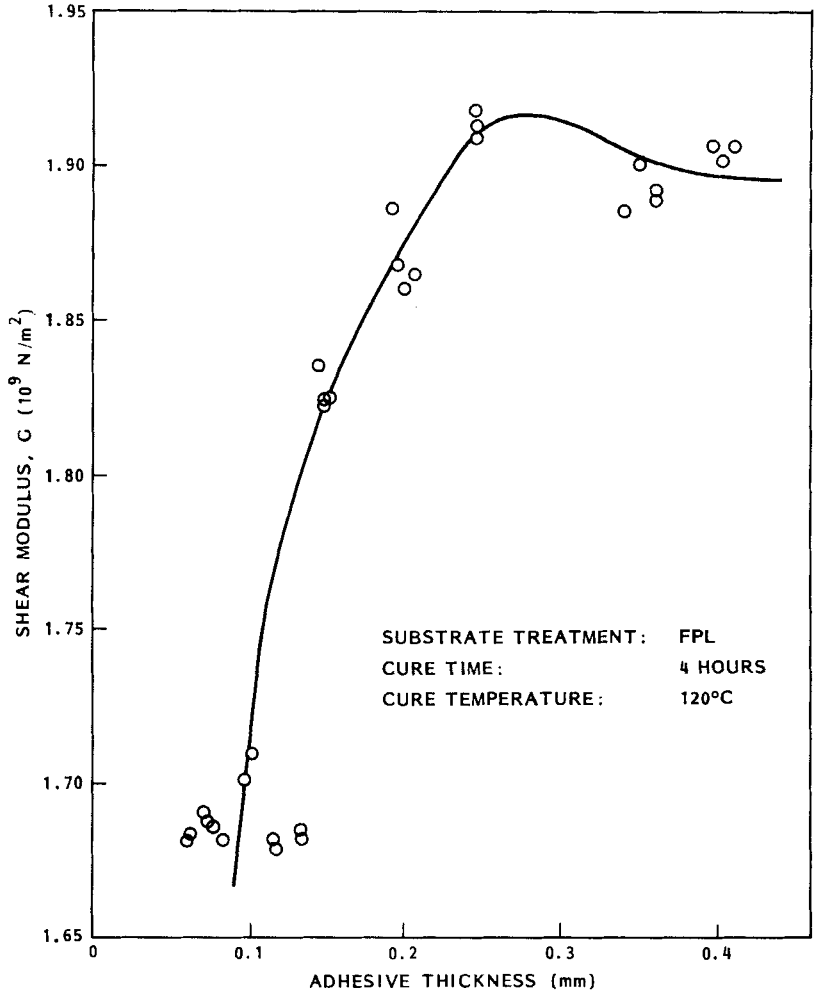

FIGURE 6 Shear modulus of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for FPL treatment of substrate surface and adhesive cure time of 4 hours.

In the calculations of shear modulus, the Rayleigh parameter K appearing in Eq. (2) was found to be K = 1.07. This value was obtained from Eq. (3) for Poisson's ratio $\sigma = 0.35$, which was determined independently from separate measurements of compressional and shear

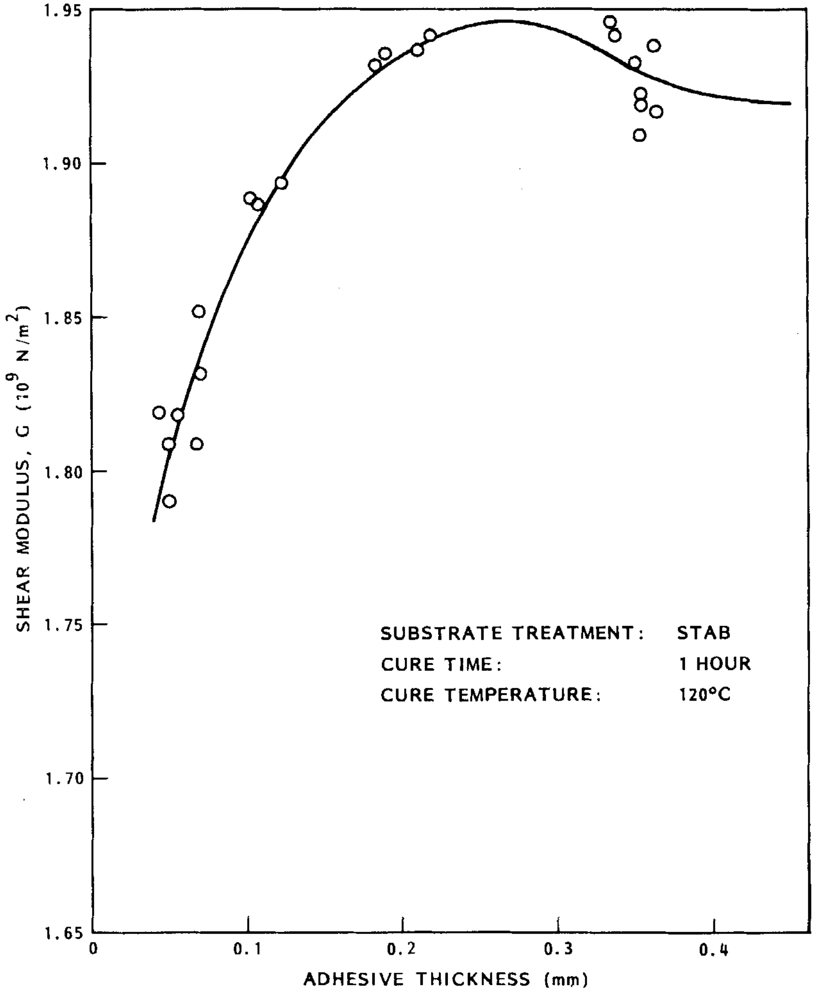

FIGURE 7 Shear moduls of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for STAB treatment of substrate surface and adhesive cure time of 1 hour.

soundwave speeds in FM 73 adhesive material. The density ρ appearing in Eq. (4) was taken as the density of bulk FM 73. Justification for this act was based on the results of previous density measurements made

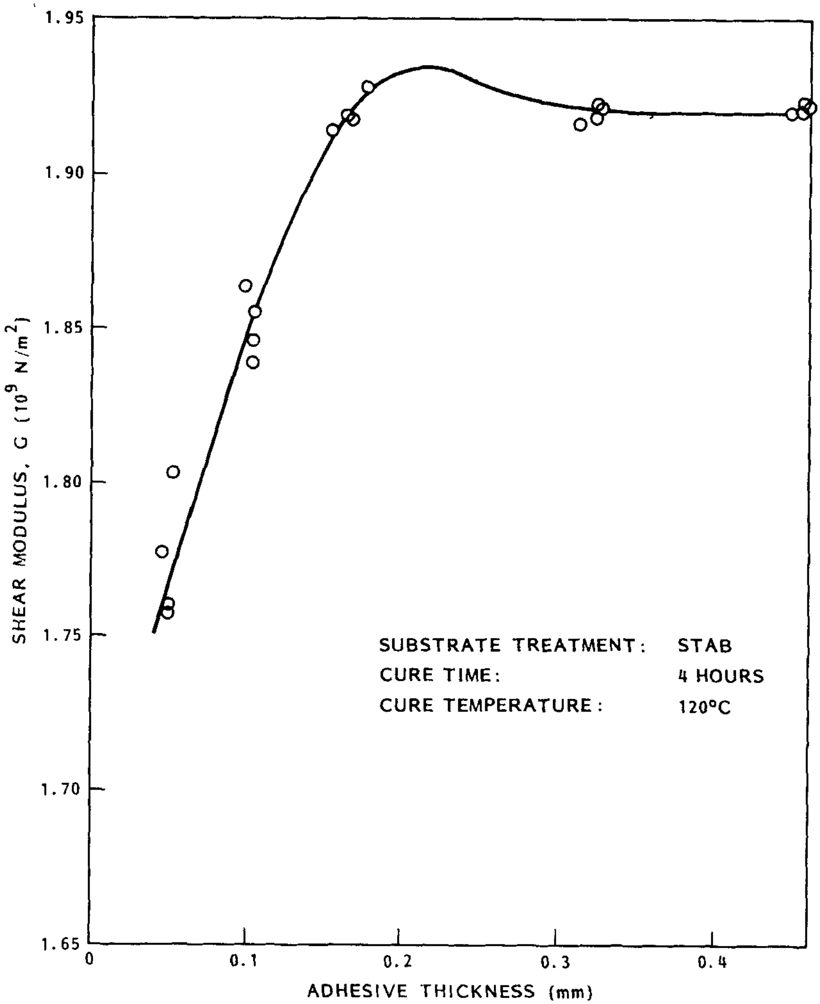

FIGURE 8 Shear modulus of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for STAB treatment of substrate surface and adhesive cure time of 4 hours.

as a function of adhesive bond thickness through the IAZ.[1] These data reveal the density to be a constant (the bulk value) within the limits of experimental error.

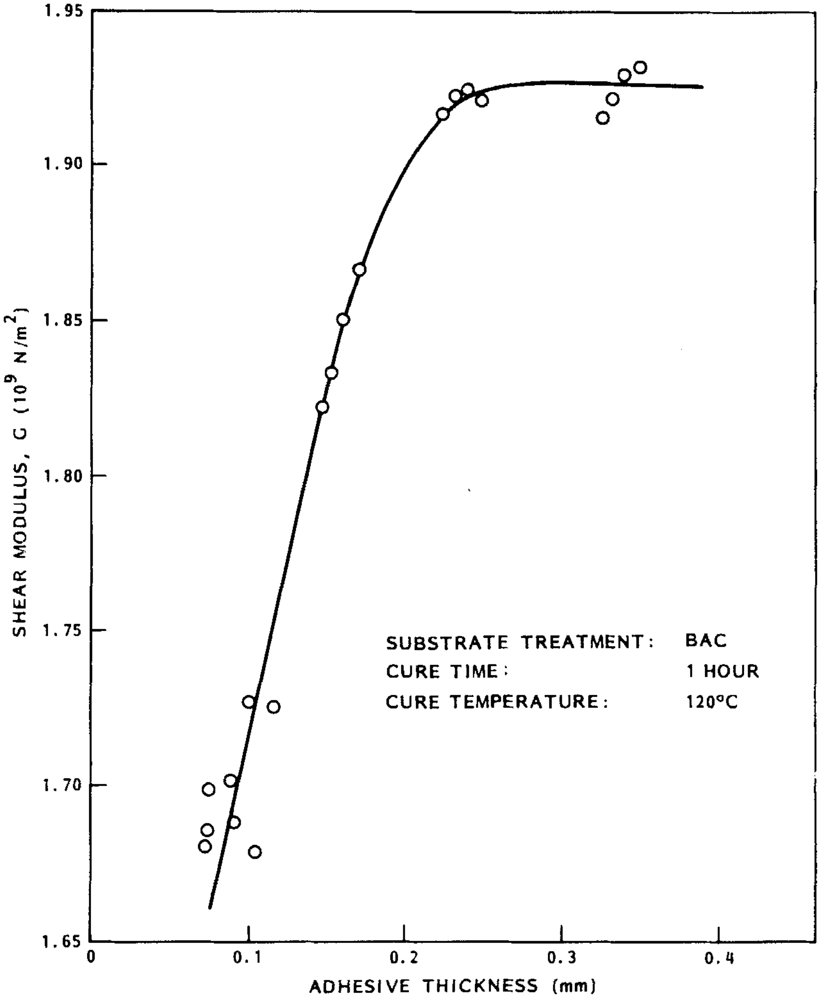

FIGURE 9 Shear modulus of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for BAC treatment of substrate surface and adhesive cure time of 1 hour.

7. DISCUSSION

The experimental results which are plotted in Figures 5 through 10 show that the shear modulus of FM 73 increases fairly linearly through the

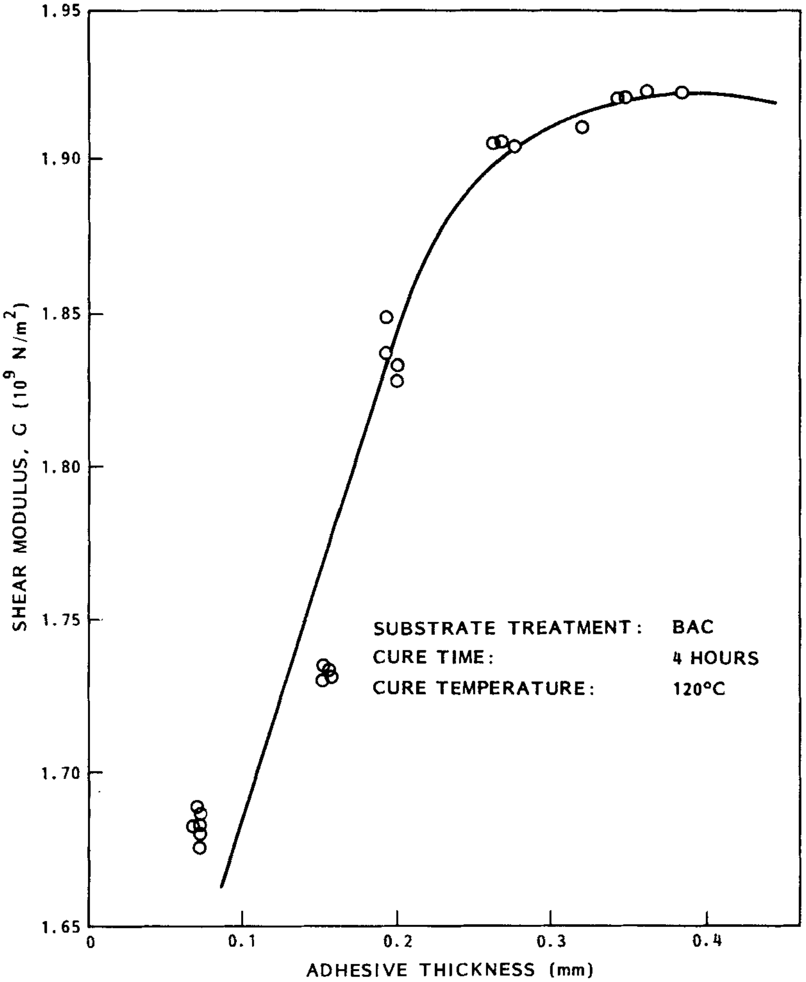

FIGURE 10 Shear modulus of FM 73 in the IAZ plotted as a function of adhesive bond thickness from the aluminum substrate, for BAC treatment of substrate surface and adhesive cure time of 4 hours.

IAZ of the adhesive bond. The gradient in modulus extends to at least 0.20 mm in all cases represented by the figures. Farther from the adhesive-adherend interface the modulus tends toward a constant (bulk) value G_B.

Shear modulus gradients in the IAZ for the various substrate treatments and cure times are best compared by normalizing the data of Figures 5 through 10 with respect to G_B. The shear modulus G_B in the region beyond the IAZ was determined by averaging the shear modulus data obtained in that region (not included in Figures 5 through 10) for all samples having identical surface treatment and cure time. Table II lists these averages of shear modulus in the bulk adhesive, for the three substrate surface treatments and two FM 73 cure times involved in the present study.

TABLE II
Shear modulus of FM 73 adhesive beyond the IAZ, averaged for all samples having identical surface treatment and cure time

Substrate treatment	Cure time (hrs)	Average G_B (10^9 N/m^2)
FPL	1	1.928
FPL	4	1.910
STAB	1	1.940
STAB	4	1.915
BAC	1	1.922
BAC	4	1.910

The data in Table II for an adhesive cure time of 1 hour are quite similar, as are the values of G_B corresponding to 4-hour cures. In fact, averaging the tabular values for 1- and 4-hour cure times yields G_B (1 hour) = 1.930 and G_B (4 hours) = 1.912. One might expect that the elastic moduli of bulk adhesive would differ somewhat depending on the cure time involved.

Plots are presented in Figures 11 and 12 of the normalized shear modulus, G/G_B, as a function of adhesive thickness for each substrate treatment. The curves appertaining to a cure time of 1 hour are plotted together in Figure 11, whereas those for 4-hour cure times are contained in Figure 12. As already stated, all cure temperatures were 120°C.

Comparison of the curves in Figure 11 and those in Figure 12 reveals that the slope of shear modulus in the IAZ of FM 73 bonded to aluminum is essentially independent of surface treatment. Overlaying Figures 11 and 12 shows that the gradient in shear modulus is also independent of adhesive cure time.

The extent of the IAZ appears to be larger for the condition of BAC substrate treatment than with FPL or STAB surface preparations. Among the latter two, not much difference exists in the range of the

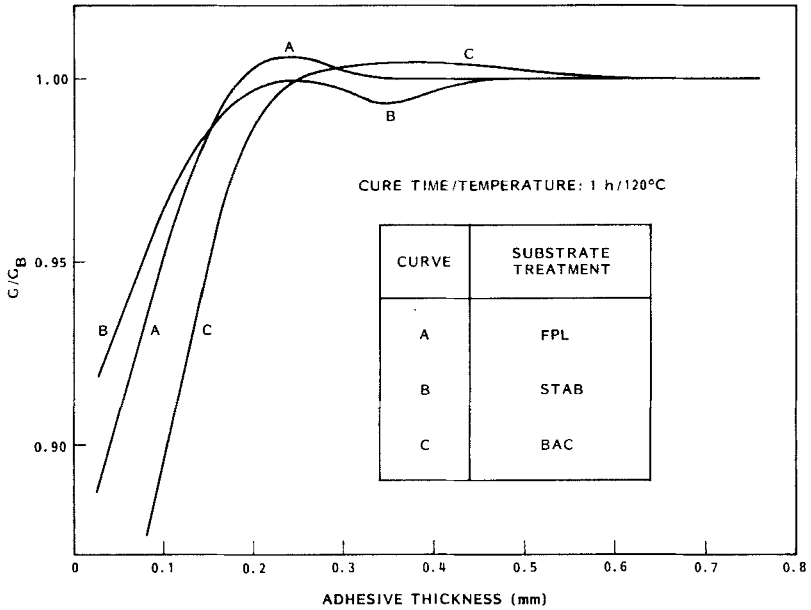

FIGURE 11 Normalized shear modulus of FM 73 versus adhesive bond thickness from the aluminum substrate, for three different treatments of substrate surface and adhesive cure of 1 hour at 120°C.

IAZ for the normal cure time of 1 hour. With 4-hour adhesive cures, the extent of the IAZ for FPL treatment appears to be somewhat greater than occurs with the STAB preparation.

Cure time has little or no effect on the extent of the IAZ for FPL and STAB treatments of the substrate surface. However, with BAC substrate preparation, the IAZ is somewhat larger with a 4-hour cure time than with a 1-hour cure.

8. CONCLUSIONS

A technique involving acoustic surface waves or ultrasonic Rayleigh waves (URW) is well suited for studying the elastic properties of an adhesive bond through the interfacial region. Measurement of the Rayleigh angle at variously exposed layers of the adhesive bond leads to a determination of the shear modulus as a function of distance from

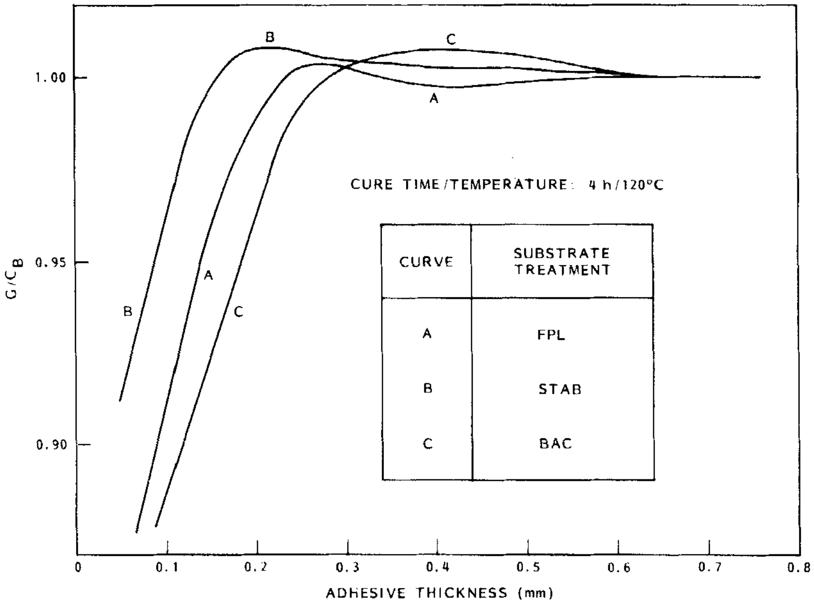

FIGURE 12 Normalized shear modulus of FM 73 versus adhesive bond thickness from the aluminum substrate, for three different treatments of substrate surface and adhesive cure of 4 hours at 120°C.

the adhesive-adherend interface into the interfacial accommodation zone (IAZ).

With FM 73 adhesive bonds on an aluminum substrate, a decided gradient in shear modulus exists through the IAZ. This almost linear variation of shear modulus with distance from the substrate is independent of substrate surface treatment and adhesive cure time, when conventional surface preparations and usual cure times are employed. Of course, standard procedures were followed in preparing the substrate and in handling the adhesive. Cure temperature was that recommended by the manufacturer for FM 73 adhesive.

In general, under normal circumstances of substrate and adhesive preparation, the shear-modulus gradient, if it exists, is expected to depend only on the nature of the material. However, the extent of the IAZ may depend on the nature of the substrate surface preparation and the adhesive cure time. For FM 73, preparing the aluminum substrate with the BAC treatment results in an IAZ of greater extent than occurs with FPL or STAB treatments. With the former treatments, the IAZ is larger for a 4-hour cure than with a 1-hour cure time.

Adhesive cure time seems to affect somewhat the shear modulus beyond the IAZ of an FM 73 bond. This quantity in the bulk material has a consistent value for the 1-hour adhesive cure time, no matter the substrate surface treatment which was used. A lesser value arises for the 4-hour cure period, also independent of substrate preparation. The fact that the bulk adhesive is oblivious to the residuals on the substrate is not surprising.

Shear-modulus gradients in the IAZ of an adhesive may be due in whole or in part to residual strain. Moiré measurements have been made in the laboratory on several exposed surfaces of FM 73 at different depths in the IAZ. The resulting strain-field fringes show that residual strains indeed exist and decrease with distance from the adhesive-adherend interface. Since an inverse relationship exists (for metallics) between residual strain and shear modulus,[17] the Moiré findings correspond to the URW results of shear modulus as a monotonic increasing function of adhesive thickness through the IAZ.

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