JOURNAL OF MATERIALS SCIENCE 25 (1990) 1794-1802

Non-destructive evaluation of the quality (cure) of polymeric coatings on steel food cans by means of high frequency Lamb wave propagation: a preliminary study

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Lamb wave propagation in the frequency range from 13 to 30 MHz has been used to monitor structural variations in thin polymer coatings on steel plate used in the food packaging industry. The amplitude of compressional waves reflected from water-plate interfaces was measured as a function of a continuously variable angle of incidence, to a precision of ±0.05 dB. The minima in these reflectivity curves, which signal the onset of Lamb wave propagation, were measured to a precision of ±0.1°. This precision was adequate to allow shifts in Lamb wave phase velocities due to changes in polymer structure and polymer-metal delamination, to be distinguished from changes due to overall thickness variations in the plate and structural inhomogeneities in the steel. This conclusion was reached from a statistical analysis of a large amount of data taken with polymer coatings of variable cure obtained by varying annealing times from 1 to 20 min and annealing temperatures from 170° to 237° C. The lack of systematic relationships between phase velocities and the heat treatment variables suggested that besides the degree of cure, the object of interest, the structure of the batch of polymer coatings studied also varied in other ill-defined ways. However the data remains well worth reporting to introduce a novel technique.

1. Introduction

Internal polymer coatings on steel containers are widely used in the packaging industry to prevent the contamination and impairment of flavour of food by absorbed metal. The performance of the coating as a barrier is determined by the degree of polymer cure and there is continued interest in evaluating the cure by non-destructive means. Here we report on the use of ultrasonic Lamb waves for polymer coating inspection. The degree of crosslinking affects both the isotropic elastic moduli and the density of the polymer. Correspondingly the acoustic impedance of the polymers for both bulk compressional and shear waves will be dependent on the degree of crosslinking. Wave absorption by relaxation mechanisms will also be a function of crosslinking. Therefore on two grounds, the boundary conditions containing the Lamb wave modes that may propagate in polymer coated plates, may be a function of a degree of cure.

2. Theoretical background

A theoretical résumé of wave propagation in plates will help the subsequent discussion of the experiment. In an isotropic and linearly elastic medium of density ϱ, the vector particle displacement, ψ, is related to the Lamé constants μ and λ by the equation [1]:

$$\mu\nabla^2\psi + (\lambda + \mu)\nabla(\nabla \cdot \psi) = \varrho\ddot{\psi} \tag{1}$$

For propagation in an infinite plate, the solution of this equation, subject to the boundary condition that the normal and tangential components of stress must vanish over both surfaces of the plate, produces the following dispersion relationships for the infinite but discrete set of permitted wave modes [2].

$$\frac{\tanh\,(pq/2)}{\tanh\,(qd/2)} = \frac{K^2 + q^2}{4K^2\varrho q} \quad \text{(symmetrical case)} \tag{2}$$

$$\frac{\tanh\,(pd/2)}{\tanh\,(qd/2)} = \frac{4K^2\varrho q}{(K^2 + q^2)^2} \quad \text{(anti-symmetrical case)} \tag{3}$$

Here

$$p = K(1 - c^2/c_L^2)^{1/2} \tag{4}$$

and

$$q = K(1 - c^2/c_T^2)^{1/2} \tag{5}$$

where $K = 2\pi/\omega$ is the wave vector (i.e., ω is the angular velocity) and c is the phase velocity (i.e. ω/K) for the Lamb waves; c_L and c_T are the bulk longitudinal and shear wave velocities obtaining in an unbounded medium of the same material as the plate and d is the plate thickness. For steel, the subject of the present study, the dependence of c on fd (where

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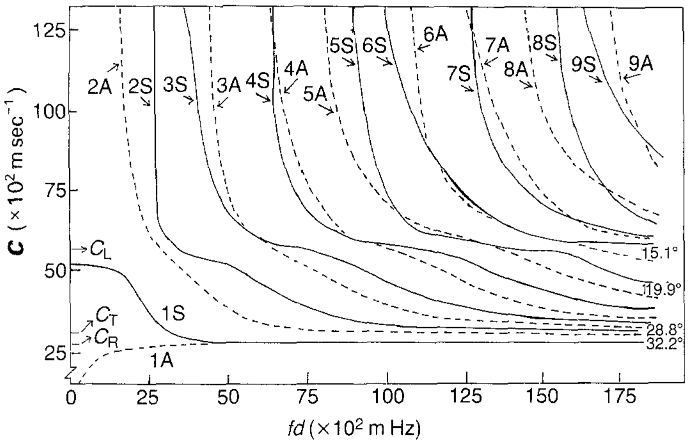

Figure 1 Dispersion relationships (phase velocity c against frequency (f) × thickness (d) for Lamb wave modes in steel plates, redrawn after Worlton [3]. Subscripts L, T and R, refer to isotropic bulk, shear and Rayleigh wave velocities in an infinitely extended medium. The angles denote the angles of incidence in water at which various modes with asymptotic phase velocities are generated. A and S denote asymmetrical (- - -) and symmetrical (——) modes, respectively.

f is frequency) for the first few symmetrical and asymmetrical modes is plotted in Fig. 1 [3, 4].

By propagating a particular mode in a frequency regime such that c is insensitive to fd, small changes in thickness of the plate or coating should not affect c. Therefore it should be feasible to detect any effect of a variation in the properties (e.g. cure) of the coating on c. As implied in the first paragraph one might expect that c (amongst other wave properties) would depend on polymer structure through a perturbation in the boundary conditions of Equation 1. Thus the basis of our technique is to measure c for selected wave modes and frequencies.

3. Experimental techniques and instrumentation

A high precision ultrasonic goniometer [5–7] was used to launch the Lamb waves. Two probes, one transmitter and one set to receive a specularly reflected signal, rotate in a plane and the vertical axis of rotation coincided with the coated surface of the plate under test. If c_w is the velocity of compressional waves in the immersion fluid (usually water) and θ is the angle of incidence, the phase velocity of the fluid measured along the surface of the plate is $c_w/\sin\theta$ [7]. For a given fd value and Lamb wave mode, the mode can be excited by the incident compressional wave providing c, as given by Equations 2 to 5, satisfies the condition [7]

$$c = c_w/\sin\theta \qquad (6)$$

The range of θ permitted by the goniometer design was from 6° to 75° corresponding to an experimental range of from 1500 to 15 000 msec^{-1} for c. Experimentally a Lamb wave excitation shows up as a sharp dip in the plot of angular dependence of the power reflection coefficient of incident compressional waves. Since c is a single valued function of fd (see Fig. 1) and modes of the same symmetry do not intersect, it is in principle always possible, knowing the value of fd, to identify the order of mode corresponding to a reflectivity maximum at a given angle. Although modes of the same orders but with different symmetry do intersect in the c–fd plots it is usually possible to identify the mode symmetry as well.

The samples for this project consisted of 34 steel plates, both sides containing a 4 μm coating of tin and one side containing a further outer coating of epoxy phenolic lacquer about 1 μm thick. Twenty samples were annealed at a temperature of 202° C for a time of from 1 to 20 min at 1 min intervals. The others were cured at temperatures of from 170 to 237° C at 5° C intervals for 10 min. The overall thickness of the plates averaged over the area of impact of the ultrasound beam was 180 μm with one standard deviation of $\pm 3\,\mu$m, when measured by a micrometer.

The high sensitivity pulse echo instrumentation and the high power narrow band immersion probes employed have been described elsewhere [8]. The 1 cm diameter air-backed probes were operated on high harmonics to produce operating frequencies of 13.6 and 30 MHz, corresponding to fd values of 2.38×10^3 and 5.25×10^3 m Hz for the thinnest samples. Inspection of Fig. 1 shows that at 13.6 MHz the 1st asymmetrical mode will have c fairly insensitive to fd, whilst at 30 MHz both the 1st order modes will have $\partial c/\partial d(fd) \rightarrow 0$. This is the condition, mentioned earlier, required to separate the effects of sample structure and thickness on Lamb wave propagation.

4. Measurements

For every sample plots were taken of reflectivity (R) against θ. In several cases these plots of coated and uncoated samples were repeated many times with the incident beam incident on different parts of the sample. This was in order to take account of possible local variations in material properties. Apart from documenting the positions of all reflectivity minima, thus identifying the wave modes present (Table I), it was also considered useful to evaluate the shape of the minima, i.e. the depth, and the width at the 3 dB drop points. In Figs 2 to 5 typical R–θ plots are shown. They have been chosen to represent the various shapes of plots (with respect to depth and width of minima and the slope of the plot outside the region of the minima, etc.) rather than equal intervals of temperature and curing times. The important features of all plots are quantified in Tables II to V and the reflectivity minima are labelled as 1st, 2nd or 3rd in order of increasing angle.

5. Statistical analysis of the angular positions of reflectivity minimum

At 13.6 MHz the corresponding mode propagations are the 2nd asymmetrical, the 1st symmetrical and the 1st asymmetrical modes, conveniently abbreviated as

TABLE I Typical analysis of propagation modes in the polymer coated plates. Illustrated for the coating cured at 202° C for 12 min.

Frequency (MHz)	Angle of incidence (degree)	Phase velocity ($\mathrm{m\,sec^{-1}}$)	Frequency × thickness ($\times 10^2\,\mathrm{m\,Hz}$)	Thickness measured (μm)	Possible Lamb wave mode consistent with measured phase velocity
13.6	10.4	8026	2.90	160	2nd A*
			4.80	353	3rd A
			7.39	544	4th A
			9.22	678	5th A
			11.90	872	6th A
			14.60	1072	7th A
			2.72	200	2nd S
			4.55	334	3rd S
			6.93	510	4th S
			9.78	719	5th S
			12.00	883	6th S
			14.00	1029	7th S
	18.5	4572	4.24	312	2nd A
			8.45	625	3rd A
			12.60	930	4th A
			2.03	159	1st S*
			6.38	470	2nd S
			10.40	765	3rd S
			14.60	1074	4th S
	32.2	2718	26.70	196	1st A*
30.5	15.8	5309	5.79	170	2nd S*
			8.92	292	3rd S
			12.90	421	4th S
			3.48	114	2nd A
			7.16	235	3rd A
			10.90	356	4th A
			14.60	480	5th A
	21.6	3937	2.49	815	1st S
			7.59	249	2nd S
			12.40	406	3rd S
			4.90	161	2nd A*
			9.86	323	3rd S
			14.73	483	4th S
	29.7	2921	4.65	152	1st S*
			11.20	366	1st A

*Actual wave excited.

13.6(2A), 13.6(1S) and 13.6(1A) respectively. At 30 MHz the corresponding mode propagations are the 2nd symmetrical, the 2nd asymmetrical, and the 1st symmetrical or asymmetrical modes, abbreviated as 30.5(2S), 30.5(2A) and 30.5(1S/1A) respectively. The change in angle of a minimum caused by a change Δd in sample thickness is given by

$$\Delta\theta_d = -[\partial c/\partial(fd)]\,(f/c)\tan\theta\Delta d \qquad (7)$$

The best estimate for $\Delta\theta_d$ we can obtain for the present samples is obtained from Fig. 1, i.e. treating the entire sample to be made of steel. Thus one obtains

$$\begin{bmatrix} 13.6(2A) & [\partial c/\partial(fd)] \approx & -7 \\ 13.6(1S) & [\partial c/\partial(fd)] \approx & -1.6 \\ 13.6(1A) & [\partial c/\partial(fd)] \approx & 0.06 \\ 30.5(2S) & [\partial c/\partial(fd)] \approx & 0.5 \\ 30.5(2A) & [\partial c/\partial(fd)] \approx & -0.8 \\ 30.5(1S/2A) & [\partial c/\partial(fd)] \approx & 0 \end{bmatrix} \qquad (8)$$

In separate thickness measurements, averaged over the area of impact of the ultrasound beam with a digital micrometer, one standard deviation in thickness reading was $\pm 3\,\mu$m and about 90% of the data lay within $\pm 5\,\mu$m of the mean, as could be expected approximately, if Gaussian statistics held. Thickness variations from sample to sample and point to point on a given sample were undetectable outside the above spread of data. Therefore it seems reasonable to take $\Delta d = \pm 5\,\mu$m to estimate the limits between which $\Delta\theta_d$ will be for the majority of the samples. Then taking normal c and θ values from Table I, the theoretical sample-to-sample variations in θ due to thickness tolerances are given by

$$\begin{bmatrix} 13.6(2A) & \Delta\theta_d & = & \pm 0.6^\circ \\ 13.6(1S) & \Delta\theta_d & = & \pm 0.45^\circ \\ 13.6(1A) & \Delta\theta_d & = & \pm 0.5^\circ \\ 30.5(2S) & \Delta\theta_d & = & \pm 0.23^\circ \\ 30.5(2A) & \Delta\theta_d & = & \pm 0.7^\circ \\ 30.5(1S/1A) & \Delta\theta_d & = & \pm 0.0^\circ \end{bmatrix} \qquad (9)$$

Now by inspection of Table V and Fig. 1, taking averages over all modes and frequencies, the maximum deviation in the angle of a minimum from point to point along the surface of a single sample is only ±0.175° and ±0.13° for an uncoated and coated sample, respectively. These relatively low values imply that the few randomly selected samples inspected in

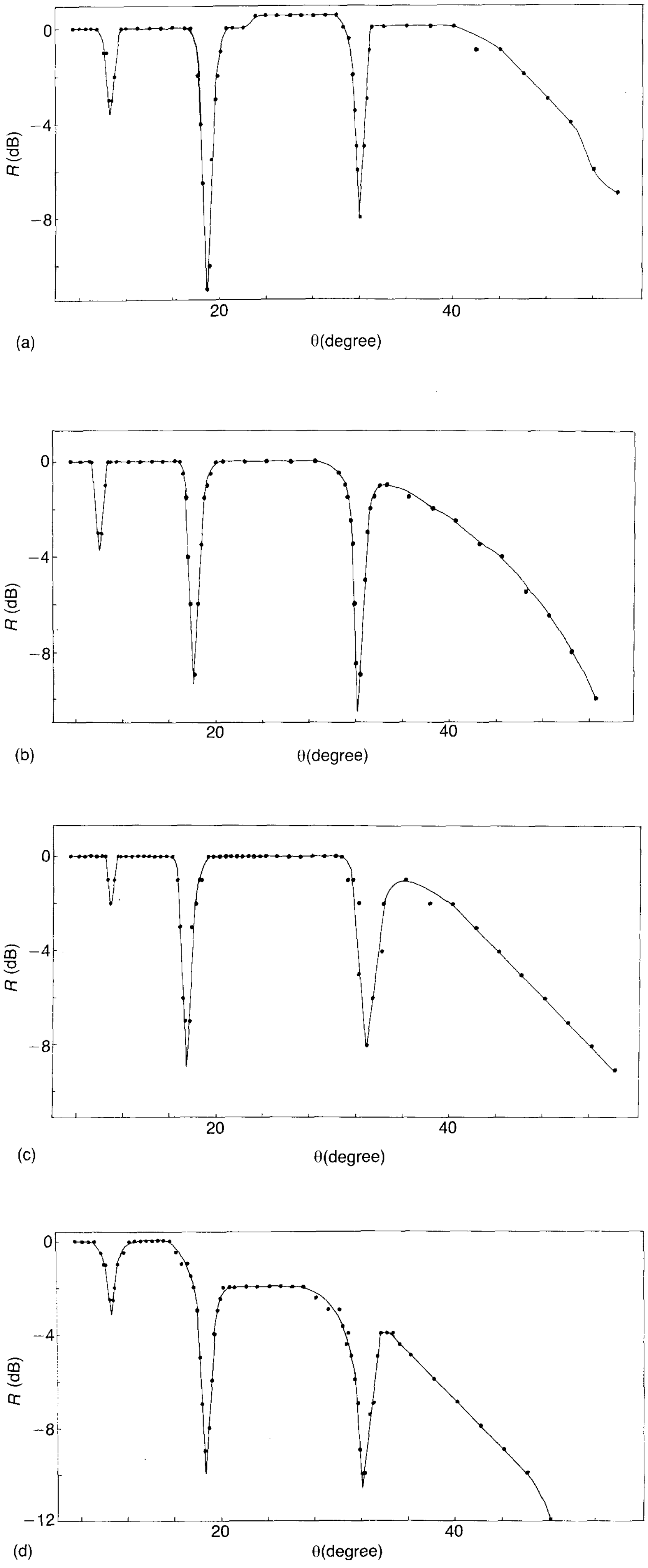

Figure 2 Dependence of reflectivity *R* on angle of incidence θ for 13.6 MHz compressional waves incident on polymer-coated steel plates. Polymer annealed at (a) 202° C for 17 min, (b) 237° C for 10 min, (c) 202° C for 9 min, (d) 202° C for 16 min. *R* is measured in decibels (dB) relative to the maximum value obtained in the vicinity of the smallest angle of measurement.

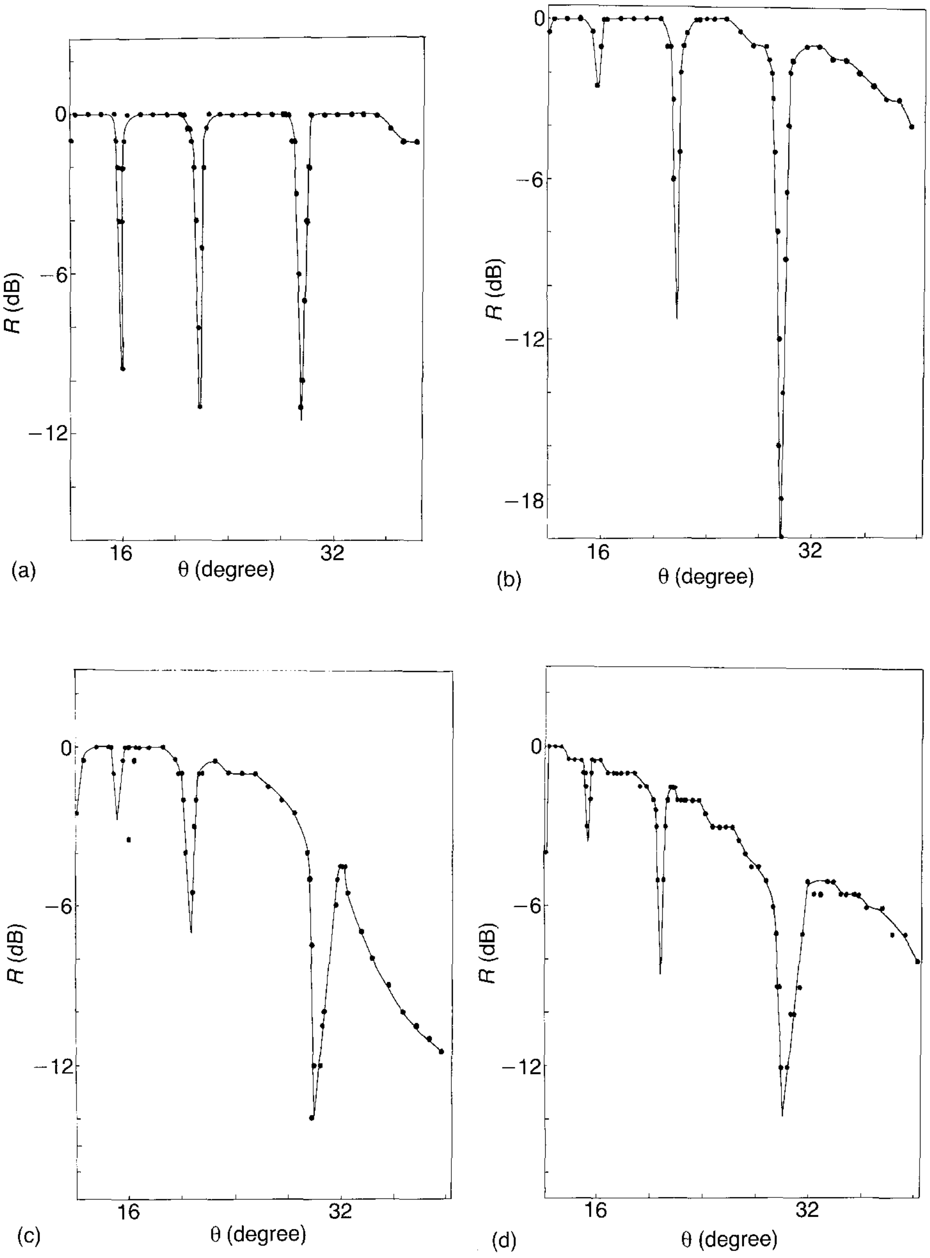

Figure 3 Plot of R against θ as Fig. 2, for 30.5 MHz ultrasound. Polymer annealed at (a) 210° C for 7 min, (b) 202° C for 7 min, (c) 202° C for 4 min and (d) 202° C for 2 min.

this way were spatially uniform, i.e. of homogeneous cure with local variations in thickness of less than $\approx 1.5\,\mu$m (standard deviation). Clearly the standard deviations in micrometer thickness measurements mentioned earlier stem primarily from error in the measurement instrument. Thus the data in Equation 8 may be compared directly with experimental variations in the angles of reflectivity minima between samples having polymer coatings of different cure (given in Table V). The maximum deviations from sample to sample are

$$\begin{bmatrix} 13.6(2\mathrm{A}) & \Delta\theta & = & \pm 0.7^\circ \\ 13.6(1\mathrm{S}) & \Delta\theta & = & \pm 1.0^\circ \\ 13.6(1\mathrm{A}) & \Delta\theta & = & \pm 0.65^\circ \\ 30.5(2\mathrm{S}) & \Delta\theta & = & \pm 0.45^\circ \\ 30.5(2\mathrm{A}) & \Delta\theta & = & \pm 1.2^\circ \\ 30.5(1\mathrm{S}/1\mathrm{A}) & \Delta\theta & = & \pm 0.5^\circ \end{bmatrix} \qquad (10)$$

Comparisons of Equations 9 and 10 give clear evidence of a contribution to $\Delta\theta$ arising from a source other than thickness variations, presumably the state of cure or other microstructural variations in the polymer coatings or the underlying metal. Denoting this contribution by $\Delta\theta_c$ and assuming

$$[\Delta\theta]^2 \approx [\Delta\theta_d]^2 + [\Delta\theta_c]^2 \qquad (11)$$

then for the different mode-frequency combinations listed in the order given in Equations 9 and 10 we have

$$\begin{bmatrix} 13.6(2\mathrm{A}) & \Delta\theta_c & = & \pm 0.36^\circ \\ 13.6(1\mathrm{S}) & \Delta\theta_c & = & \pm 0.89^\circ \\ 13.6(1\mathrm{A}) & \Delta\theta_c & = & \pm 0.65^\circ \\ 30.5(2\mathrm{S}) & \Delta\theta_c & = & \pm 0.38^\circ \\ 30.5(2\mathrm{A}) & \Delta\theta_c & = & \pm 0.97^\circ \\ 30.5(1\mathrm{S}/2\mathrm{A}) & \Delta\theta_c & = & \pm 0.5^\circ \end{bmatrix} \qquad (12)$$

with a mean value of ± 0.6° which is six times greater than the experimental error in an individual angular measurement. Now from a study of a limited number of samples without polymer coatings the maximum deviations $\Delta\theta$ from sample to sample were found to be

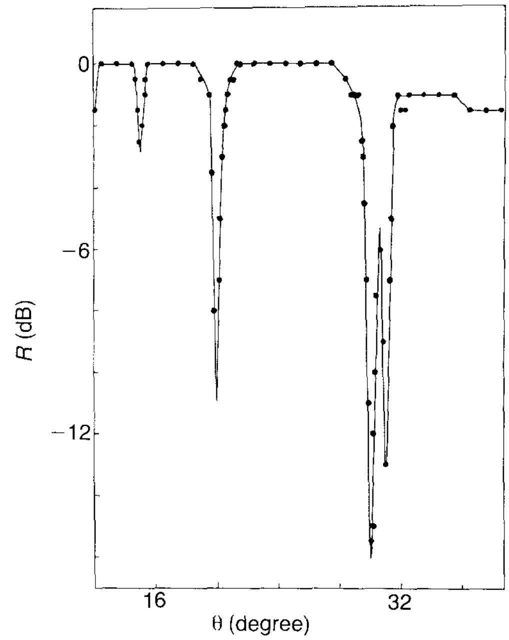

Figure 4 Plot of R against θ as Fig. 3, but illustrating peak splitting of one minima due to surface wave excitation. Polymer annealed at 180° C for 10 min.

(see Figs 5a and b)

$$\begin{bmatrix} 13.6(2A) & \Delta\theta & = & \pm 0.6^\circ \\ 13.6(1S) & \Delta\theta & = & \pm 0.4^\circ \\ 13.6(1A) & \Delta\theta & = & \pm 0.1^\circ \\ 30.5(2S) & \Delta\theta & = & \pm 0.2^\circ \\ 30.5(2A) & \Delta\theta & = & \pm 0.4^\circ \\ 30.5(1S/1A) & \Delta\theta & = & \pm 0.2^\circ \end{bmatrix} \qquad (13)$$

From Equations 9, 11 and 13 the maximum deviations in $\Delta\theta_c$ between uncoated samples are

$$\begin{bmatrix} 13.6(2A) & \Delta\theta_c \approx 0^\circ \\ 13.6(1S) & \Delta\theta_c \approx 0^\circ \\ 13.6(1A) & \Delta\theta_c \approx 0.1^\circ \\ 30.5(2S) & \Delta\theta_c \approx 0^\circ \\ 30.5(2A) & \Delta\theta_c \approx 0^\circ \\ 30.5(1S/2A) & \Delta\theta_c \approx 0.2^\circ \end{bmatrix} \qquad (14)$$

with a mean value of 0.05, which are comparable with the experimental errors in individual angular measurements. Thus no variations in metal microstructures from sample to sample are detectable within the limits of experimental error, and the much larger values of $\Delta\theta_c$ of Equation 12 applying to polymer coated samples, can be attributed unequivocally to variations in polymer microstructure.

6. Statistical analysis on the depths of reflectivity minima

Performing a similar averaging exercise on the depth of the reflectivity minima, the maximum deviation in depth in point-to-point measurements in an uncoated sample is 1.34 dB, whilst the figure for a coated sample is not much higher, ≈ 2.5 dB. The latter figure also applies (see Figs 5a and b) for variations from one uncoated sample to another, whereas the average of the maximum deviations from one coated sample to another due to cure time and temperature variations is ± 3.5 dB, i.e., ± 2.16 dB (a factor of 1.5) greater. The conclusion is that variations in polymer microstructure do affect the depth of the reflectivity minima but not very strongly, i.e. the effect is only marginally detectable above the "background" spatial and sample-to-sample variations typical of uncoated samples.

TABLE II Variations of the angular position of reflectivity minima. Probe-specimen separation was 10 cm for a frequency of 13.6 MHz and 6 cm for 30.5 MHz.

(a) Variation with annealing times for a temperature of 202° C

Period of heating (min)	Angular position (degree)					
	1st minimum		2nd minimum		3rd minimum	
	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz
1	10.90	15.80	18.80	22.00	32.00	29.90
2	10.90	15.20	17.40	20.80	33.20	30.10
3	10.70	15.70	18.60	21.80	32.00	29.60
4	10.90	15.20	17.20	20.70	33.20	30.10
5	10.90	15.70	18.90	21.70	32.00	29.70
6	11.00	15.30	17.40	20.70	33.40	30.20
7	10.60	15.70	18.50	21.80	32.30	29.80
8	10.60	15.70	18.60	21.60	32.20	29.40
9	10.90	15.40	17.50	20.80	33.00	30.10
10	11.00	15.20	17.50	20.90	33.30	30.00
11	10.90	15.10	17.30	19.80	33.30	29.80
12	10.40	15.80	18.50	21.60	32.20	29.70
13	10.90	15.20	17.40	20.80	33.20	30.20
14	11.00	15.10	17.40	21.90	33.40	30.00
15	10.50	15.90	18.60	21.90	32.40	29.60
16	10.60	15.80	18.70	21.70	32.20	29.60
17	10.80	15.90	19.00	21.90	32.10	29.60
18	10.90	15.80	18.80	22.20	32.20	29.70
19	11.50	15.50	18.20	21.60	33.10	30.40
20	11.00	15.90	19.20	22.20	32.00	29.60

(b) Variation with curing temperatures (cure time, 10 min)

Curing temperature (°C)	Angular position (degree)					
	1st minimum		2nd minimum		3rd minimum	
	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz
170.00	10.60	15.90	18.60	22.00	31.90	29.80
175.00	10.70	15.20	17.00	20.40	33.00	30.20
180.00	10.70	15.10	17.10	20.00	32.90	30.10
185.00	10.60	16.00	18.60	22.20	31.80	29.60
190.00	11.00	15.10	17.40	20.50	33.00	30.10
195.00	10.90	15.20	17.30	20.60	33.00	29.90
200.00	10.80	15.60	18.80	21.70	31.80	29.50
205.00	10.60	15.70	18.50	21.70	32.00	29.50
210.00	10.40	16.00	18.40	21.90	32.00	29.60
215.00	11.20	15.40	17.40	21.00	33.10	30.00
220.00	10.90	16.00	18.70	22.20	31.90	29.70
225.00	11.20	15.30	18.00	21.20	33.00	30.00
230.00	11.30	15.40	18.20	21.20	33.00	30.00
237.00	10.10	15.60	18.10	21.00	32.20	29.60

7. Other general aspects of the results

For the 30.5(1S/2A) and 13.6(1A) cases, i.e. thickness insensitive combinations, the average value of the angles of the reflectivity minima are 1° higher for coated specimens than for uncoated samples. For other four mode-frequency combinations, i.e.

TABLE III Variations of the width and depth of the reflectivity minima at operating frequencies of 13.6 and 30.5 MHz. Probe-specimen separations were 10 and 6 cm for the transmitters and receiving probes respectively

(a) Variation with curing temperatures (cure time, 10 min)

Curing temperature (°C)	Width of 2nd minimum (mm)		Depth (dB)							
			1st minimum		2nd minimum		3rd minimum		4th minimum	
	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz
170.00	3.50	2.00	2.50	5.00	9.40	8.75	8.30	12.60	–	–
175.00	3.50	2.00	2.50	2.40	7.70	7.35	8.30	14.35	–	13.65
180.00	4.00	1.50	2.40	2.30	7.90	10.80	8.00	15.30	–	12.50
185.00	3.50	2.00	3.00	6.30	10.00	8.35	7.90	11.00	–	–
190.00	3.00	1.00	2.50	2.70	9.00	12.40	8.70	13.05	–	15.95
195.00	3.00	1.50	2.30	3.00	7.70	10.20	8.40	10.85	–	11.75
200.00	2.50	0.50	3.20	4.30	11.30	15.00	8.30	15.80	–	–
205.00	3.00	1.00	2.70	4.60	9.80	12.50	8.00	14.60	–	–
210.00	4.00	1.00	3.30	9.50	9.10	11.00	8.40	11.70	–	–
215.00	3.00	1.00	2.60	2.70	9.30	12.75	8.50	12.50	–	14.70
220.00	3.00	1.50	3.30	5.00	10.40	8.40	8.30	12.50	–	–
225.00	3.50	1.00	2.30	5.00	9.70	13.75	8.90	14.05	–	–
230.00	3.50	1.00	2.50	4.00	9.00	11.00	8.30	11.00	–	13.60
237.00	3.00	1.50	3.50	2.75	9.20	11.25	10.00	18.00	–	–

(b) Variation with curing times at a temperature of 202° C

Curing time (min)	Width of 2nd minimum (mm)		Depth (dB)					
			1st minimum		2nd minimum		3rd minimum	
	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz	13.6 MHz	30.5 MHz
1	3.5	1.5	3.0	5.6	9.5	10.7	7.5	11.7
2	4.5	2.0	3.0	3.1	7.5	7.4	8.2	10.1
3	2.5	2.0	3.0	4.0	10.5	8.5	9.2	11.0
4	4.5	3.0	2.0	2.7	7.7	5.2	10.0	10.5
5	3.0	1.5	2.5	3.8	10.9	9.5	8.2	13.2
6	4.0	2.0	2.0	2.9	7.9	9.5	8.0	15.2
7	5.0	1.0	3.0	2.6	8.0	11.8	8.5	18.8
8	3.0	2.0	3.0	3.0	10.3	9.0	7.0	15.5
9	3.5	1.0	2.0	2.5	8.5	12.5	7.6	11.5
10	3.0	1.5	3.0	2.8	8.9	9.5	8.0	11.0
11	3.0	1.5	2.3	2.0	9.0	11.0	8.5	13.0
12	4.0	1.5	3.0	4.5	9.0	10.0	8.0	16.2
13	3.0	1.0	2.5	3.0	9.0	11.4	8.5	11.7
14	3.5	1.0	2.2	3.0	8.8	15.0	10.1	12.5
15	3.0	2.0	3.0	3.8	10.6	8.0	8.1	10.7
16	4.0	2.0	2.1	4.3	8.6	8.0	7.3	14.0
17	3.0	1.5	3.3	4.3	11.3	8.7	8.2	11.2
18	3.5	1.5	3.0	3.0	9.3	9.5	8.5	9.5
19	3.0	1.5	2.3	3.8	11.0	10.8	10.0	14.8
20	3.5	2.0	3.0	3.8	9.7	8.0	8.5	10.2

thickness-sensitive cases, there is no statistically significant difference between the two averages. This situation reflects the large negative values of $\Delta\theta_c$ (with $|\Delta\theta_c| > |\Delta\theta_d|$) arising for some of the mode–frequency combinations. Now the polymer coating would be expected to have lower values of c_L and c_T than does the steel and tin substrate. Correspondingly the frequency equations would predict a lower value of c for a given fd in the coating, i.e., we could expect the coating to lower slightly the mean value of c averaged over the volume of the specimens. Thus the shift of $+1°$ in the angles of the reflectivity minima for the 30.5(1S/1A) and 13.6(1A) cases is plausible whilst the negative shifts obtained in some samples with some of the other mode–frequency combinations are difficult to understand.

Finally whilst a dependence of both the positions and the depths of the reflectivity minima on the structure of polymer coatings has been established, there is no systematic relationship between these quantities and the variables of heat treatment. Since c_L, c_T and, therefore, c should increase with the degree of cross-linking in the polymer it would have been feasible to expect the reflectivity minima to shift back towards the positions occurring with an uncoated sample as the time and temperature of heat treatment are increased from small values. It seems possible that there are variations in polymer structures from sample to sample which are caused by factors other than heat treatment.

Surface analysis of a number of specimens shows that there is evidence of areas of delamination between the polymer coating and the underlying metal (dark regions in Fig. 6), which will undoubtedly have a major influence on Lamb wave propagation [7]. A striking feature of the reflectivity-θ plots for uncoated

TABLE IV Typical variations in the depth and angular position of reflectivity minima caused by varying the position of intersection of the probe beam along a line across the sample surface. (Zero position is arbitrary and does not relate to a sample edge; operating frequency is 30.5 MHz in all cases).

(a) Sample cured at 170° C for 10 min

Probe beam position (mm)	Depth (dB)					
	1st minimum	2nd minimum	3rd minimum	1st minimum	2nd minimum	3rd minimum
0.00	5.00	6.00	9.50	16.00	21.80	29.60
10.00	5.00	7.00	9.00	16.00	21.70	29.80
20.00	3.30	7.20	12.00	16.00	21.90	29.80
30.00	4.60	8.50	11.00	15.80	21.80	29.70
40.00	6.00	9.50	6.50	16.00	22.00	29.80
50.00	3.50	8.00	12.80	15.90	22.00	29.70
60.00	4.90	8.00	12.00	16.00	22.00	29.80
70.00	7.00	11.50	11.50	15.90	22.30	29.80
80.00	3.75	10.00	12.50	16.00	22.20	29.80
90.00	4.20	8.50	12.00	16.00	22.10	29.80

(b) Sample cured at 200° C for 10 min

Probe beam position (mm)	Amplitude at normal incidence (dB)	(mm)	(dB)
0.00	24.00	50.00	25.00
5.00	24.00	55.00	25.00
10.00	25.00	60.00	25.50
15.00	24.50	65.00	25.00
20.00	25.00	70.00	25.50
25.00	24.00	75.00	25.50
30.00	25.00	80.00	25.00
35.00	25.00	85.00	25.50
40.00	24.50	90.00	26.00
45.00	25.00		

(c) Sample without a polymer coating

Probe beam position (mm)	Depth (dB)			Angular position (degree)		
	1st minimum	2nd minimum	3rd minimum	1st minimum	2nd minimum	3rd minimum
0.00	3.9	6.3	7.2	15.2	20.9	28.7
20.00	4.0	7.5	10.0	15.2	21.2	28.8
40.00	5.3	8.0	8.7	15.4	21.2	28.7
60.00	5.7	8.0	8.5	15.3	21.0	28.8
80.00	4.9	6.5	12.2	15.2	21.2	29.0

TABLE V Ranges of the angular position and depth of the 1st, 2nd and 3rd reflectivity minima for samples with and without polymer coatings. Frequencies used were 13.6 and 30.5 MHz. This range covers such variables as samples, position of impact of beam and curing conditions. Only the 1A mode at 13.6 MHz, and the 1S/1A modes at 30.5 MHz produce angles of minima insensitive to thickness variations. The effect of position variations alone on the depth of minima occurring with laquered samples are almost (though not quite) as small as the corresponding variations arising with unlacquered samples (see Table IV).

Range of angular position of minima (degrees) ±0.1

Frequency used (MHz)	Actual mode excited	Lacquered samples		Unlacquered samples
		Samples of a constant curing temperature	Samples of a constant curing temperature	
13.6	2A	10.4–11.5	10.1–11.3	10.3–10.8
	1S	17.2–19.2	17.0–18.8	18.5–18.6
	1A	32.0–33.4	31.9–33.1	31.4–31.6
30.5	2S	15.1–15.9	15.1–16.0	15.2–15.6
	2A	19.8–22.2	20.0–22.2	20.9–21.4
	1S	29.4–30.4	29.5–30.2	28.7–29.2
13.6	2A	2.0–3.3	2.3–3.5	2.5–3.1
	1S	7.5–11.3	7.7–11.3	11.3–13.8
	1A	7.0–10.1	7.90–10.0	10.5–13.1
30.5	2S	2.0–5.6	2.30–9.5	3.2–5.3
	2A	5.2–11.8	7.35–15.0	6.3–9.5
	1S	9.5–18.8	10.85–18.0	7.2–12.3

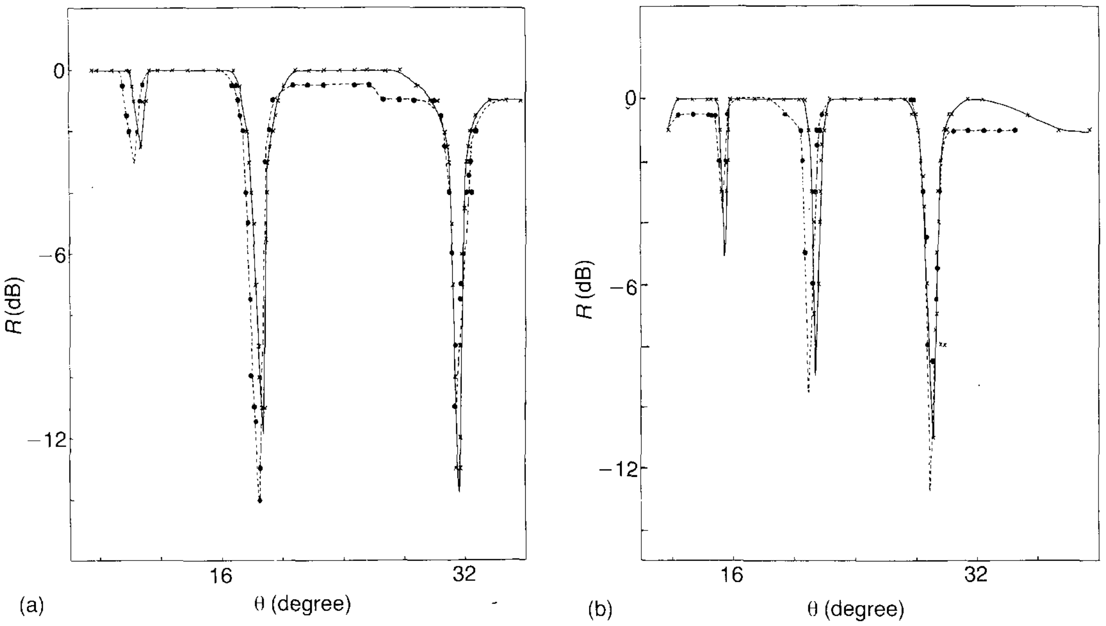

Figure 5 Comparison of the dependence of reflectivity (R) of ultrasound for two steel plates without polymer coating, showing the typical maximum differences in the positions and depths of the minima obtained. (a) 13 MHz and (b) 30.5 MHz. (R measured as in Fig. 2.)

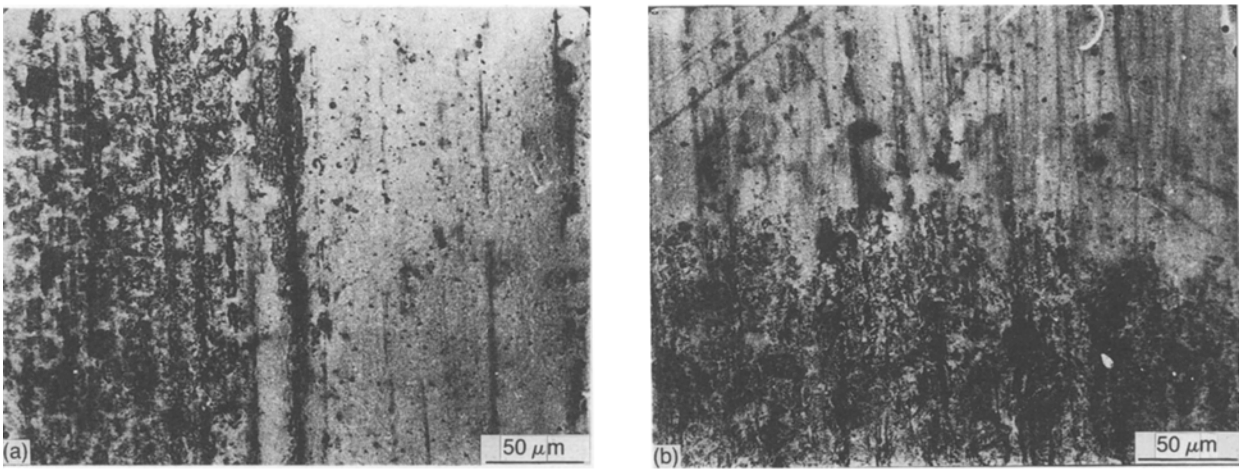

Figure 6 Typical microstructures (× 325 microscope photographs) taken from two different positions on a sample annealed at 200° C for 10 min. (a) (b)

samples is the flat nature of the plots to each side of each minima. In contrast for many, though not all, polymer-coated samples, the plots display a pronounced droop, with the reflectivity falling off rapidly with increasing angle, outside the regimes where Lamb wave propagation takes place. It is quite plausible that this effect is associated with disbonding between the polymer and metal.

8. Conclusions

Changes in the phase velocity and other properties associated with high frequency Lamb wave propagation can be measured with sufficient accuracy to detect a sensitivity of these properties to the microstructure of thin polymer coatings. Further experiments seem worthwhile provided that a range of specimens with more carefully controlled microstructural variations are employed.

Acknowledgement

The authors would like to thank the Metal Box Co., Wantage, Oxon, for the provision of samples.

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Received 4 October 1988
and accepted 28 February 1989