

MEASUREMENT OF ADHESIVE-ADHEREND INTERLAYER PROPERTIES USING ACOUSTIC MICROSCOPY

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INTRODUCTION

There is considerable uncertainty about the mechanism of adhesive bonding and, in particular, the changes occurring during environmental attack which greatly reduce the bond strength [1]. This lack of understanding hampers the development of better adhesive systems and also makes the development of non-destructive evaluation methods very difficult since it is not certain what properties should ideally be measured.

The standard surface pre-treatments used on aluminum adherends in aerospace applications produce a honeycomb-like oxide structure on the adherend surface, and the adhesive (or primer if one is used) penetrates some distance into the honeycomb cells, the depth of penetration depending on the pre-treatment used and on the viscosity of the primer or adhesive. The overall thickness of this 'interlayer' between the bulk adhesive (or primer) and the bulk adherend in a typical aluminum-epoxy joint is typically only of the order of $1\mu\text{m}$ and, even over this distance, its properties may be a function of depth depending on the adhesive penetration and the honeycomb structure. It is therefore extremely difficult to measure the mechanical properties of the interlayer.

Recent developments in acoustic microscopy have made it possible to carry out accurate wave velocity measurements at frequencies up to 1 GHz where the wavelength approaches $1\mu\text{m}$, the velocity being obtained by Fourier analysis of the $V(z)$ curve [2]. If these measurements could be carried out on samples with the complex structure found in the interlayer of adhesive joints, it would be possible to measure the velocity of a surface wave whose energy is predominantly contained within the interlayer. This opens up the possibility of measuring the properties of the interlayers produced by different surface preparations, and also of monitoring the changes which occur during environmental attack.

Most previous quantitative acoustic microscopy of multi-layer systems has been done at frequencies around 200-400 MHz, and has been limited to relatively simple, low attenuation systems such as gold plated silicon wafers (see, for example, [3,4]). It was therefore necessary to demonstrate that satisfactory measurements could be obtained on the much more complex structures found in adhesive joints where a honeycomb oxide structure is partially penetrated by an attenuative polymer (the adhesive or primer). In order to do this, tests have

been carried out using 225, 820 and 980 MHz center frequency lenses on plain, polished aluminum, polished aluminum coated with thin layers of polymer, anodised aluminum and anodised aluminum coated with polymer. This preliminary study is reported here.

EXPERIMENTS

An aluminum/lithium alloy (8090) was used as the substrate for the experiments. Quantitative Acoustic Microscopy (QAM) requires a good surface finish, ideally with local flatness to within a tenth of a wavelength, or about $0.3\text{ }\mu\text{m}$ at 1 GHz. It was therefore necessary to polish the aluminum prior to measurement.

For the initial experiments on coated samples, it was desirable to use specimens coated with a small, well controlled thickness of polymer. This was most easily achieved by spin coating PMMA onto a polished aluminum substrate, rather than by attempting to bond a very thin layer of adhesive to the substrate. Various concentrations of PMMA dissolved in toluene were therefore spin coated onto polished aluminum substrates. Adhesion to the substrate was not found to be a problem, and the resultant coating was reasonably uniform, with PMMA concentrations of 3% and 10% yielding coating thicknesses of approximately $0.2\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ respectively, as measured by optical spectrophotometry.

The anodised specimens were produced by phosphoric acid anodisation (PAA) of polished aluminum substrates, the thickness on the samples used in this investigation being approximately $0.2\text{ }\mu\text{m}$. The thickness was determined by taper polishing, and checked by examining the cross-section in a scanning electron microscope.

Measurements were taken using three different acoustic lenses, with center frequencies of 225, 820 and 980 MHz. The 225 MHz lens had a cylindrical cavity, while the other two lenses had spherical cavities. When using the higher frequency lenses it was necessary to heat the water used as couplant to about 50°C , in order to reduce the attenuation. Twenty five measurements were made at each frequency over a small area of the surface, and this enabled an assessment of the accuracy at each frequency, as well as giving an indication of the scatter due to the inhomogeneity of the samples.

RESULTS

General

It had initially been thought that the highly inhomogeneous nature of the oxide might preclude acoustic measurements, but it was found that good quality $V(z)$ s were easily obtainable between 225 and 980 MHz. A second potential source of difficulty, namely the attenuative nature of the PMMA coating, was not significant for the thicknesses of coating employed. Figs 1a, 1b, 1c, 1d, 1e and 1f show $V(z)$ curves obtained with the 225 MHz lens for polished aluminum, anodised aluminum, polished aluminum coated with a $0.2\text{ }\mu\text{m}$ layer of PMMA, polished aluminum coated with a $1.0\text{ }\mu\text{m}$ layer of PMMA, anodised aluminum coated with a $0.2\text{ }\mu\text{m}$ thick layer of PMMA and anodised aluminum coated with a $1.0\text{ }\mu\text{m}$ thick layer of PMMA respectively. Fig 2 shows the corresponding results obtained with the 980 MHz lens. The signal-noise ratio is much poorer on the $V(z)$ curves at 980 MHz, but satisfactory analysis could still be carried out.

There are two main qualitative differences in the raw data between the various specimens. The first is a difference in the periodicity of the oscillations near focus: the oscillations are associated with various types of acoustic wave propagating along the surface, and a change in the periodicity represents a change in the velocity of the wave. This effect is small for most of the specimens, and not easily detectable by eye. The second difference is much more striking, and may be seen by comparing the $V(z)$ s at 225 MHz obtained on aluminum coated with $0.2\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$ layers of PMMA (Figs 1c and 1d). A second mode with a larger periodicity begins to dominate the $V(z)$, particularly at higher negative defocus. This mode is called a pseudo-Sezawa wave, and is characteristic of certain coating-substrate combinations. The pseudo-Sezawa wave is highly dispersive, and QAM is therefore extremely sensitive to changes in the thickness or elastic constants of the layer when this mode is strongly excited.

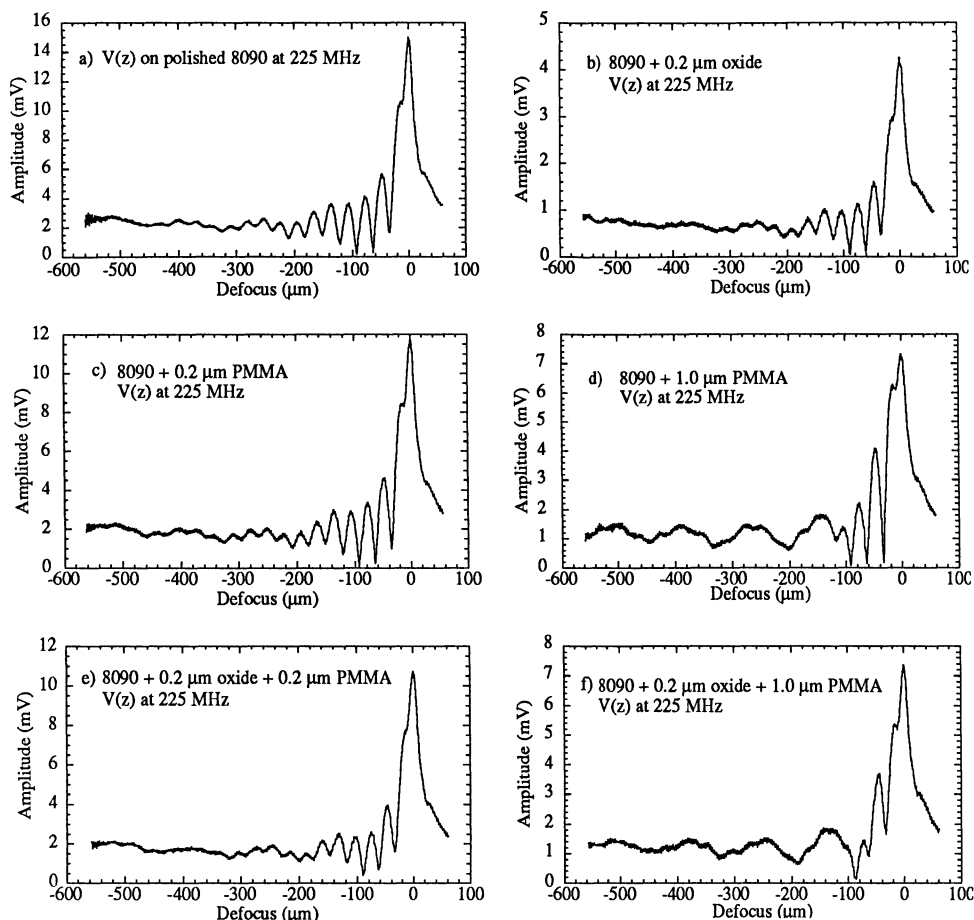


Figure 1. $V(z)$ curves at 225 MHz on different samples.

Figure 3 shows the velocities of the mode closest to focus, i.e. the Rayleigh type mode, obtained at 25 points within a 4 mm² area for the polished aluminum and a 1 mm² area for the anodised materials. One reason for the scatter in velocity is the polycrystalline nature of the substrate. At 225 MHz, the insonified area averages over approximately 10 grains at average values of defocus. When the frequency is increased to 980 MHz, the insonified area is comparable to that of a single grain. This indicates the sensitivity of the technique, since the error at each individual point is usually much smaller than the overall scatter. Aluminum is only weakly anisotropic, and any effects due to texture are not noticeable for this orientation of 8090. Summaries of the Rayleigh type mode velocities measured at each frequency are presented in Table 1. The scatter in velocity is quite high for some of the materials, and this can result from surface roughness, weak excitation of the SAW, or non-uniformities in the layer thickness. These effects are discussed in more detail in the next section. It would be expected that the Rayleigh wave on the polished aluminum sample would be non-dispersive, so the velocities at 225, 820 and 980 MHz would be the same. The difference between the measured velocities at 225 MHz and the two higher frequencies exceeds the estimated error bounds due to random effects and appears to be due to a small systematic difference between the measurements made with the three lenses.

Errors in QAM

The best figures quoted for line-focus beam acoustic microscopy at 225 MHz are a relative error of 0.01% and an absolute accuracy of 0.05% in the velocity [5]. Such figures

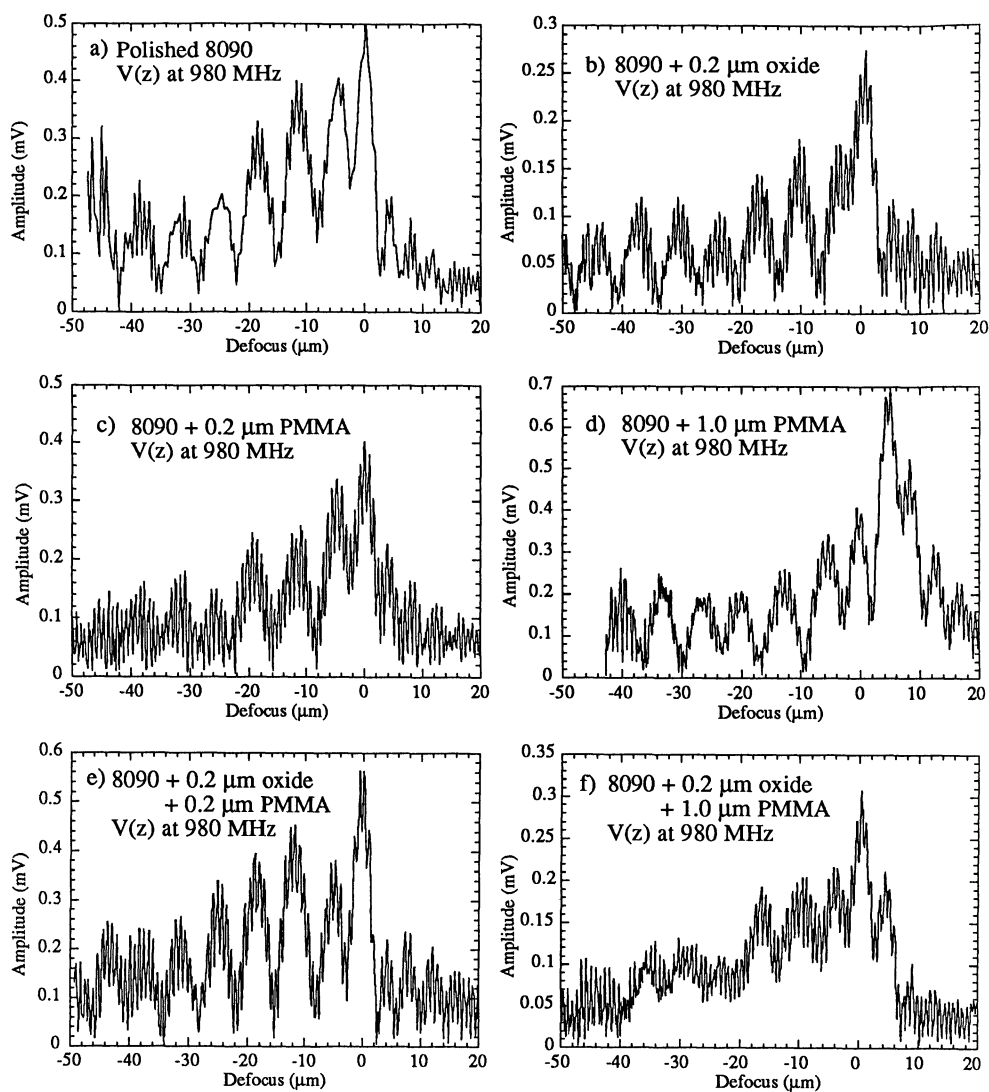


Figure 2. $V(z)$ curves at 980 MHz on different samples.

Table 1. Summary of measured SAW velocities. (The quoted errors refer to the scatter across the material, and do not include systematic errors in the analysis.)

Specimen	SAW velocity (m/s)		
	@ 225 MHz	@ 820 MHz	@ 980 MHz
Polished Al (8090)	3225 ± 5	3250 ± 15	3275 ± 20
Polished Al + 0.2 μm PMMA	3215 ± 5	3120 ± 55	3285 ± 30
Polished Al + 1.0 μm PMMA	3140 ± 25	-	3180 ± 90
Anodised Al	3205 ± 10	3270 ± 100	3320 ± 40
Anodised Al + 0.2 μm PMMA	3175 ± 10	3165 ± 75	3205 ± 100
Anodised Al + 1.0 μm PMMA	3060 ± 25	3200 ± 200	3100 ± 150

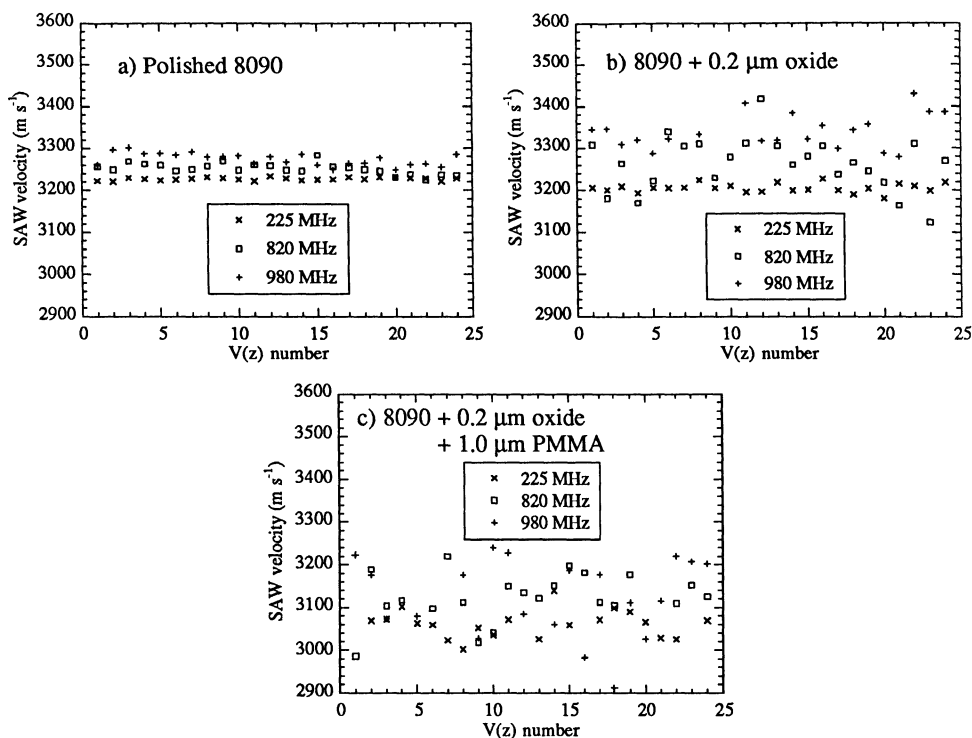


Figure 3. Measured SAW velocities at 25 positions in (a) a 4 mm² area of plain, polished aluminum; (b) a 1 mm² area of anodised aluminum; (c) a 1 mm² area of anodised aluminum coated with 1 µm PMMA.

apply only to ideal single crystal materials, and the errors are considerably higher for the inhomogeneous materials studied here. One cause of increased error is surface roughness. Li [6] has calculated the effect of periodic surface roughness on Rayleigh wave velocities as measured at 225 MHz in the LFB acoustic microscope. He found that the change in velocity from that for a smooth surface varied from 0.2% for a height/period ratio of 0.1 with 1 µm period, to 3% for a height/period ratio of 0.3 with 3 µm period.

A second cause for increased errors is inhomogeneity, since this increases scatter in the near surface region. In mild cases, the predominant effect is to increase the attenuation of the SAW. If the attenuation is sufficient to reduce the number of oscillations to two or three, then the errors in the estimation of the velocity from the Fourier analysis can become as high as a few percent. A similar effect can arise when more than one mode is present in the $V(z)$. An example is shown in Fig 1f, where the Rayleigh-type mode, i.e. the mode closest to focus, is not the predominant mode at 225 MHz. Only two or three oscillations associated with this weakly excited mode are present in the $V(z)$, and this can lead to large systematic errors in the analysis as mentioned. Although it is possible to correct for the peak position in the FFT of a highly attenuated sinusoid [4], this is again only really effective on reasonably homogeneous materials.

Table 2. Estimated standard deviations in velocity for $V(z)$ analysis on polished aluminum.

	Frequency (MHz)		
	225	820	980
Relative error at a single point (m/s)	2.0 (0.06%)	10 (0.3%)	8 (0.25%)
Absolute accuracy (m/s)	10 (0.3%)	40 (1.2%)	30 (0.9%)
Scatter along specimen (m/s)	3.5 (0.1%)	15 (0.5%)	18 (0.6%)

The difficulties with inhomogeneity and roughness tend to increase as the frequency is increased, and there are two reasons for this. Firstly, the wavelength is decreased, and secondly, a smaller area is insonified by the acoustic lens, since the focal length of the lens must be reduced owing to higher attenuation in the water at high frequencies. The shorter focal length means that less negative defocus is available. This in turn can result in fewer oscillations being available, which decreases the accuracy of the analysis. Particularly at high frequencies, the combination of two modes, roughness and inhomogeneity can make the $V(z)$ extremely difficult to interpret. An indication of the errors for the Rayleigh mode obtained in tests on the plain, polished aluminum sample is given in Table 2.

The relative error in Table 2 refers to a series of 25 $V(z)$ s taken at the same point on the specimen. At high frequencies, the values are considerably greater than at 225 MHz since the measurements themselves are considerably noisier, and a smaller range of negative defocus is available. The absolute accuracy refers to uncertainty in the analysis for a single $V(z)$, and has been estimated by conducting the analysis using windows of different shapes [7], and over different regions of the $V(z)$. Temperature effects and differences between the lenses, which might result in an offset in the velocity are not included in these figures. The accuracy is lower at 820 MHz than at 980 MHz because the range of negative defocus is the same for both lenses, and hence fewer oscillations are available for analysis at 820 MHz. The scatter has been estimated by taking 25 $V(z)$ s in an area of 4 mm², and is higher at high frequencies since averaging is only over one or two grains for any single measurement, and reflections from grain boundaries are more significant. All the figures in Table 2 are approximately two to three times higher than on a more uniform material such as glass.

PMMA on polished aluminum

The aluminum substrate and PMMA coating were modelled as isotropic materials using literature values for the elastic constants and density. The calculated SAW dispersion is shown by the solid and dashed lines in Fig 4, whilst the measured velocities are marked by crosses, circles and squares for frequencies of 225 MHz, 820 MHz and 980 MHz respectively.

The pseudo-Sezawa mode in Fig 4 begins with a predominantly longitudinal polarisation, and is excited fairly weakly. However, the shear vertical component increases quickly with increasing frequency or thickness, so it becomes strongly excited in the acoustic microscope. The measurements agree well with the calculated dispersion curve, although measurements at intermediate frequencies would help greatly to fill the curves out. At higher thicknesses and frequencies, there are a large number of available modes, and a $V(z)$ calculated from the reflectance function will probably provide the easiest method of determining which mode is excited most strongly.

Anodised aluminum

Figure 5 shows the measured velocities on the plain and anodised samples, together with predictions for different levels of porosity made using the model described by Wang and Rokhlin [8] and also used by Cawley and Pialucha [9,10]. The curve labelled A was obtained using the properties which were found to fit best to the properties of a 43 μm thick sulphuric acid anodised (SAA) oxide layer [10]. The measured velocities at 820 and 980 MHz have been reduced by 25 and 50 m/s respectively in order to remove the apparent systematic error discussed above, so making the results with the three lenses the same on the plain, polished sample (the zero frequency-thickness points). The large error bars in the frequency-thickness direction for the measurements on the anodised sample are due to uncertainties in the thickness of the oxide layer which varied from its average 0.2 μm in the region of grain boundaries.

It can be seen that the measured velocities are not consistent with any of the calculated curves. However, the predictions as a function of porosity were made using cell wall properties corresponding to pure, fully compacted alumina, whereas the cell wall material formed during anodisation is more likely to be a relatively open array of amorphous alumina

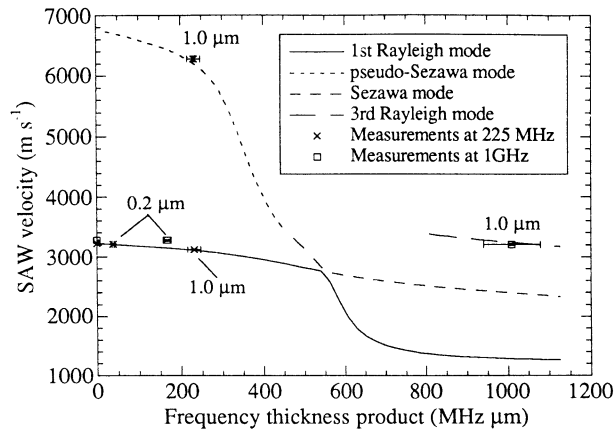


Figure 4. SAW dispersion curves for PMMA coatings on polished aluminum.

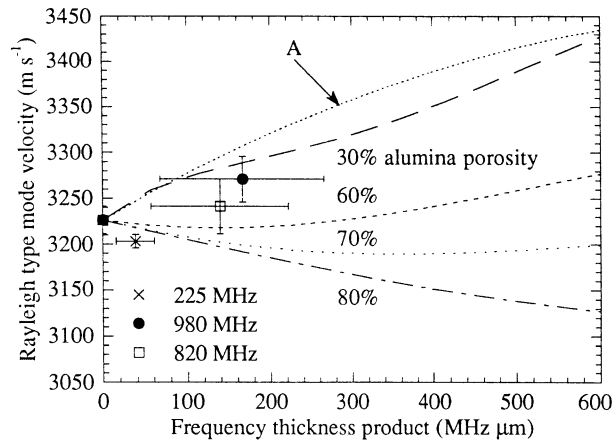


Figure 5. SAW dispersion curves for anodised aluminum. Measured results are for oxide thickness 0.2 μm .

microcrystallites, permeated by molecular water and with the surfaces of the crystallites carrying hydroxyl ions or groups [11]. The material is also likely to contain as much as 12-15% by weight of acid anions. Some discrepancy with the predictions would also be expected since the model assumes that the oxide cell structure is uniform with all the cells oriented normal to the interface. However, this is unlikely to be the case [11]. It is therefore

not surprising that the acoustic measurements do not give good agreement with the calculations. The measurements also do not correspond to the predictions using the properties measured on an SAA oxide layer. However, the SAA layer on which the earlier results were obtained was 43 μm thick compared with the 0.2 μm thick layer tested here, and phosphoric, rather than sulphuric, acid anodisation was employed in the current tests. The morphology and composition of the oxide layers can vary significantly with the anodisation conditions [12], so good agreement with the earlier work would not necessarily be expected. It is proposed to obtain high resolution transmission electron micrographs of the oxide layer in order to obtain more information about its morphology, and also to test a variety of oxide layers formed under different conditions. It should be noted that the oxide layer tested here was only 0.2 μm thick, compared with the industry standard 0.6 μm thickness for PAA surface treatment and 3.5 μm for CAA (chromic acid anodisation). Larger changes in velocity would be expected with these thicker layers.

CONCLUSIONS

Quantitative acoustic microscopy has been used to measure surface wave velocities on polished and anodised aluminum substrates, both with and without PMMA coatings spun onto the surface. Good quality $V(z)$ s were obtained at frequencies between 225 and 980 MHz, and demonstrated the sensitivity of the technique to the presence of a 0.2 μm oxide layer and a 1.0 μm PMMA coating. It was thought to begin with that the anodised surface might be too rough or the PMMA coating too attenuative for successful measurement at 980 MHz, but neither of these effects has proved problematic. The highly dispersive nature of the pseudo-Sezawa mode excited on some of the coatings means that QAM is extremely sensitive to small changes in the material parameters.

Good agreement has been obtained between the SAW dispersion measured on the PMMA coated aluminum, and that calculated by a simple isotropic layer model. Work on predicting the dispersion behaviour on the anodised aluminum is at an early stage, more information about the morphology and composition of the oxide layer being required. This study is continuing and it is hoped to present more results at future meetings.

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