Damage evaluation of unsaturated polyester resin using zero-group velocity Lamb waves in non-contact matter *

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Abstract
In this study we attempted to evaluate the degree of degradation of an unsaturated polyester resin when it was degraded by exposing it to hot water at 90°C, using the frequency of zero-group-velocity (ZGV) Lamb waves. The energy of ZGV Lamb waves does not propagate while the phase velocity remains finite. We generated ZGV Lamb waves with a Q-switched YAG laser and detected them with a focused air-coupled transducer at the same area: an irradiation point of the YAG laser in con-contact matter. A change in measured frequencies of ZGV Lamb waves decreased with increase of exposed period to hot water and are corresponding to the change in Young's modulus and thickness of the plate near the surface exposed to 90°C water for 0 to 72 h

Key words: Nondestructive evaluation, zero-group-velocity Lamb waves, unsaturated polyester resin.

1. Introduction

A lot of glass fiber reinforced plastic (GFRP) tanks and containers are used in chemical and food production plants as an alternative to steel tanks with rubber or polymer lining. Glass fiber reinforced tanks have superior anti-corrosion performance. In Japan, the number of GFRP tanks that are over twenty years old is increasing and degradation in old GFRP tanks is becoming a problem.

In early stages of degradation of GFRP, the matrix resin absorbs liquid in the tank, and a chemical reaction between the resin and liquid occurs. Therefore, a detection method for the degradation of a matrix resin is required. Unsaturated polyester resin is commonly used as a matrix of GFRP. However, as the changes in the elastic properties of unsaturated polyester resin are very small in the early stages of degradation, it is difficult to detect this stage with conventional ultrasonic inspection. Recently, Lamb waves with zero group velocity (ZGV) have received attention as a new approach for local measurement of the elastic properties and thickness of plates.\(^{(1)}\)\(^{(2)}\)\(^{(3)}\)

In general, Lamb waves that propagate in plate structures are widely used for nondestructive inspections for characterizing a defect in large plate structures because of their tendency to have low attenuation. In ZGV Lamb waves, the energy of the waves does not propagate while its phase velocity remains in a given finite value and ZGV Lamb waves cause a kind of resonance. It is reported that the resonance frequency of ZGV Lamb waves reflects elastic properties and thickness within an area where ZGV lamb waves excite. S. D. Holland et al.\(^{(2)}\) reported that symmetric (S\(_{0}\)) mode ZGV Lamb waves can be generated and detected with two air-coupled transducers located at each side of a polymethyl methacrylate
plate. They reported that the amplitude of the ZGV Lamb waves is approximately 10 dB larger than that of thickness resonant mode longitudinal waves, and this method allows visualization of small thickness variations within several tens of μm by an amplitude of a ZGV Lamb wave.

D. Crenence et al. (3) proposed a method for measuring ZVG Lamb waves with a laser-based technique. With a pulsed-YAG laser for generation and a laser interferometer for detection, ZVG Lamb waves can be measured with one-side access. Poisson’s ratio in an isotropic plate was estimated from two resonance frequencies of ZGV Lamb waves (\(S_1\) mode and \(A_2\) mode), simultaneously generated. Recently, they also reported that elastic anisotropy of a Si single crystal wafer can be characterized by utilizing ZGV Lamb waves (4). ZVG Lamb waves have a potential to characterize local elastic properties and thickness of a plate.

In this study, we attempted to detect and evaluate the degree of degradation of an unsaturated polyester resin using the resonance frequency of \(S_1\) mode ZGV Lamb waves. A ZGV Lamb wave was generated with a Q-switched YAG laser and was detected by a focused air-coupled transducer. The generation and detection points of the ZGV Lamb wave are on the same side of the plate. Distribution of change in resonance frequency of the ZGV Lamb waves for a degraded plate by exposing it to hot water was obtained by scanning the sample with a two-dimensional mechanical stage.

2. Zero-group velocity Lamb waves

Figure 1 show dispersion relation of Lamb waves for an unsaturated polyester resin plate used in this study calculated with software DISPERSE (5). Dispersion relation is plotted as variation of the frequency thickness product \(fd\) versus the thickness to wavelength ratio \(d/\lambda\). Longitudinal and shear velocity of the resin plate with thickness of 10 mm were measured by through-transmission method and 2.2×10³ m/s and 1.5×10³ m/s at 2 MHz, respectively. Density of the sample is estimated as 1.2×10³ kg/m³. The Dotted lines indicate anti-symmetric modes and the solid lines indicate symmetric modes. The fundamental symmetric and anti-symmetric mode (\(S_0\) and \(A_0\)) does not exhibit any cutoff frequency. In \(S_1\) mode and \(A_2\) modes, the slopes which equal to group velocities \((d\omega/dk)\) vanished at \(d/\lambda = 4.9×10^{-2}\) and \(6.5×10^{-2}\), respectively, by indicating with arrows in Fig. 1. While at these frequencies, phase velocities \((\omega/k)\) of the two modes remain finite. Figure 2 shows profiles of in-plane (dotted line) and out-of-plane displacement (solid line) across thickness.
of the plate of ZGV resonance for $S_1$ mode Lamb waves calculated with software DISPERSE. The out-of-plane displacement at the surface is relatively large and is appropriate for measuring with a laser interferometer and an air-coupled transducer which are sensitive to out-of-plane displacement. In subsurface area, these two profiles imply that resonance frequency of ZGV lamb waves are affected by elastic constant parallel to surface because strain estimated from the slope of displacement profile is relatively large.

3. Specimen and experimental setup

We prepared an unsaturated polyester plate 70 mm x 70 mm square with a thickness ranging from 5.06 mm to 5.35 mm. The predicted frequency of ZGV $S_1$-mode Lamb waves for the plate with a thickness of 5.0 mm is 221 kHz. In order to produce four different degrees of degradation in the one plate, the specimen was covered with silicone sealant and separated into four areas as shown in Fig. 3. The covered sample was immersed into 90 °C water and the silicone sealant was removed from one separated area every 24 h. As a result, the sample surface in area A was exposed to hot water for 72 hr and the sample surface in area D was not exposed to it. No visible change in color occurred when specimens were immersed.

Figure 4 shows photos obtained with an optical microscope for the sample in area A (72-h exposure) and area D (0-h exposure) after measuring ZGV lamb waves. In area D, a lot of small cracks were observed within depth of 0.5 mm. Those small cracks were probably introduced by mechanical machining for flattening the sample. In area A, no cracks were observed because these small cracks were closed due to swelling as water penetrated the sample. The disappearance of the cracks is proof of degradation of the sample with hot water.

Figure 5 shows an experimental setup for measuring $S_1$-mode ZGV Lamb wave resonance. ZGV Lamb waves were generated by a Q-switched YAG laser with a half duration period of 10 ns and a wavelength of 1064 nm. The energy of one shot of the pulsed YAG laser was controlled to 3.0 mJ and was below the ablation threshold of the sample. The beam diameter of the laser was adjusted to around 5 mm and almost equaled the half wavelength of the predicted ZGV lamb waves for the sample. It is reported that the efficiency of ZVG Lamb waves generation is high when the diameter of the ultrasonic generation region equals the half of wavelength of interest Lamb wave mode$^{(6)}$. Generated ZGV lamb waves were detected with focus-type air-coupled transducers with focal lengths of 150 mm at the same side of the sample as the laser incident area. Resonance frequencies of the transducer ranged from 150 kHz to 250 kHz.
Distance from the sample surface to the transducer was aligned to 135 mm so as to set a measuring area of the transducer to approximately 5 mm. A signal detected with the transducer was amplified with a pre-amplifier by 40 dB and was fed to a digital oscilloscope. The sampling interval and points were 100 ns and 16384 points. For improving the signal to noise ratio, the signal was averaged 64 times (processed in the oscilloscope). In order to enhance frequency resolution in the frequency domain, data points were increased to 131072 by the zero-padding method and the resolution was 76 Hz. For comparison, we used a laser interferometer for detection of generated ZGV waves. The interferometer measured out-of-plane displacement at the opposite side to the sample surface, where the ZGV wave was generated with the YAG laser.

For measuring the ZGV lamb waves with the interferometer, thin gold film was deposited on the sample surface at interferometer detection side by sputtering. The sample was set on a two-dimensional mechanical stage (X-Y stage) and moved each direction by 5 mm step for measuring distribution of the resonance frequency of the $S_1$ mode of ZGV lamb waves for the degraded sample.

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![Fig. 5 Experimental setup for measuring zero-group-velocity Lamb waves](image)

4. Experimental results

Figure 6 shows waveform detected with the transducer and laser interferometer, and their amplitude spectra for the sample through 72 h of exposure. In the waveform detected with the focused air-coupled transducer shown in Fig. 6 (a), large oscillations started at approximately 400 $\mu$s and decayed gradually. 0 $\mu$s corresponded to trigger timing of the YAG. Three distinct peaks were observed in the amplitude spectra at 170 kHz, 223 kHz and 260 kHz. Peaks at 170 kHz and 260 kHz were derived from intrinsic response of the transducer used in this study.

The waveform shown in Fig. 6 (c) was detected with a laser interferometer. We can observe a small oscillation with a relatively long duration time of 100 $\mu$s followed by a large positive pulse and a clear peak at 223 kHz corresponding to the oscillation. Using both methods of measurement, the laser interferometer and the transducer, the peak at the similar frequency of 223 kHz was almost identical to the predicted one (221 kHz).

Figure 7 shows the distribution of change in resonance frequency of $S_1$ mode Lamb waves measured with a focused air-couple transducer and thickness measured with a micrometer having minimum scale of 0.01 mm. Each contour map was displayed with gray scale shown above each graph. The lighter color signifies a decrease in the frequency and an increase of thickness. Dotted lines mean the boundaries of the areas and numbers written in the maps indicate the exposed period. Measured frequencies obviously decreased with an increase of the exposed period and a maximum decrease of 16 kHz was obtained at area A,
corresponding to 72-h exposure. The thickness of the sample increased as the exposed period increased, due to the sample swelling with absorbed water. Slight changes in the frequency and the thickness in a region along the borderline shown as the dotted white line in area D were observed due to diffusion of absorbed water at other exposed areas toward area D.

![Waveform with the air-coupled transducer](a)

![Amplitude spectrum of (a)](b)

![Waveform with the interferometer](c)

![Amplitude spectrum of (c)](d)

Fig. 6 Waveforms and their amplitude spectra of ZGV Lamb waves

![Change in the frequency](a)

![Change in thickness](b)

Fig. 7 Change in ZGV frequency and thickness of degraded specimen.

Figure 8 shows an average amount of change in the frequency and thickness of the specimen in each area. The horizontal axis indicates the exposed period corresponding to each area. A linear decrease in the resonance frequency was observed with increasing exposed period, while the thickness linearly increased. Both the thickness and elastic properties of a plate affect the resonance frequency of ZGV Lamb waves. If a change in the measured frequency derived from only change in the thickness, the predicted frequency...
change would be estimated as approximately –3.7 kHz/0.1 mm. This is smaller than the measured result. Next, we measured profiles in Young's modulus across the thickness of the plate by an indentation method. We used a micro-indenter with an applicable load from 0.1 mN to 2 N (fabricated by the Shimazu Corporation) and a Berkovich-type indenter with a tip angle of 115°. In this test, the loading speed was 13 mN/s and the maximum load was 100 mN. Indentation was performed across the thickness in steps of 2 mm at 0.5 mm, 2.5 mm and 4.5 mm from the exposed surface.

Figure 9 shows profiles of the estimated Young's modulus in each area. Young's modulus near the exposed surface decreased with longer exposed periods, down to approximately 70% in area A. At the center of the plate, the modulus is almost equal to that of the non-exposed surface area D for 0-h exposure. A change in the elastic properties of the plate occurred near the exposed surface only and was affected by the frequency of ZGV resonance. We conclude that the change in the frequency of ZGV resonance was caused by a change in the elastic properties and thickness near the exposed surface. Therefore, ZGV resonance may be a powerful tool for evaluating early-stage degradation of unsaturated polyester resins.

5. Conclusions

The degree of degradation of an unsaturated polyester resin plate caused by exposing it to hot water at 90 °C was estimated by S1 mode zero-group-velocity (ZGV) Lamb waves. The results are summarized below.

1. A non-contact measurement system for S1 mode ZGV Lamb waves was constructed with a Q-switched YAG laser for generation and a focused air-coupled transducer for detection. In this system, generation and detection of the ZGV Lamb waves can be performed on one side. With a two-dimensional mechanical stage, the distribution of the frequency of ZGV Lamb waves can be measured easily.

2. A distinct peak derived from ZGV Lamb waves for the degraded specimen was clearly observed in the frequency domain when the wave was measured with the air-couple transducer. The peak frequency is equal to that measured with a laser interferometer detected at the opposite side from the generation with a YAG laser.

3. Change in the measured frequencies of ZGV Lamb waves decreased with an increase of the exposed period and are corresponding to the change in Young's modulus and thickness of the plate near the surface exposed to the 90 °C water.

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