Experiments on focusing and use of acoustic energy to enhance the rate of polymer healing

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ABSTRACT

We consider the effects of acoustic pressure on the curing of a two-part epoxy, which can be considered analogous to the polymer healing process. An epoxy sample is loaded into a tube and monitored throughout the early stages of curing by measuring its vibrational response upon periodic impulses. By tracing the natural frequencies of the epoxy-tube system and cross-checking the temperature of the epoxy, the progress of the curing can be quantified. Acoustic stimulation at three different frequencies is investigated and compared to the unstimulated case. We find that external acoustic pressure does seem to affect the curing, though much work remains to be completed.

Keywords: Acoustic energy, polymer healing, epoxy curing, accelerated curing

1. INTRODUCTION

Minor damage to orbiting light-weight space structures can significantly affect their functionality. The damage may often be caused by collisions with space debris and micrometeorites, and it can be difficult and/or economically challenging to repair during service. It is therefore worthwhile to consider self-healing materials and structures for missions where manual recovery and repair are ruled out. A number of innovative approaches to self-healing are currently being developed around the world. While many of these developments are at the materials level, our study considers the problem from a structural point of view, while recognizing that healing occurs at the molecular/materials-level. In particular, the current emphasis is on investigating whether crack healing to the point of full mechanical recovery can be accelerated using focused acoustic energy. The first step in this study, therefore, is to determine the effect of acoustic excitation on the healing tendency of polymers.

2. CRACK HEALING

According to Wool and O'Connor,[1] crack healing in polymers proceeds in the following stages: (i) surface rearrangement, (ii) surface approach, (iii) wetting, (iv) diffusion, (v) equilibrium and randomization. The extent of healing is quantified by a parameter R, which represents the rate of recovery of mechanical properties such as tensile modulus, fracture stress, elongation to break, etc. R is a function of time, molecular weight, temperature, and pressure at the site of the crack.

Acoustic waves cause stress variations, which result in altered pressure and temperature under the disturbance. Thus, highly localized pressure and temperature changes may be caused by a propagating narrow pulse. Focusing and repeated magnification of such a pulse at the crack site should in theory enable the pressure and temperature at the crack to be altered enough to accelerate the rate of healing by increasing the recovery rate R. In applications where damage and healing may occur concurrently, such an increase could tip the balance in favor of the local healing process, leading to eventual healing instead of structural failure.

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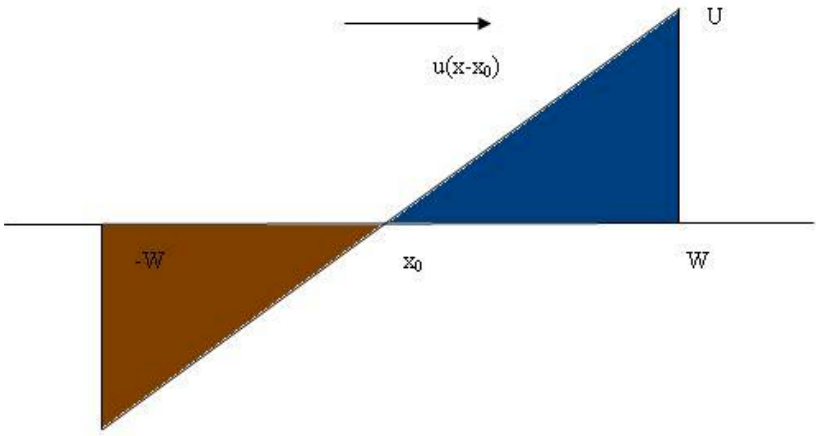

Figure 1. Pulse shape to be focused through time reversing. The maximum height U over the half pulse width W determines the slope.

Here we focus on just the effect of localized pressure (as caused by a focused, sustained acoustic pulse) on crack healing. Based on Wool and O'Connor's work, for instant wetting (as in cracks with small, smooth surface areas), the recovery rate

$$R = R_0 + Kt^{\frac{1}{4}}/\sigma_\infty \tag{1}$$

$$R_0 = \sigma_0^2/2YE_\infty \quad \text{and} \quad K = qn_0/(2D_c)^{\frac{1}{4}} \tag{2}$$

where E_∞, σ_∞, and Y: fracture energy, fracture stress, and tensile modulus respectively. Other symbols have the meaning defined below.

σ_0: stress due to wetting or surface attraction,

D_c: reptation diffusion coefficient,

q: relates the stress σ_d due to interpenetration $\perp$ the surface to the number of constraints in the interpenetration volume,

n_0: related to the bulk density, molecular weight, Avogadro's number, etc.

Acoustically caused localized stress is here taken to determine σ_0, which for uni-directional propagation is approximately related to the localized strain according to

$$\sigma_0 = E\frac{\partial u}{\partial x} \tag{3}$$

for a pulse propagating in the x direction causing localized displacement $u(x,t)$. For this reason, both the shape and amplitude of the focused pulse are important. For a step function distribution of strain, the deflection pulse propagating over the polymer membrane needs to be ramp/saw-tooth shaped, as shown in Figure 1.

Based on a prescribed combination of breaking strength, molecular weight, number of chains, density, and other properties reflected in the Wool and O'Connor crack healing theory, calculations were carried out for various levels of pulse slope involved in the time reversal procedure. The slope directly determines the strain over the pulse, which determines the stress across the crack when the pulse is centered at the defect. This stress influences the healing rate in a manner described by simple analytical expressions presented by Wool and O'Connor. Sample results from these calculations are shown in Figure 2.

Our goal in the experimental work that follows is to investigate the effect of pressure on the healing rate. Crack healing in polymers is often considered analogous to the curing process. For this reason, we study below the curing of a two-part epoxy with and without acoustically applied pressure. For the purpose at hand, it is sufficient to consider harmonic acoustic waves illuminating the entire epoxy sample.

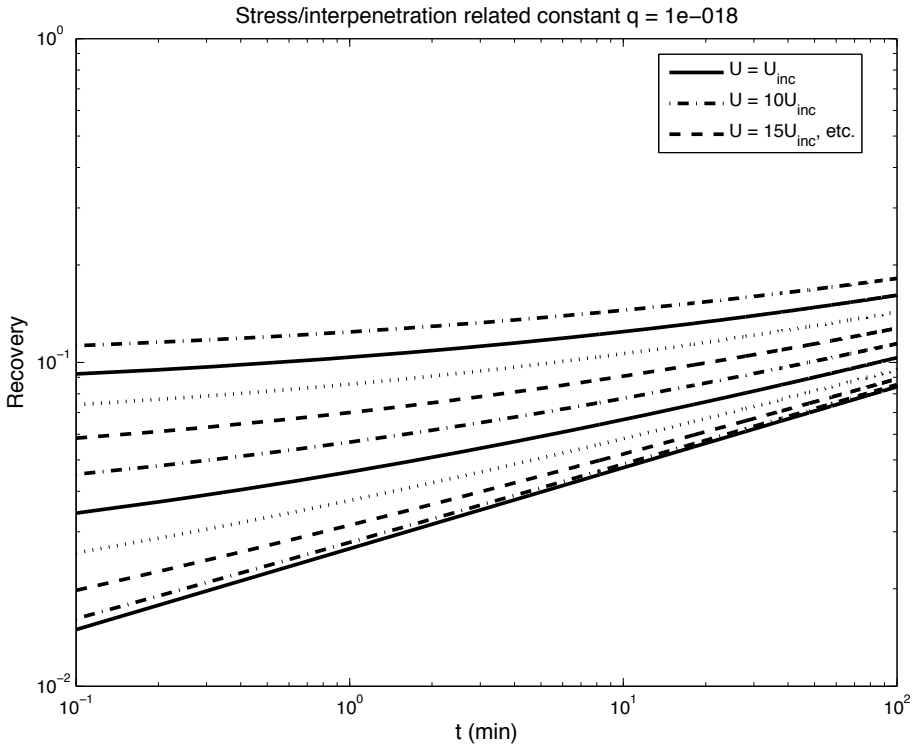

Figure 2. Recovery rate for various initial pulse height U values (for the same W).

3. EXPERIMENTAL WORK

In order to emulate the polymer healing process, we examine the polymerization of a two-part epoxy composed of Huntsman's Araldite GY 6010 resin and its accompanying hardener, HY 955. Araldite 6010 is constituted mainly of bisphenol A and epichlorohydrin, two typical resin components. The hardener is a low-viscosity polyamide consisting of a modified liquid amidoamine. When mixed at room temperature, the epoxy fully cures in approximately 24 hours, with a set time of about an hour. This two-part system was chosen for its availability and long cure time, which allows for a detailed look at the curing process at normal temperatures with our relatively slow apparatus.

Because we wish to track the health of polymers remotely by recording vibrational responses with transducers, the same approach is used here. To monitor the epoxy curing progress, a system was put in place to record a sample's vibrational response upon sustaining periodic impacts. After mixing, the epoxy is poured into a half-inch diameter brass cylinder one foot in length. The cylinder is taped at both ends to prevent leakage and a small thermistor is inserted into one end in order to keep track of the epoxy temperature (Fig. 3). This acts as an additional measure of the curing progress. The tube with epoxy and thermistor is then placed in the testing apparatus (Fig. 4), which has two compact discs to act as knife-edges and support the tube near its ends. In addition to the tube mounts, the apparatus contains a marble-dropping device that produces solid, consistent impacts on the tube. After securing the tube, a small accelerometer is affixed with putty at one mark (see Fig. 3), while the arm of marble dropper is positioned above the other. The marks are made near, but not at, intervals of one-third the length of the tube, in order to excite all vibrational modes. If running a test with acoustic excitation, a large speaker playing a specific tone is switched on and placed on top of the box facing the sample. Once the connections are made, the elevator motor of the marble-dropping device is switched on and measurements are begun. This typically occurs between six and ten minutes after the epoxy is mixed.

The accelerometer waveform, thermistor resistance, and time are recorded for each impact, which are 27 seconds apart. A fast Fourier transform (FFT) is then computed from the waveform and the five strongest peaks

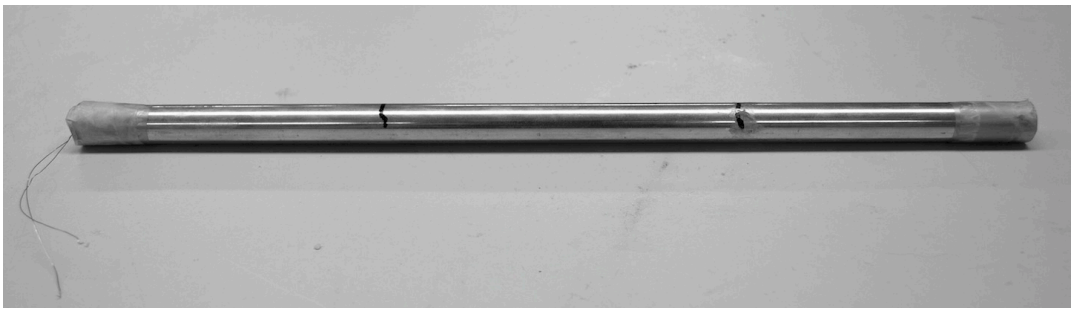

Figure 3. Brass tube containing epoxy and taped at both ends. The wires protruding from the left come from the thermistor. The marks at approximately one- and two-thirds the length of the tube indicate the positions of the marble impacts and accelerometer, respectively.

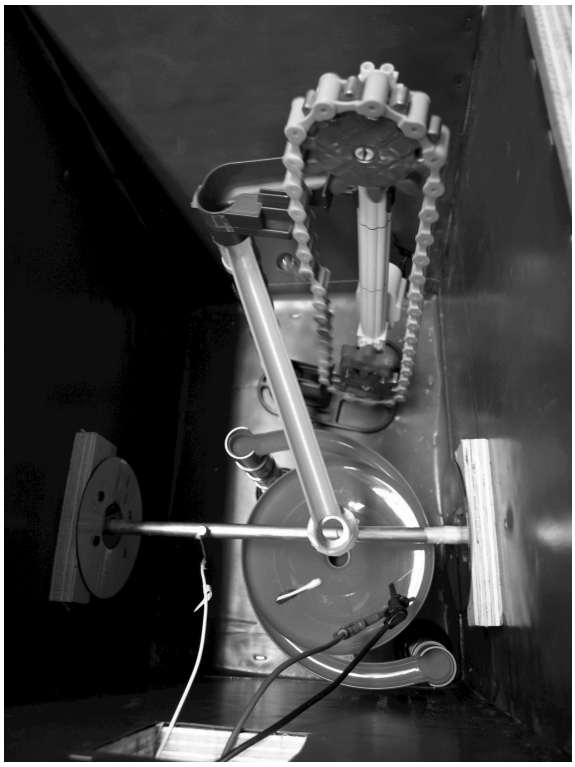

Figure 4. The testing apparatus contains mounts for the brass tube, a marble elevator and marble tracks. The accelerometer is attached to the tube on the left and the connection to the thermistor leads can also be seen. After impact, the marble is collected by the spiral-armed dish below the tube and returned to the elevator queue. The box is lined with rubber to facilitate future tests that may utilize ice to slow the curing process.

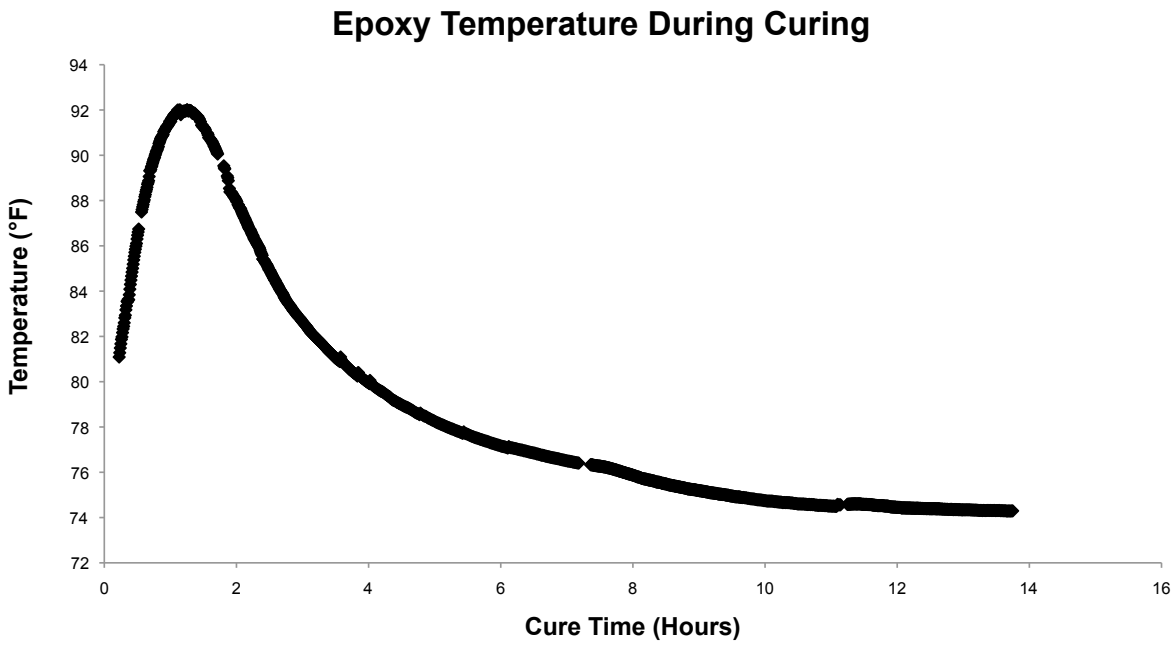

Figure 5. Temperature of the epoxy over fourteen hours of curing, without acoustic excitation.

are tabulated, while the resistance value is converted into a temperature and also included in the table. By tracking the changes in frequency and amplitude for each event, as well as monitoring the temperature, we hope to develop a method for determining the extent of curing.

4. RESULTS AND DISCUSSION

Figure 5 shows the temperature of an unexcited epoxy sample over a fourteen hour period. Although both the resin and hardener are stored and mixed at room temperature, the first data point shows a significantly increased epoxy temperature. This can be explained by the time delay between the mixing and testing phases, and an estimated extrapolation backward to the zero of the time scale, which corresponds to when the mixing is completed, confirms that we start near room temperature. A similarly long test for an epoxy sample subjected to acoustic pressure is yet to be conducted, however we do see differences in the briefer tests described below.

Figure 6 shows the temperature of the epoxy as a function of time for four different samples. One sample was not excited during curing while the other three were subjected to harmonic acoustic waves throughout the entire process at the frequencies indicated on the graph. While these preliminary results suggest that high frequency excitation delays the temperature turning point, which we consider a useful point of reference in the curing process, it must be noted that strict temporal alignment has not been performed. Initially, we did not track the time from mixing, but rather the time from the first impact. We estimate that each trial begins approximately six to ten minutes after mixing the epoxy, but the precise time has not been recorded until very recently (as in Fig. 5). In addition, peak temperatures of unexcited epoxy samples can vary by a few degrees Fahrenheit, as seen when comparing Fig. 5 to the unexcited sample in Fig. 6. Thus, we cautiously suggest that external acoustic stimulation does affect epoxy curing, insofar as the temperature turning point is concerned. The meaning of this feature will be investigated in the future, but for now we view it as a useful metric for comparison with changes in the power spectrum, which are the main emphasis here.

The FFT that is performed on each recorded accelerometer waveform can be seen to change significantly over the course of the test. Figure 7 shows a typical FFT for the sample a few minutes after mixing, as well as a typical FFT for a fully cured sample. We can clearly see that the solid, fully cured epoxy produces much

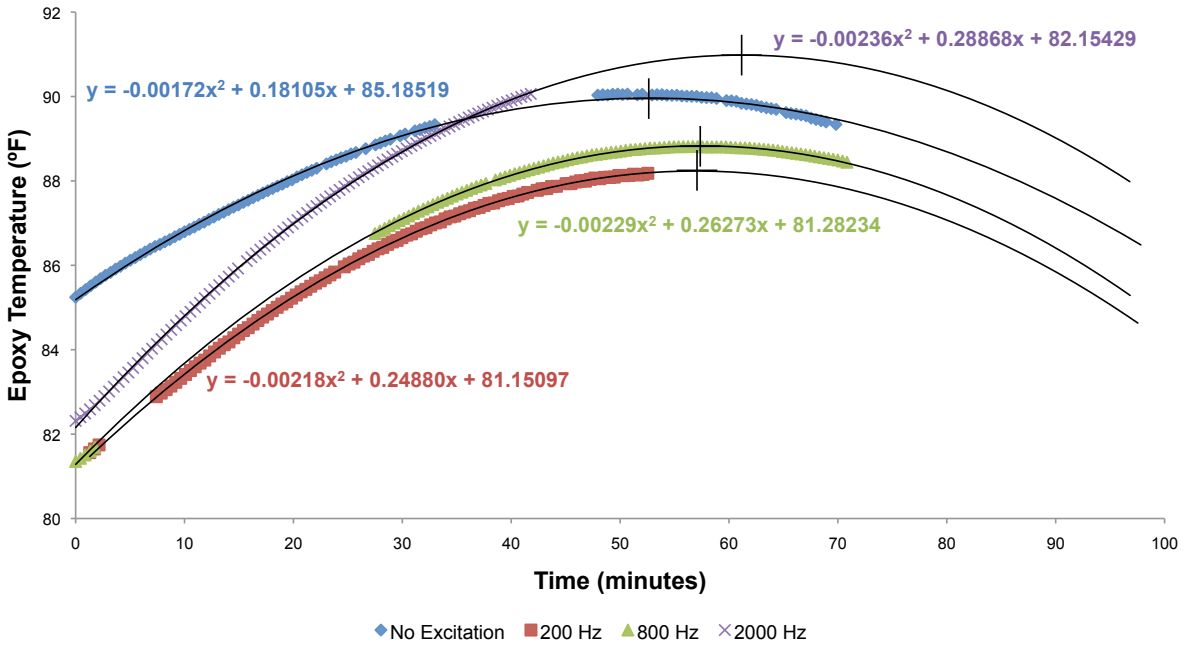

Figure 6. Temperature of the epoxy during curing. Quadratic trend lines and vertical bars indicating turning points are plotted along with the data. The series of diamonds indicates a sample that was allowed to cure with no external acoustic excitation, while the other three series were excited by a speaker producing a tone at the indicated frequencies.

sharper peaks than the thick liquid epoxy, but the transition between the two distributions can be tracked by following the power and frequency of the strongest peak of the FFT. Figure 8 shows the peak frequency in the FFT, which is fairly constant around 1100 Hz throughout of the first two hours of curing and then switches to the 5100 Hz range. Unfortunately, our desire to record an FFT spanning 20 kHz reduces our precision to 20 Hz, and a closer look at the dominant frequency early in the curing process shows only a handful of alternating, discrete values, which is not a particularly helpful diagnostic. The peak near 5100 Hz, however, undergoes a change of approximately 500 Hz in about ten hours, as shown in Fig. 9. As this may prove to be a useful measure of the progress of epoxy polymerization, future tests will be fine-tuned to this frequency to get a precision better than 20 Hz.

Another changing parameter is the power of the strongest peak in the FFT, which is shown in Fig. 10. First, we note that there is a noticeable downward shift of the average maximum power around two hours in, which corresponds to the abrupt change in peak frequency. Despite the considerable vertical spread, the average power of the strongest frequency seems to increase almost linearly (in dBV) for the next four hours before leveling off. This is another trend that may be useful in future tests, though efforts will have to be made to make impacts more consistent, as they are likely the reason for the spread in neighboring data points. If such improvements can be made, tracking the maximum power in the FFT of early impacts may, in addition to tracking the frequency of the 5.1 kHz peak, provide a complete way of measuring the stage of curing. We will also look at tracking other peaks that change significantly throughout the curing process, such as the ones near 7 kHz and 11 kHz. A better analysis of the evolution of these and other peaks may help shed some light on the temperature turning point, which does not seem to correspond to any other major event at the moment. Longer tests will also be conducted in the future during which the samples will undergo acoustic stimulation, in order to see if these long-term changes occur at the same time in their respective FFTs.

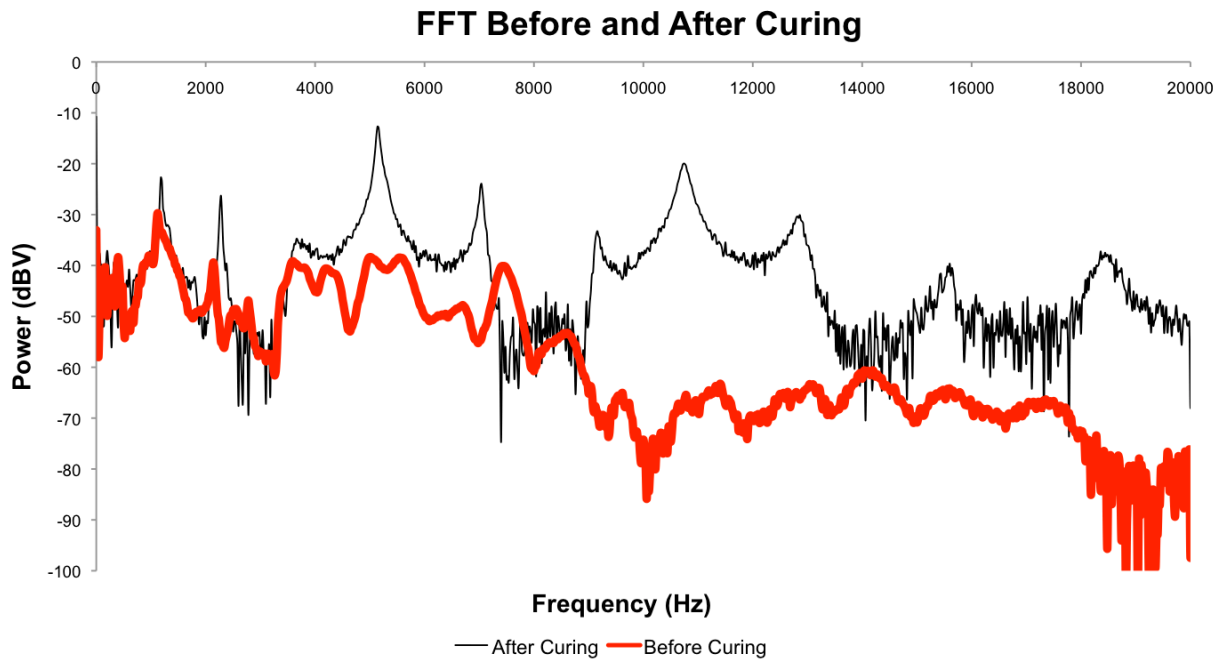

Figure 7. Representative fast Fourier transforms of the actuator waveform upon impact in the unexcited state. The thick line corresponds to a trial within a few minutes of mixing, while the thin line corresponds to an impact twenty-four hours after mixing, when the epoxy is fully cured.

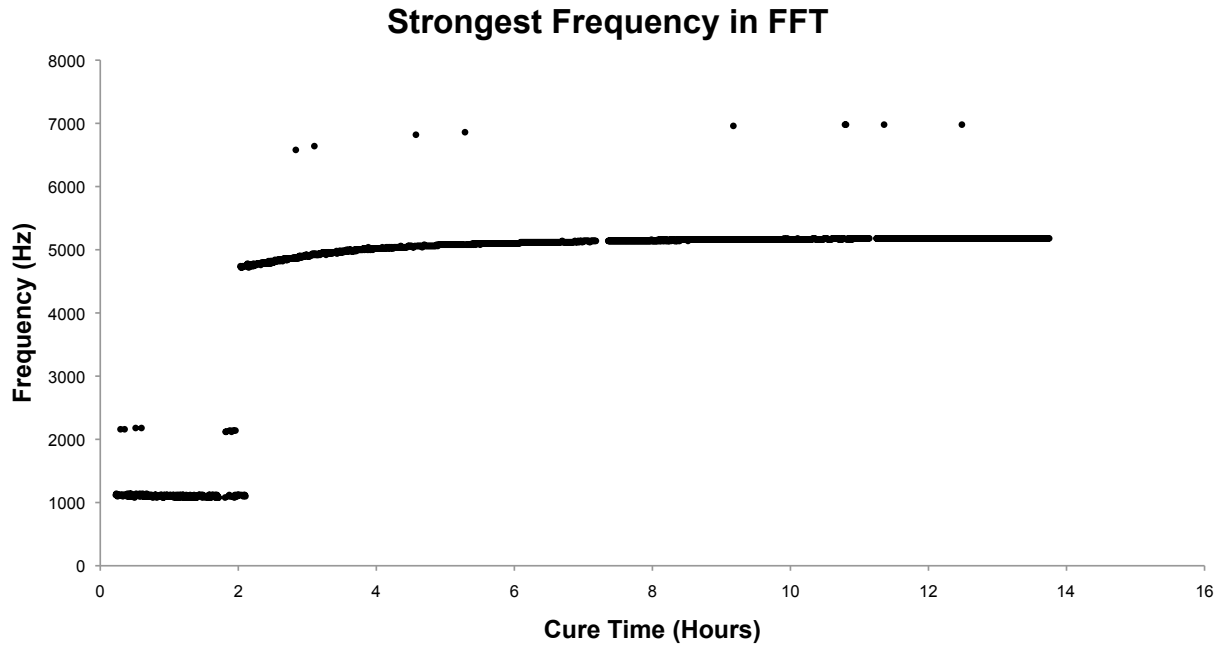

Figure 8. Frequency of the strongest peak in the fast Fourier transform over time.

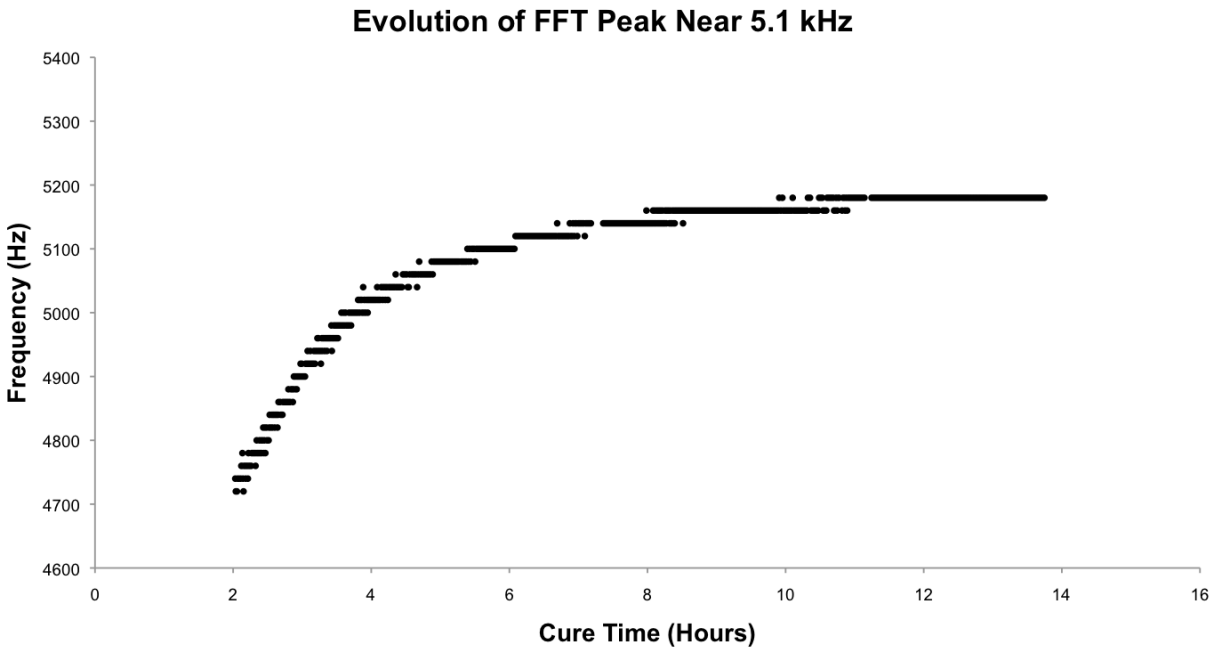

Figure 9. The change in frequency of an FFT peak near 5.1 kHz over time. Vertical gaps are 20 Hz wide.

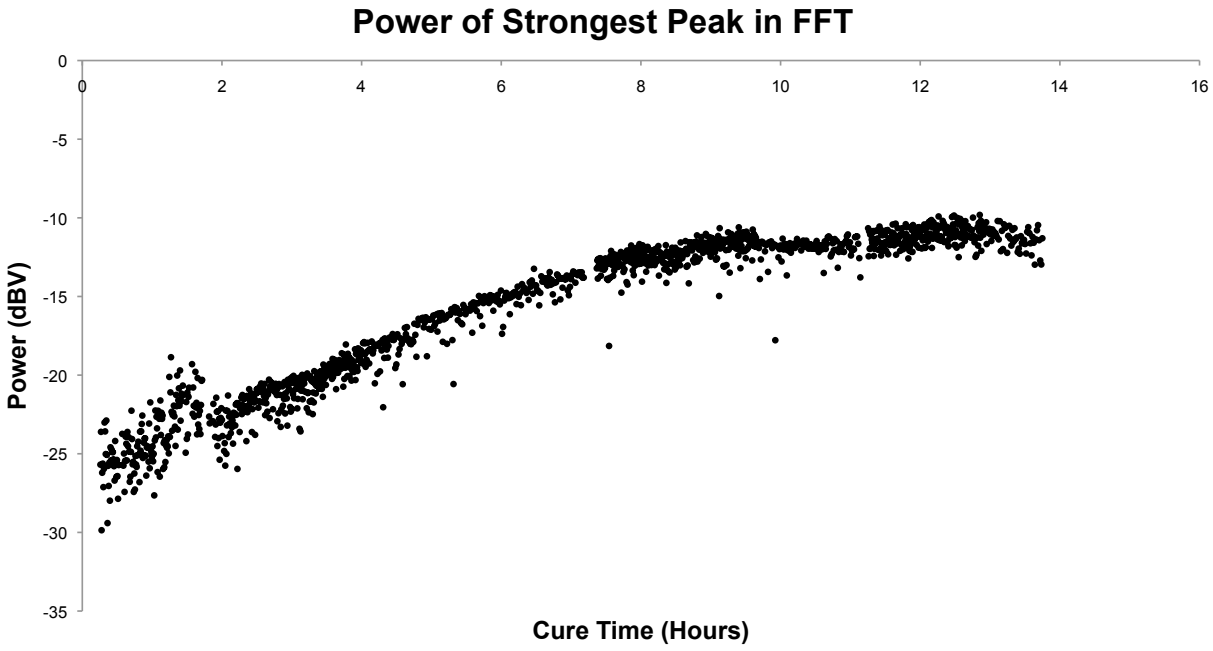

Figure 10. Power of the strongest peak in the fast Fourier transform over time.

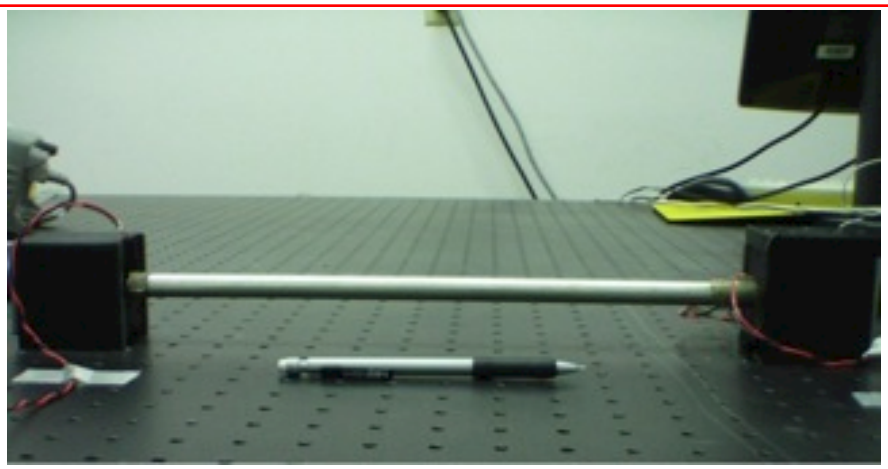

Figure 11. Steel rod with PZTs undergoing time reversal testing.

5. TIME REVERSAL METHODS

Acoustic waves will be used more accurately in the future to accelerate the self-healing process. This work will involve focusing the waves at the point of the defect by implementing a time reversal[2] (TR) algorithm. The version of TR that we will be using exploits the amplitude combination that occurs with waves of the same frequency and phase. When two or more of these waves meet, they form a larger wave that has an amplitude roughly equivalent to the amplitudes of the smaller waves summed together. There is then a focusing at the point where the waves meet.

Our current aim is to achieve focusing in one-dimension using the TR method. We use a steel rod as our wave-propagation medium and two piezoelectric ceramic stacks (PZTs) for signal actuation and reception. The stacks are placed on each end of the steel rod, as shown in Fig. 11. The idea is to send a single sinusoidal pulse from one of the PZTs through the rod and towards the other PZT. While this pulse is in transit for a discrete amount of time, both PZTs will be put into receiving mode and have their signals recorded. Once the wave travels through the rod and strikes the receiving PZT, that PZT will read the wave as it is reflected back towards the sending PZT. When the sending side PZT reads this reflection, it will look just like the original pulse it sent, but 180 degrees out of phase. This is all the data that the TR method requires: the pulse hit on the receiving side and the reflection pulse on the sending side. All other data is zeroed out. The pulses are then centered on zero, rescaled, reversed, and played back. The sending PZT plays back the reflection pulse it received, and it travels through the rod towards the receiving PZT. As this pulse reaches the receiving PZT and begins to reflect back, that PZT then plays out the initial pulse it had recorded previously. These two waves then combine with each other and head towards the sending PZT where they create a larger response and focus on that point. Tests are ongoing and recent results have been both encouraging and very promising.

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