Accelerating the self-repair rate of a polymer via acoustic energy

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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 curing process by measuring the amplitudes of its natural frequencies in response to periodic mechanical impulses. The progress of the curing process can be quantified by tracing the natural frequencies and temperature of the epoxy-tube system. Studies described in our last report continue and work completed in this reporting period has sought and achieved repeatable test results by making slight modifications to existing procedures and protocol.

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

1. INTRODUCTION

Minor damage caused by collisions with micro-meteoroids and other space debris can significantly affect the functionality of orbiting lightweight space structures. Because this damage is nearly impossible to repair using conventional methods, such as reaching the site manually, it is important to consider self-healing materials and structures in these applications.[1] Currently there are numerous innovative approaches to self-healing being developed worldwide and focused at the materials level.[2–8] 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. Because crack healing in polymers is often considered analogous to the curing process, the first step in our study has been to determine the effect of acoustic excitation on the healing tendency of polymers. Our experiments monitor the curing process of a two-part epoxy with and without acoustic pressure. For the purposes at hand, it is sufficient to consider harmonic acoustic waves illuminating the entire epoxy sample. Also discussed at the end of this report are our most recent studies and findings relating to the use of time reversal in polymer healing. We hope to use these methods to detect and focus acoustic energy at a damaged point within a structure in order to accelerate the rate of recovery.[9, 10]

2. METHODOLOGY

Studies and attempts to quantify the curing of epoxies while achieving repeatable test results have led to the current test methods and practices. Data collection has evolved from hand-tracing periodic vibrational responses to a computer-assisted system tracing results from tests conducted in a temperature-controlled environment. We feel the vibrational data we collect, when compared to other tests or different periods of the same test, is sufficient for us to speak of the epoxy's cure progress. Testing procedures will be explained in detail in this section but will be briefly described as follows: a two-part liquid epoxy system is mixed together and injected into a brass tube. A thermistor is also inserted and the tube ends are sealed to contain the epoxy. An accelerometer is then attached to the tube, an automated marble dropper started, and the tracing of vibrational responses and internal temperatures begins. After a 30 hour test is conducted, data is compiled into several different graphs, and it is from these that visible results emerge. The remaining sections under the heading of methodology will add to and more accurately describe the steps introduced.

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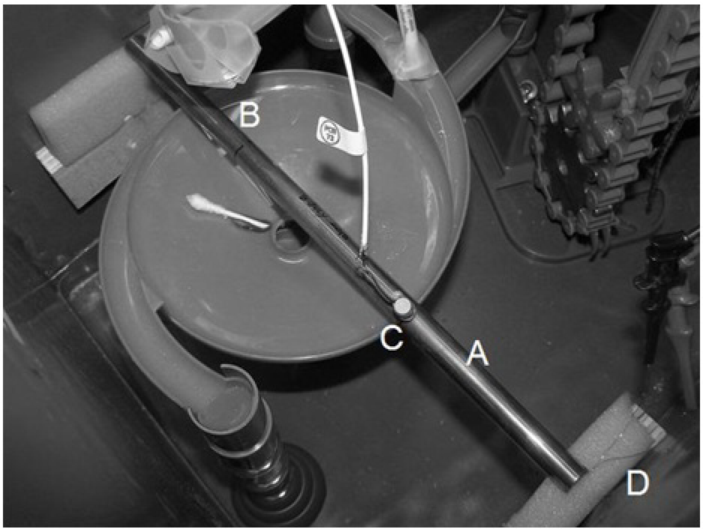

Figure 1. An overhead view of a test in progress. Seen diagonally across the picture is the epoxy-filled tube (A) supported by foam supports at each end. Marbles are dropped by the elevator onto the mark approximately 1/3 down from the far end of the tube (B) and are collected by the round dish directly beneath the tube. Vibrations are received by the accelerometer seen in the center of the picture (C) and also visible are thermistor leads emerging from the bottom end of the tube (D).

2.1 Preparation

The resin and hardener are drawn out of storage containers in measured amounts before being mixed thoroughly by hand for 4-5 minutes, drawn into an open-ended syringe, inverted, and then placed into a vacuum chamber. This chamber holds $25inHg$ of vacuum for approximately 5 minutes, during which time all sizeable gas bubbles ($0.4mm$ diameter and larger) are drawn out of the opening of the syringe. Consistently filling the brass tube with degassed epoxy while excluding air has historically been a difficult task, but it has been found that injecting the epoxy from the bottom of the tube provides satisfactory results. Ends of the tube are sealed with a hot melt adhesive and tape combination, and a thermistor is also inserted at this time. This sealed brass tube is then placed into our testing apparatus (Figure 1) where it is subjected to periodic marble impacts from an automatic dropper. The mixing, degassing and injection steps take approximately 15 minutes; the time of record starts as the mixing begins. Frequency responses of the tube-epoxy system are recorded as well as the internal temperature by the attached accelerometer and the imbedded thermistor, respectively.

2.2 Testing

Once a tube has been placed in our apparatus, a marble elevator is switched on and testing begins. In the case of an acoustically-excited test a ten-inch speaker is placed directly over the test: in all others a piece of Plexiglas is substituted and serves to contain the box's elevated temperature. A custom computer program traces frequency responses and temperatures of the tube-epoxy system and records waveforms, temperatures and fast Fourier transforms in a spreadsheet document. Sampling intervals are usually 2 minutes for the duration of the test and provide sufficient detail and resolution to monitor and quantify the curing process.

2.3 Procedural changes made during the reporting period

In previous testing, the epoxy-filled tube was supported at the ends by compact discs acting as knife edge supports. It had been observed that the interaction between the tube and CDs upon marble impact created small inconsistencies in the readings from the oscilloscope, and the CDs have since been replaced with a soft, open-cell foam rest at either end. Tape was used previously to seal the ends of the tubing, but a hot-melt adhesive/tape combination is now being used and has proven more effective at retaining epoxy and excluding air. Inconsistent marble strikes have been another cause of cloudy test data. To correct this, slight modifications

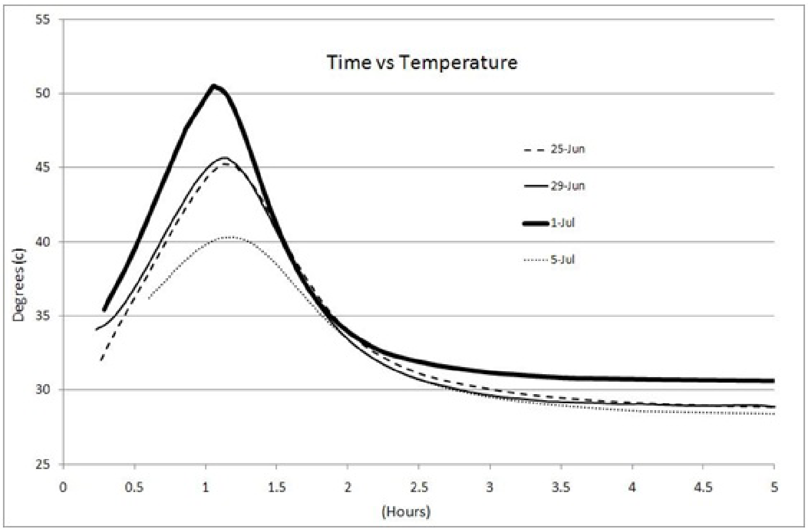

Figure 2. A four-test comparison of peak temperatures. Date labels are the date at which that particular test started. Seen on the right-hand side of the graph are temperatures returning to and holding at the ambient air temperature during the time of testing. Note that only small increases in ambient temperature (a $2°C$ spread at the 4 hour mark) correspond to a much wider disparity in peak temperatures ($10°C$ between highest and lowest peak temperatures). Also, higher peak temperatures tend to occur earlier than lower ones (there is a 9 minute separation between the peaks of 1-Jul and 5-Jul).

to the marble dropper have been made. Weight-matched marbles are being used and more consistent impacts from the marble elevator are now being achieved.

3. DATA AND RESULTS

Data is recorded into spreadsheets by our testing program and is compiled afterwards to make graphs. Recorded each test 'cycle' is the time of the sampling, the temperature of the epoxy and an FFT of the epoxy-tube system. The remainder of this section will display and describe the graphs constructed to quantify the cure progress of an epoxy.

3.1 Temperature

The curing reaction is exothermic and creates an appreciable amount of heat in the first 2 hours of testing. The peak occurs about an hour after mixing, and after approximately 6 hours the sample has cooled to the temperature of the surrounding air. No other recorded data seems to correspond to the internal temperature of the epoxy-tube system, but it is known that the curing rate of this epoxy is largely a function of temperature at which the reaction takes place so care is taken to ensure tests are conducted at the same temperature. The graph in Figure 2 indicates that an increase in ambient temperature as small as $1.5°C$ can cause an increase of nearly $4°C$ in the epoxy's peak recorded temperature and also causes this same peak to occur several minutes earlier in the test cycle, when compared to tests conducted during times of cooler ambient temperatures. Rather than try to strictly regulate the laboratory temperature, it has been decided to house the testing apparatus in its own temperature-controlled climate. A small thermostat and heater is used to maintain an elevated, constant temperature for tests. Temperature data in recent tests has served to confirm the consistent temperature of the test environment and is also an indicator of a test's normalcy.

3.2 Fast Fourier transforms

A plotted FFT is a favored measure of cure progress, but a small variety of graphs are also constructed with data recorded by the program. An example of one of these are amplitude and peak frequency shifts as a function of time. The results displayed in Figure 3 have been taken from a singular test and can be considered a representative sample.

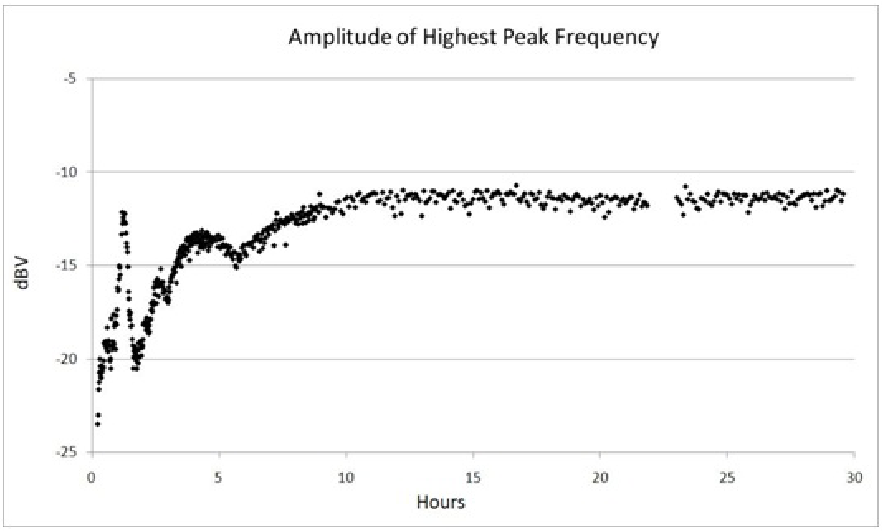

Figure 3. Seen here is the amplitude of the peak frequency as calculated in our FFT. More consistent marble impacts have significantly cleared our view of the first 5 hours of testing to reveal a pattern of rising and falling before leveling off at about 12 hours. The gap in record around the 22 hour mark was caused by a short lapse in data recording.

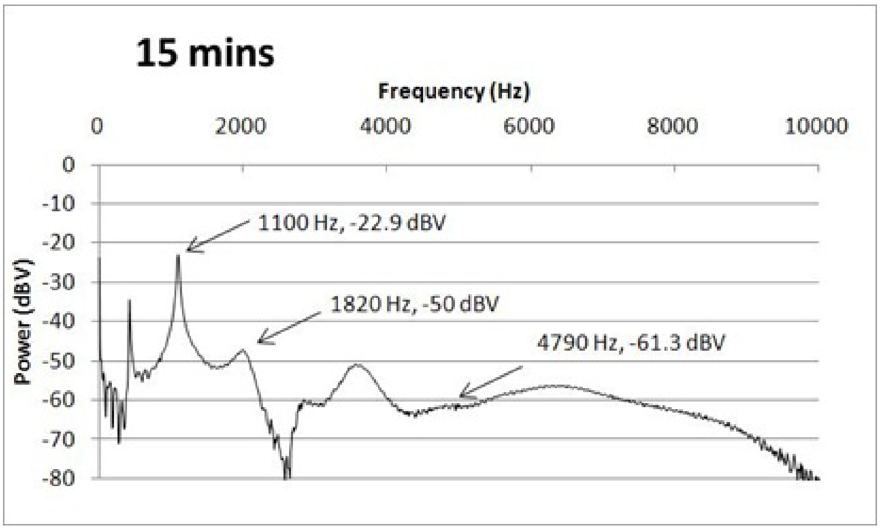

Figure 4. An FFT picture taken 15 minutes after mixing the epoxy. At this point in time the epoxy is a viscous (approximately $8Pas$) liquid.

Figures 4-7 graphically demonstrate the frequency and amplitude shifts during the cure of the epoxy. The 3 peak frequencies from the cured sample (figure 7) have been picked out of figures 4, 5, and 6 and serve to show how the rate of an epoxy's cure can be quantified by measuring frequencies and amplitudes.

3.3 Results

Tests conducted since the last report indicate an applied acoustic excitation can accelerate the curing of a two-part epoxy system. The most recent tests conducted were two: an unexcited control test and following, an acoustically excited test. Both took place in a temperature-controlled environment with the only difference being the applied acoustic pressure on the second test for the first 7 hours of the cure. A singular frequency of $1kHz$ was played during the test at an intensity of about $100dB$.

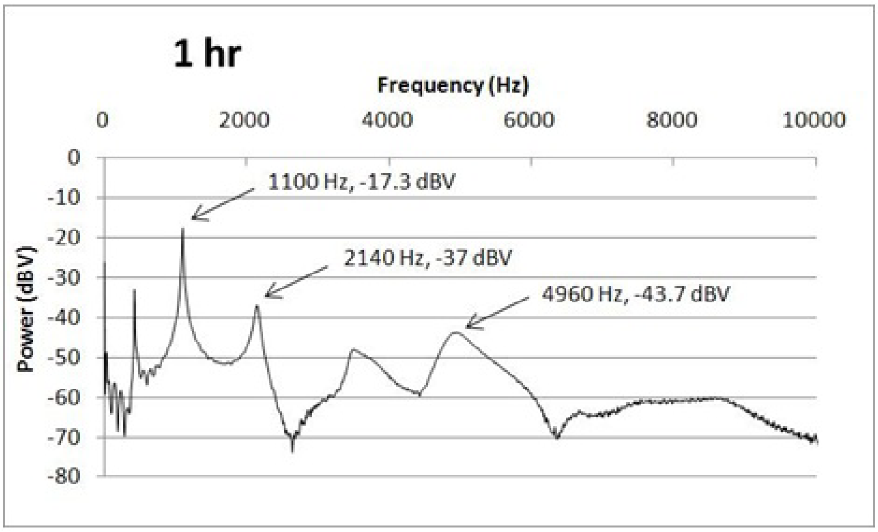

Figure 5. The same picture, now one hour from mixing. This particular epoxy has a handling life of 30 minutes and by1 hour has thickened to the point it can no longer be stirred by hand. Note the rapid growth of the peak around $5kHz$ between figures 4, 5, and 6.

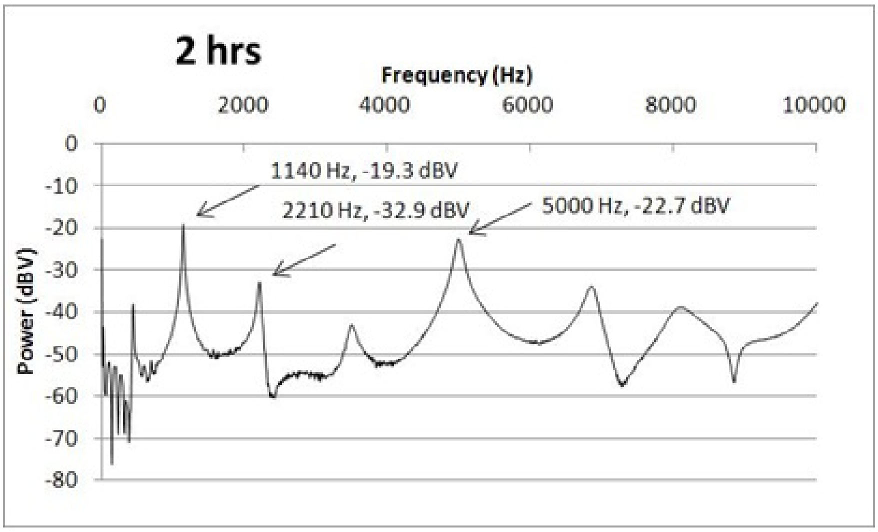

Figure 6. Two hours. Note that the amplitude of the peak near $1kHz$ has decreased since figure 5 but has again elevated and plateaued by figure 7.

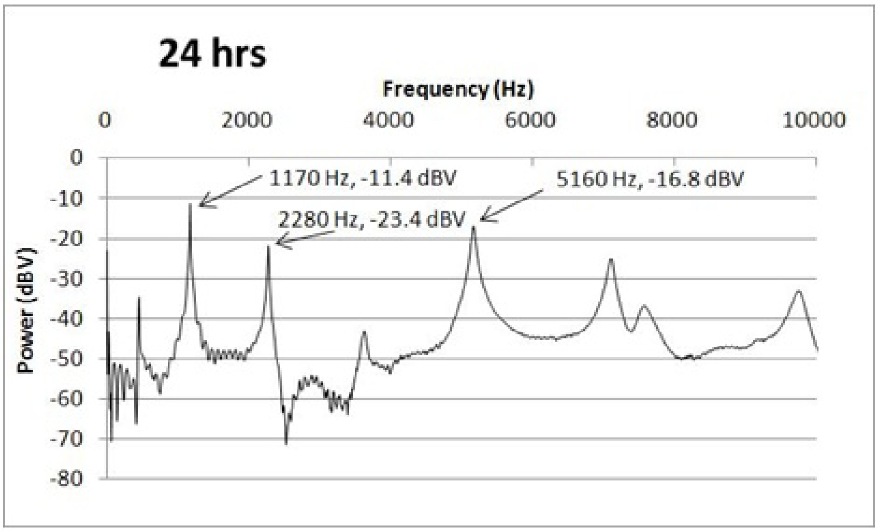

Figure 7. An FFT of a fully-cured sample. The final FFT is unique for every test conducted but maintain predictable patterns in both peak frequencies and amplitudes.

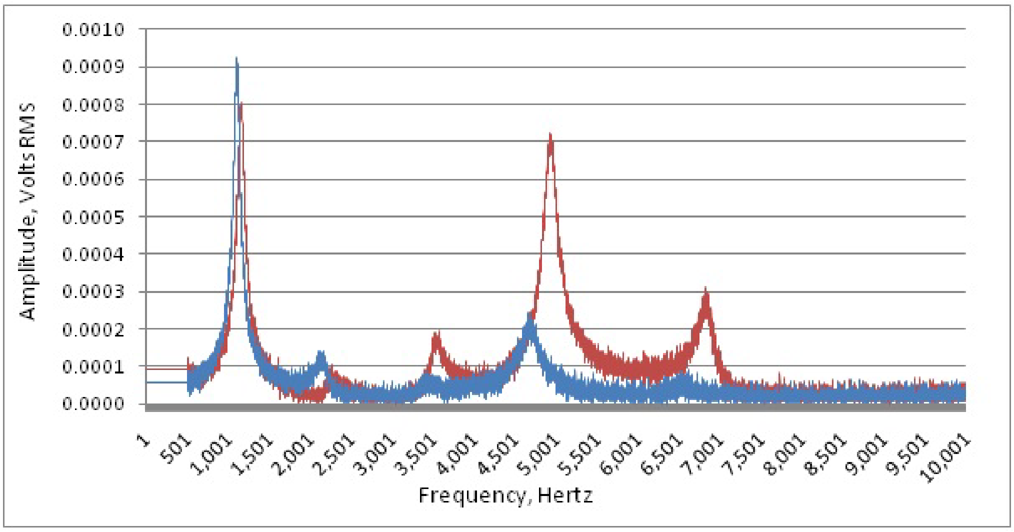

Figure 8. Fast Fourier transforms taken at 2 hours (blue) and 30 hours (red) of the unexcited test.

To compare cure progress, an FFT snapshot taken 2 hours from the time of mixing is plotted on top of the FFT of the same, fully-cured sample. Once in this format disparities between the peaks of the FFT can be measured and expressed as a percentage with the understanding that as the epoxy cures, its FFT approaches that of the final, or cured, FFT and the disparity percentages approach zero for both frequency and amplitude shift. Peak frequencies slowly increase (that is, get numerically higher) during the cure process and amplitudes of these peaks increase or decrease depending on the peak and the sample studied. Presented in figures 8 and 9 are these 2 hour vs. 30 hour FFTs for the unexcited and excited tests, respectively.

Assembled into the table in figure are comparisons between the two tests of average frequency and average amplitude disparity. It will be seen that the excited test displays smaller differences between the 2 hour and 30 hour samplings than those of the unexcited test, suggesting that its cure progress has been accelerated. Comparisons between 3 hour and 30 hour samplings of the two tests confirm this result and the average frequency and amplitude differences between the 2 hour and 30 hour excited test are comparable to a 2.6 hour/30 hour

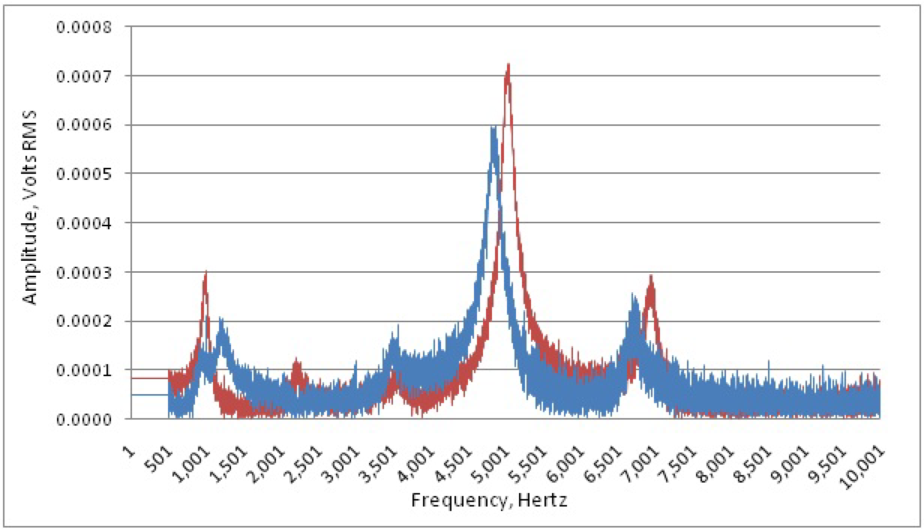

Figure 9. Two hour (blue) and 30 hour (red) FFTs taken of the acoustic test.

Control Test

Frequency Disparities (Hz)

Peak (L-R)	2 hrs	30 hrs	% difference
1	1,106	1,154	4.2%
2	2,088	2,235	6.6%
3	3,355	3,514	4.5%
4	4,660	4,916	5.2%
5	6,478	6,822	5.0%
		Average	**5.1%**

Amplitude Disparities (VRMS)

Peak (L-R)	2 hrs	30 hrs	% difference
1	0.000925	0.000796	-16.2%
2	0.000132	0.000096	-37.9%
3	0.000078	0.000179	56.3%
4	0.000245	0.000725	66.2%
5	0.000075	0.000310	75.9%
		Average	**50.5%**

Acoustic Test

Frequency Disparities (Hz)

Peak (L-R)	2 hrs	30 hrs	% difference
1	915	978	6.4%
2	2,032	2,194	7.4%
3	3,469	3,557	2.5%
4	4,805	5,019	4.3%
5	6,687	6,936	3.6%
		Average	**4.8%**

Amplitude Disparities (VRMS)

Peak (L-R)	2 hrs	30 hrs	% difference
1	0.000146	0.000295	50.5%
2	0.000091	0.000124	26.4%
3	0.000178	0.000108	-64.8%
4	0.000595	0.000719	17.2%
5	0.000256	0.000293	12.6%
		Average	**34.3%**

Figure 10. Comparison of the test without acoustic excitation vs the test with acoustic excitation

comparison of the unexcited test.

4. ACOUSTIC FOCUSING TESTS

Two separate experiments were performed for the acoustic focusing portion of the self healing project. The first was an experiment designed to determine if ringing in the system due to natural frequency oscillations would become a problem. The second set of tests look at our ability to focus acoustic energy at damaged point within a finite rod using a time reversal method.

4.1 Ringing Tests

The ringing experiments used the same test setup that was designed for our previous acoustic focusing tests. This setup uses a steel rod as the transmission medium for the acoustic energy. A ceramic piezo-electric transducer (PZT) is placed on each end of the steel rod. This system is then placed under compression. An FPGA data

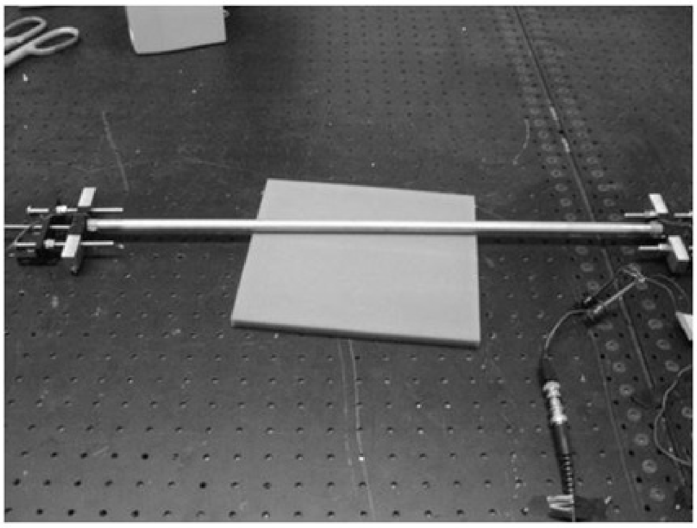

Figure 11. Setup for the ringing tests.

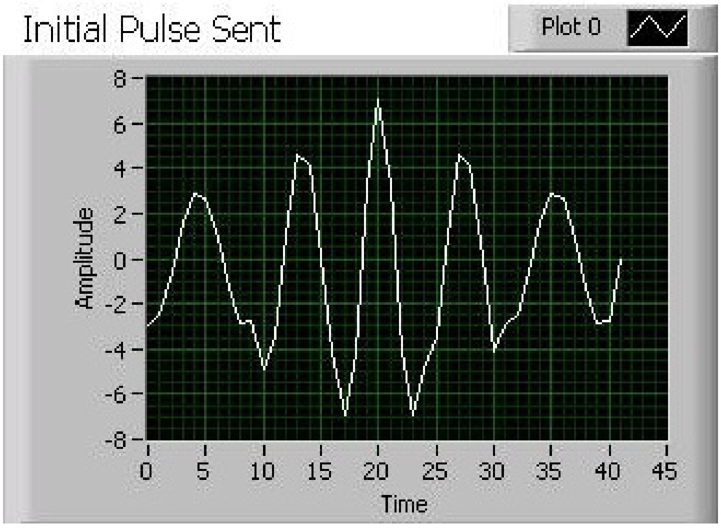

Figure 12. The multi-tone pulse that is used in both the ringing and acoustic focusing tests.

acquisition card is used to send signals to and read signals from the PZTs. A custom voltage/current amplifier enables a larger response from the transducers to be achieved.

Two test algorithms were used to determine the rate at which the amplitude of the natural frequency oscillations decayed. The first algorithm simply sent out a single 14 V pulse from one of the transducers. Samples were then taken from each PZT and then analyzed to see the effects of the ringing. The second test method was similar, except that a multi-tone wave is used instead of a single pulse.

4.2 Time reversal focusing tests

The time reversal tests are an extension of our previous focusing tests in which we were able to focus waves at the end of a steel rod. The previous testing used the same setup as described above in our ringing tests. Our current tests use a very similar setup with one change; we add a second rod segment and a third transducer to the system. The rod segment attaches to one of the PZTs in the old setup so that the PZT is now sandwiched between the two rods. This PZT will both reflect and transmit energy which is characteristic of a crack. That

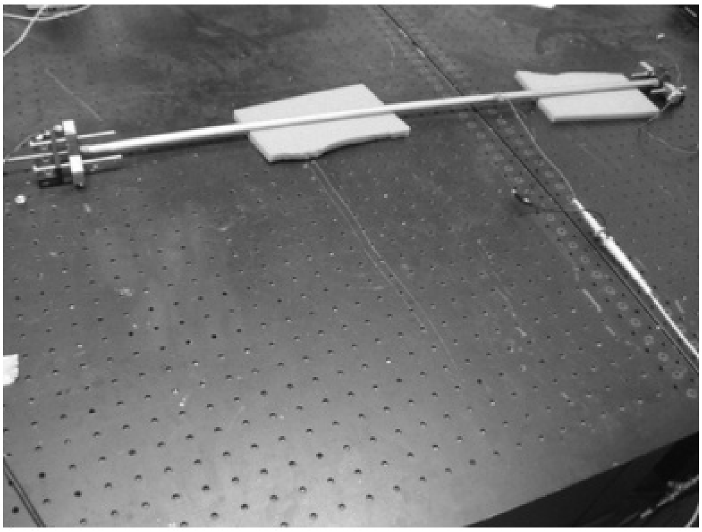

Figure 13. The setup used for the acoustic focusing tests. Notice that it is the same setup that is used for the ringing tests with an additional rod segment and transducer.

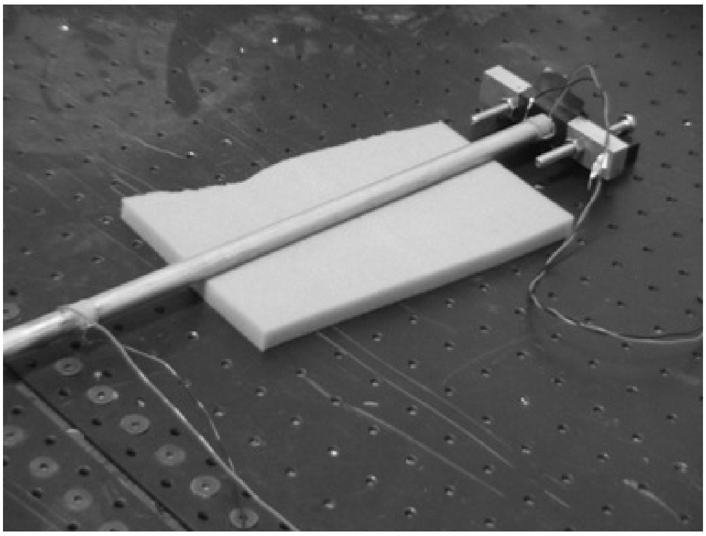

Figure 14. Close up of the second rod segment. Also notice the transducer between the two rod segments. This is the point that we attempt to focus acoustic energy.

middle PZT will be the point at which we attempt to focus acoustic energy by using time reversal to exploit the transducer's effect on traveling waves. A third transducer is placed on the open end of the new rod segment.

The test algorithm sends a multi-tone pulse through one of the end PZTs. Data samples are then read from all three PZTs. The initial response at the middle, or "defect", PZT is recorded. In order to extract the desired waves, a normalized correlation filter is applied to the signals that were read by the end PZTs. These extracted waves are then rescaled to maximum amplitude, reversed, and then played back on their respective channels. Data is again sampled from all of the transducers. The response from the "defect" PZT during the time reversal phase is compared to that of the response during the initial phase.

5. CONCLUSIONS

In this study we detailed our recent experiments on accelerating the curing rate of a polymer using acoustic energy. Our results suggest that an externally-applied acoustic pressure will accelerate an epoxy's cure rate. This represents one crucial piece of our overall work to use time reversal to enhance the recovery rate of a self healing material. We are hopeful that focused pressure within a structure will serve to more effectively and efficiently quicken the natural healing tendency of a cracked polymer (versus using unfocused acoustic energy). We will also continue on our research on polymer curing with unfocused acoustic excitation using different frequencies, methods of application and pressures.

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