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Materials Characterization of Propellants Using Ultrasonics

by

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1. Introduction

Solid rocket propellants under consideration for this work are normally composed of cross-linked rubbery polymers, which are blended into a prepolymer slurry, curing agent added and the slurry is then cast into a rocket motor. The operational properties of the resulting solid propellant are very dependent on the morphological and mechanical properties of the as cast material.[1,2] Since a considerable amount of propellant development is given to optimizing the propellant's physical properties for a given requirement, the ability to characterize the current state of the propellant at any given time is very worthwhile. For example, the physical properties are a direct result of the both the nature of the binder network and the degree and kind of binder-filler interaction. Hence the manufacturer can exercise a considerable amount of control over the physical properties of a propellant.

The objective of the solid rocket motor design capability is to design the configuration of the grain, the liners, or the grain support in such a way that excessive stresses will not occur and so there will be no failure. Static and dynamic loads and stresses are imposed on the propellant grains during manufacture, transportation, storage, and operation. Structurally the rocket motor is a thin shell of revolution almost completely filled (80-90% of the total weight) with propellant. The propellant is a viscoelastic material is time-history dependent and provides a need to monitor the cumulative effect of loads with time. Their properties change as a function of prior loading and damage history. Howevr, they are able to reheal and recover partially following damage. Chemical deteriozation will in time degrade the properties of propellants, making it difficult o completely characterize these materials and predict their behavior or physical properties in engineering terms.

The modulus of the propellant is a complex function, but it normally increases if the amount of crosslinking is increased. The equilibrium modulus of a rubber can be shown , from a statistical theory of rubber elasticity, to depend directly on the number of crosslinks per unit volume. As modulus is increased, tensile strength increases and strain decreases.

The grain materials are rubber-like and nearly incompressible. The propellant, liner, and insulator all have a bulk modulus in compression of at least 1400 MPa in their undamaged state. Since there are very few voids in the a properly manufactured propellant, its compression strain is low. However, the propellant is easily damaged by applied tension and shear loads. Since grains are three-dimensional, all stresses are combined stresses and not pure compressional stresses; thus grains are easily damaged. This damage can be considered as due to a "dewetting' of the adhesion between the solid particles and the binder in the propellant and appears initially as small voids or porosity. Those small holes around the particles may be under vacuum, but they become larger with the strain growth.

Various techniques have been used to compensate for the nonelastic behavior by using allowable stresses that are degraded for nonlinear effects and/or an effective modulus that uses a complex approximation based on strain test data. For instance a stress relaxation modulus can be defined in which maximum stress-strain at maximum stress is plotted against temperature compensated time to failure. It is constructed from data collected from a series of uniaxial tests at constant strain rate (3-5%) performed at different temperatures (-55 - 43° C). The master curve then provides for time-dependent stress-strain data to calculate the response of the propellant for structural analysis. The master -curve relationship has been used extensively as a device for enlarging the effective time scale for excperimental measurements of stress-relaxation moduli.

2. Properies of Viscoelastic Materials

With elastic materials, the stress is essentially proportional to the strain and is independent of time; i.e. when the load is removed the materials returns to its original state. With a viscous fluid, distortion takes place at a rate determined by the viscosity of the liquid. No recovery occurs when stress is removed. None of these conditions holds for viscoelastic materials which depends very markedly on the rate at which they are deformed. A time-related dependency exists between stresses and strains. For small deformations the relation between stress and strain can generally be expressed as a linear differential equation, involving the stress, the strain, and their derivatives with respect to time, so that a stress which varies sinusoidally with time produces a sinusoidally varying strain.[2] The phase difference between stress and strain is a measure of the internal friction of the material. The elastic modulus for nearly all high polymers for sinusoida vibrations, increases markedly with increasing frequency while the internal friction changes comparatively little.

Using the notation of reference 1, the stress σ acting on a material volume results in a force **G** on the element. For isotropic viscoelastic materials, the constitutive equations can be expressed as:

$$\sigma = \int_{-\infty}^{t} G_\alpha(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \qquad 1)$$

where α=1 or 2 gives the deviatoric and the dilational part of the stress-strain relations. Further evaluation of these equations shows that as the frequency of excitation becomes very large, the imaginary part of the complex modulus disappears and the materials behaves elastically. Alternately, when the frequency of excitation is low, the material behaves viscously. Since the velocity of sound in a materials is related to the bulk modulus of the material,

$$v = \sqrt{E/\rho} \qquad 2)$$

the result is a varying velocity with respect to the frequency of excitation. This leads to dispersion in wave propagation phenomena in viscoelastic materials. However, it also provides a frequency range of excitation for characterizing propellant materials that are substantially higher than those obtainable with other mechanical relaxation methods.

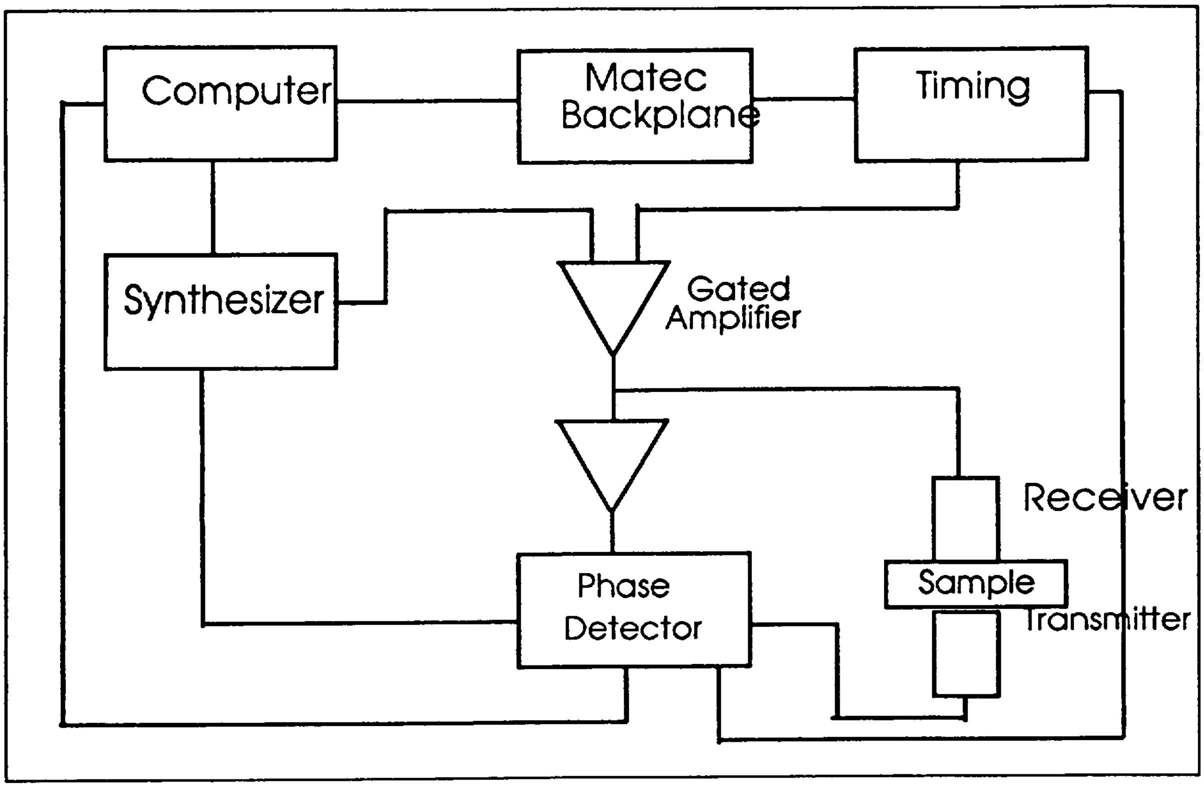
The master curve technique can also be used with acoustic dispersion data to obtain a master-curve relationship that extends over a frequency range which cannot be obtained by conventional methods.[4] The dispersion representation is equivalent to the stress-relaxation-modulus and the complex moduli representations, and it contains sufficient information to determine the propogation characteristics of a low amplitude wave.

Other recent publications dealing with the use of acoustic time-of-flight data to calculate propellant properties is given by [6,7]

3. Experimental Instrumentation

The Matec B8000 series instruments are designed for measuring ultrsonic wave velocity and attentuation in a variety of materials. The system consists of computer controller, frequncy sysnthsizer and a custom bin unit which contains the pulsers, recieivers and phase detection modules. Figure 1 shows a schematic of the typical modules contained in the Matec system.

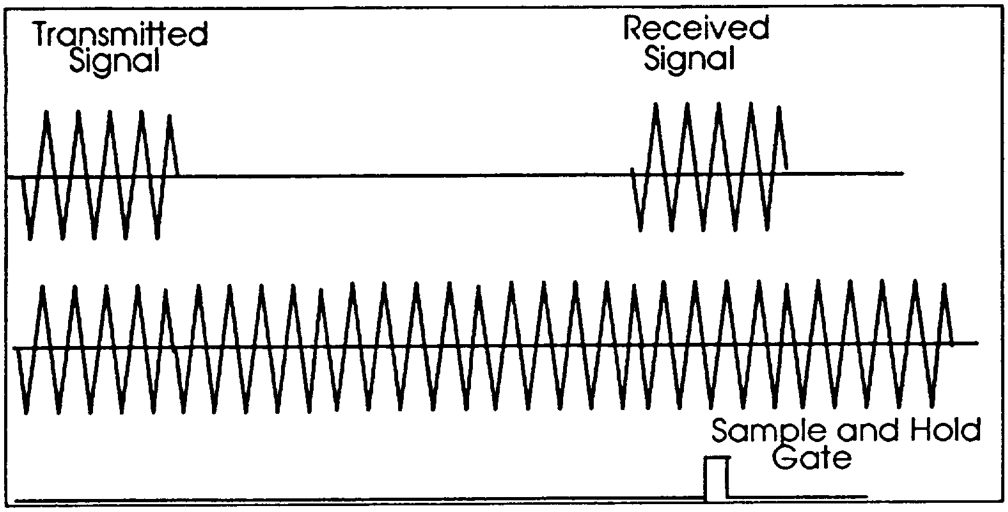
Figure 1. Architecture for the Matec Ultrasonic Measurement System



4. Theory of Operation

The Matec B8000 series instruments uses phase sensitive detection to measure ultrasonic velocities. The advantages of this approach are that automation is easily implemented and signals may often be recovered from noisy measurements using simple computer averaging techniques. The Matec provides the velocity measurement through interactive automatic control of frequency and measurement of the phase relationships. An understanding of the theory behind the phase sensitive method is given in Figure 2., in which the time duration between the ultrasonic toneburst transmitted and received ultrasonic signals are shown along the top diagram. Since a major difficulty in most methods for measuring velocity of sound is determining that the measurement is made upon the same portion of the waveform, the phase sensitive detection utilizes a continuous frequency waveform to maintain proper timing within the wave packets. In order to optimize upon the signal

Figure 2. Waveforms used by the Matec for Velocity Measurement.



The mathematical relationship:

$$t = \frac{\phi}{2\pi f} \qquad 3)$$

defines the time between the transmitted and received signals. In order to get a better handle on the phase relationships, we can differentiate equation 1 above to obtain time as a funtion of changes if phase angle and frequency.

$$t = \frac{\Delta\phi}{2\pi\Delta f} \qquad 4)$$

The Matec measurement technique is then to make incremental changes in frequency and record the new $\Delta\phi$. The incremental changes in frequency are small enough to avoid large changes in ϕ.

The Matec software performs the following procedures to calculate values for $\Delta\phi/2\pi\Delta f$.

1. The frequency synthesizer is set to an appropriate starting frequency well within the response characteristics of the transducer used and and the phase angle is measured according to equation 1.

2. The frequency is increased in small steps until the phase angle is of each echo is increased by approximately an integer value of π. The phase shifts of all echoes do not have to be equal; they only have to be multiples of π.

3. When the desired phase shift is approached, the frequency required to make the $\Delta\phi$ value exactly $M\Pi$ is calculated. Several iterations are normally performed to bring the value of $\Delta\phi$ within the desired limits. Error limits of $\pm$ 0.02 radians are relatively easy to maintain.

4. Values of $\Delta\phi/2\pi\Delta f$ are then calculated for each echo using the actual phase and frequency shifts for each echo.

5. The round trip time is then determined from the slope of the $\Delta\phi/2\pi\Delta f$ versus the echo number curve. The slope is determined from a least squares fit of the data.

5. Experimental Results

A major effort went into setting the experimental arrangement used in this work. The properties measured were longitudinal and shear velocity of sound, Poisson's ratio, elastic modulus, shear modulus, and bulk modulus. Longitudinal transducers of 100, 150, and 500 kilohertz and a shear transducer of 500 kilohertz were used for the study. Inert propellant samples supplied by Hercules were cut into square blocks of thicknesses 0.375, 0.25, and 0.125 inches. Mr. Ed White in the Materials and Processes Laboratory assisted in some of cutting operations. A fixture being fabricated by MSFC will be used in any further work in this area. As of the time of this report, it still has not appeared.

Other investigators have published results of several studies on measuring these parameters. These studies have observed that these properties vary due to the use different transducer frequencies and different sample thicknesses. Early on in this study, it was also observed that the results generated with the Matec were inconsistently wrong when compared with the general area of the gate placement signal on the oscilloscope's screen. Also since the return pulse was not very obvious on the oscilloscope display, it was concluded that the experimental operation of the sampling was being conducted in the transducer's near field. The following table shows the transducer's frequencies, diameters, and calculated near fields:

Table I. Frequency versus near field length for the transducers used in this study.

Transducer Frequency (Khz)	Transducer diameter (in.)	Near Field (in.)
100	1	0.3934
150	1.25	0.8933
500	1.25	2.6234

This analysis indicated that in order to place the propellant sample out of the near field region, a 3 inch plexiglas slab inserted between the transmitter tranducer and the sample. Once this was done, the waveforms became a little more consistent. In spite of the many attempts to optimize the experimental setup, it still required considerable effort to make sure that the measurements being taken were relevant. An example of a typical waveform for the 100 Khz transducer is shown in Figure 3. Note that the transducer is highly undamped. Setting up a proper gate for this waveform took some time.

Some measurements were taken and although these measurements displayed less variability some of the measurements were still not consistent with known values . This was remedied by placing the gate at a peak of the waveform. Usually if the gate was placed at or near one of the first five or six peaks of the waveform consistent results would result. Since the results tallied by the Matec software would not be tabulated at the initial part of the wave form, a delay was measured using the oscilloscope from the beginning of the pulse to where the gate was placed. This delay was then subtracted from each measurement and the resulting average was very close to the values attained in other propellant studies.

Figure 3. Typical Waveform for 100 Kilohertz Ultrasonic Transducer.

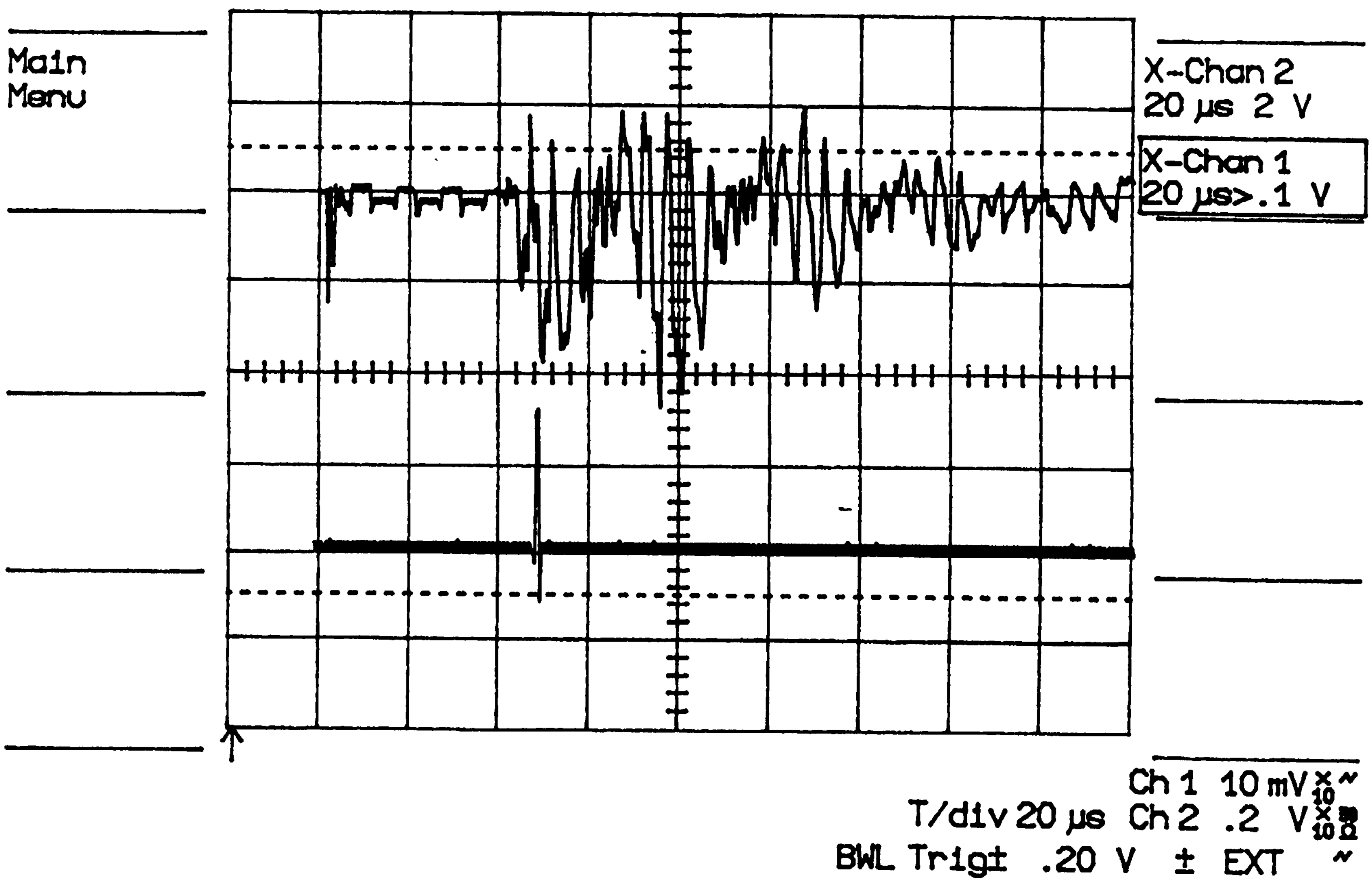


Table II. Velocity measurements obtained with the Matec Instrument. Transverse measurements are from Reference 6.

Frequency KHz	Thickness mm	Velocity (L) m/s	Velocity (T) m/s (Ref. 6.)
100	3.18	1758.9	
	6.35	1704.4	
	9.53	1589.2	191.7
150	3.18	2015.1	
	6.35	1826.8	
	9.35	1678.1	183.6
500	3.18	1511.5	
	6.35	1727.0	
	9.53	1605.4	171.3

Table III. Regression fit of data from this work plus Reference 6.

Frequency kHz	Long. Velocity m/s	Residuals m/s
50	*2019*	*234.671*
65	*1720*	*-58.6868*
100	*1614*	*-151.522*
100	1758.9	-6.62152
100	1704.4	-61.1215
100	1589.2	-176.322
150	2015.1	268.386
150	1826.8	80.08599
150	1678.1	-68.614
165	*1682*	*-59.0718*
500	1511.5	-103.561
500	1727	111.9386
500	1605.5	-9.56144

The data acquired in this work fits fairly well with the work reported in Reference 6. Both studies had some inconsistencies which are able to be explained at this time. A plot showing the data from this work, the data from Reference 6. and a regression fit including both sets of data is shown in Figure 4. The Matec technique is obviously easier to implement because the need to measure force consistently is not needed as was required in earlier work. Using the Matec instrumentation does take some getting used to setting the gates properly. The gate placements on the 500K waveform is shown in Figures 5: This should be contrasted with the 100Khz waveform shown in Figure 3.

Figure 4. Plot showing values from this work and with Reference 6.

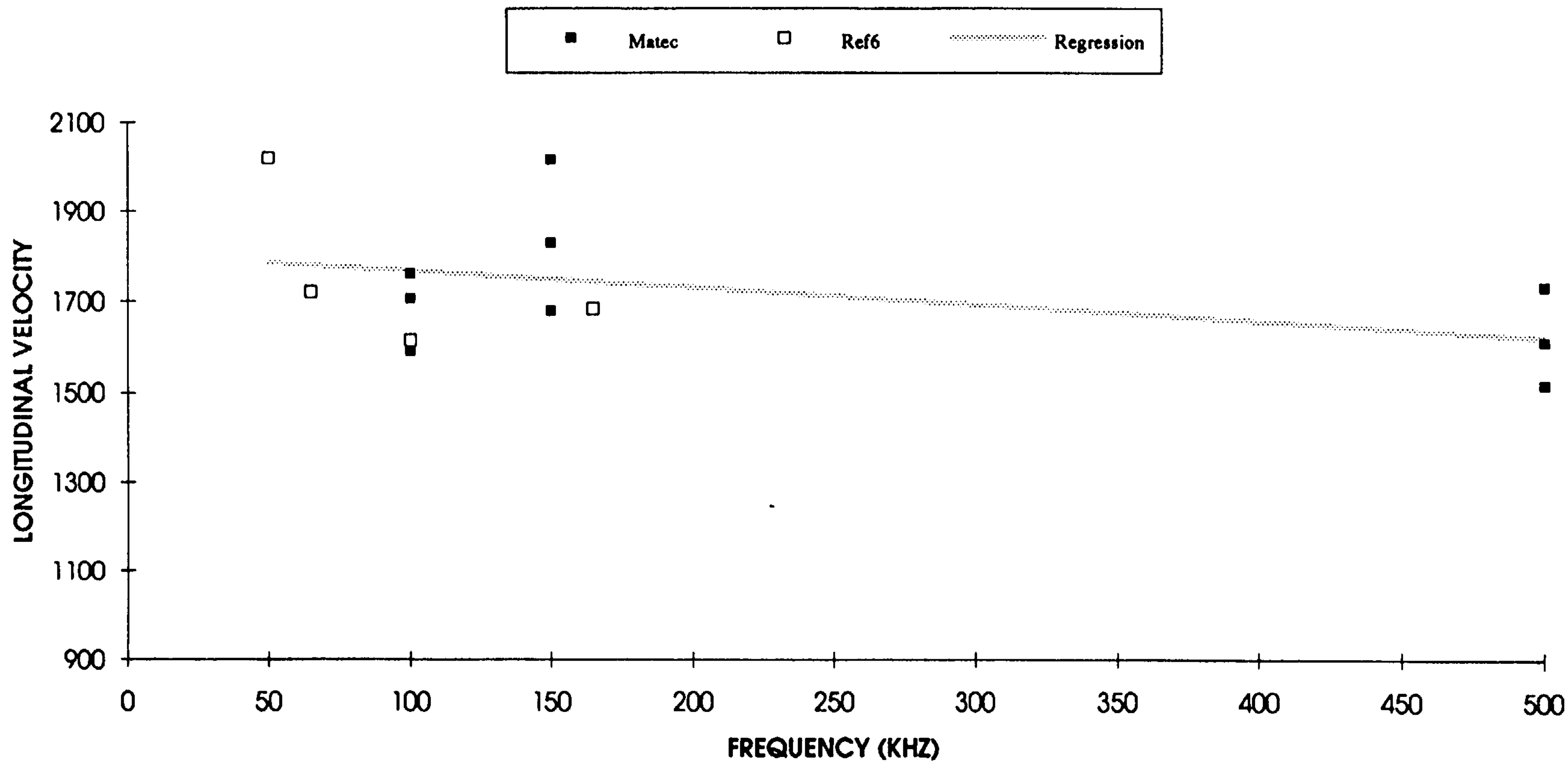
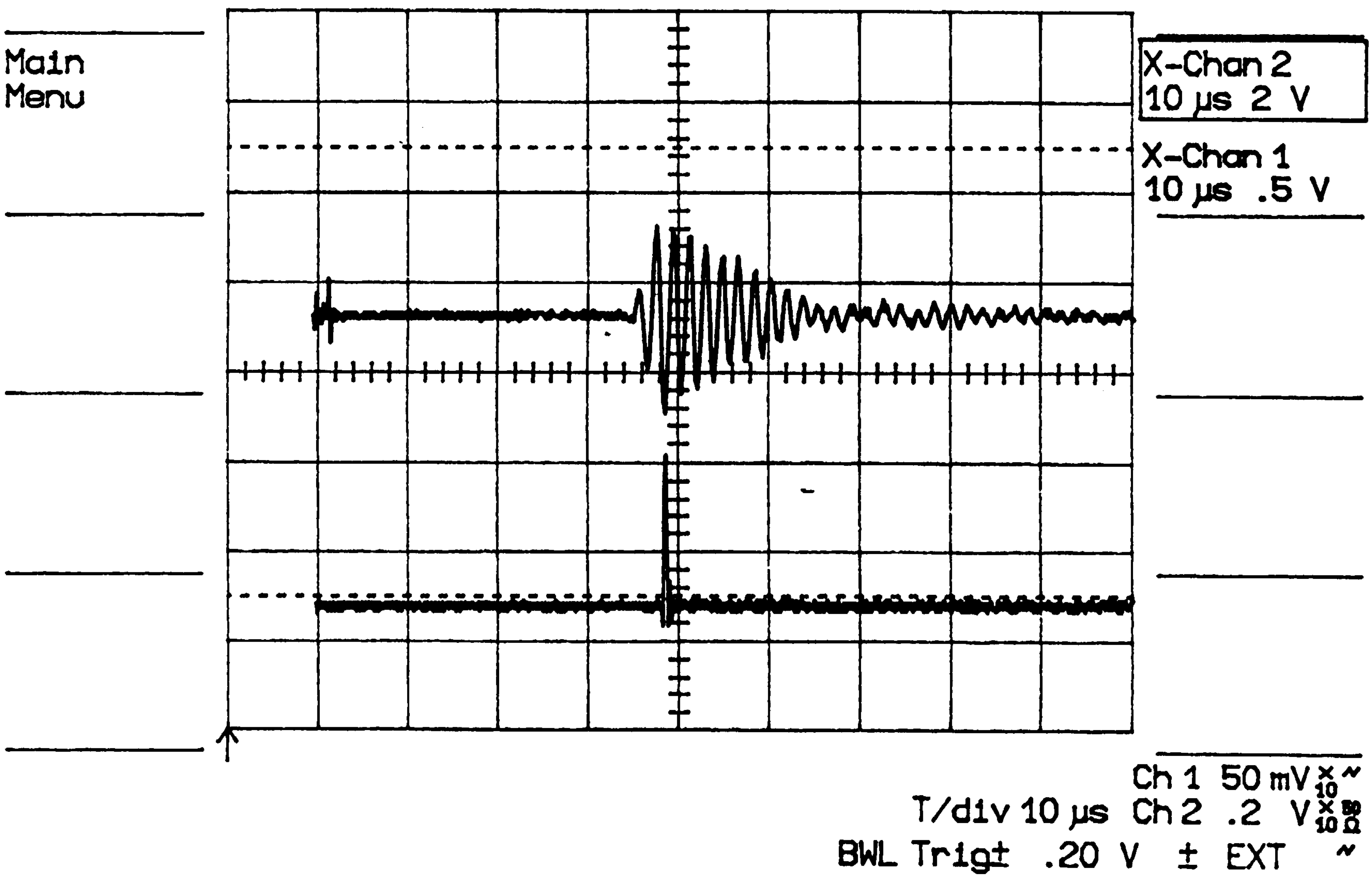


Figure 5. Waveform and Gate Position for 500 Kilohertz Transducer.



After all of the preliminary procedures were tried, a consistent procedure was developed by the student taking data, which is recommended when performing these measurements:

1. Make sure that the set up the wiring diagrams, as documented in the MATEC MBS-800 Operator's Manual, is correct. Various types of measurements do call for different set-ups. Place the sample and the transduers in the fixture as shown in Figure 2 for the velocity measurement to be performed.

2. Set the variables located on MATEC MBS-800 menu screen to the following values:

Repetition Rate: 2 milli seconds
Pulse Width: 1 micro seconds
Gate Width: 0.3 micro seconds
Receiver Gain: 47 dB
Frequency: Set to the frequency of the transducer
Filter Setting: 0 degrees, 2.5 MHz

3. Set the gate to the desired peak as shown above in Figures 4 and 5.

4. Access the measurement menu and set the menu to following measurements:

Type of Measurement: Absolute
Transducer Set-Up: Dual or Single depending on the experimental set-up.
Number of samples taken per Measurement: Between 40 and 50
Number of measurements: This is left up to the operator's judgment.
Start Measurement on Echo: Start the measurement on echo number one.

5. Press the "insert" key to start the measurement. The measurement will start out by trying to locate the frequency of the peak. This will be done by an iterative process by measuring the changes in frequency in radians. When the frequency is about to be located the change in frequency will approach zero. If the gate was placed properly, the frequency will be found within three to ten iterations. If there are more iterations but the change in frequency is still approaching zero it is a good idea to continue the measurement even though more iterations are required. However if there more than ten iterations and if the change in frequency continues to grow larger and does not appear to be converging to zero it is a good idea to stop the measurement and

reposition the gate either at another peak or at another position on the current peak. Repeat steps three through five until successful.

6. After the echo frequency has been found, the transit time measurement will begin. It is a good idea to compare the first three to five measurements with the gate placement on the oscilloscope to see if the measurements seem to be reasonable. If they are not, then terminate the measurement and repeat steps three through five. This is usually caused by improper gate placement.

7. If the measurements seem reasonable, the computer will ask the operator to either perform another measurement, return to the main menu, or save the transit times to a file. Any filename may be used to save the data. After saving the file the program returns to the main menu.

6. Conclusions

The use of ultrasonic velocity measurement for characterizing propellant materials has been demonstrated to be a valid technology for monitoring manufacturing processes. However, difficulties in actually making such measurements in situ with live rocket motors still has problems. Single-ended implementation was not practicable with the transverse transducers tried here. At the low frequencies used, through transmission longitudinal measurements worked much better. Current concepts with witness panels is still the most convenient method, although it may not be the most accurate for relecting actual material parameters in manufactured motors.

The Matec technique works well with the type of measurements performed here, as compared with earlier work. The technique also is easier to implement because the technique does not require reproducible forces between the transducers and the propellant.

7. References

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16. Abstract

Propellant characteristics for solid rocket motors have not been completely determined for its use as a processing variable in today's production facilities. A major effort to determine propellant characteristics obtainable through ultrasonic measurement techniques will be performed in this task. The information obtained in this work will then be used to determine the unifiormity of manufacturing methods and/or the ability to determine non-uniformity in processes.

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