

March 22, 2018

MASTER THESIS

# NON-DESTRUCTIVE TESTING OF SOLID PROPELLANT ROCKET MOTORS

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Document number ET.18/TM-5816

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# Summary

A lot of missiles used by the armed forces have a solid propellant rocket motor. The ageing of this solid propellant is an oxidative crosslinking process. This process starts and propagates from the free surface of the propellant material and forms a deteriorated layer.

Solid propellant missiles are used in all parts of the armed forces, this means that missiles are subjected to a wide range of handling, storage and deployment conditions. Assessment of the condition of the propellant is done on a random sample from the batch and at the moment there is no non-destructive method to assess material properties of the ageing propellant. This means expensive weapon systems are sacrificed and conclusions about the state of the material are drawn from a small number of assessed rocket motors.

This thesis investigates possibilities for vibration based non-destructive testing methods for characterizing ageing in solid propellant material and zooms in on one promising method: ultrasonic testing. The remainder of the study consists of a feasibility study on the use of ultrasound for characterizing ageing in solid propellant material.

Samples of inert HTPB (hydroxyl-terminated polybutadiene) based propellant are aged and experiments are conducted to research the effects of ageing on the ultrasonic signal, the frequency content of the pulses and the sound velocity. Although an expected reflection off the interface between pristine and aged material is not observed, it is found that an increase in sound velocity is measurable, which indicates a rise in Young's modulus of the material. This suggests that ultrasound is a promising technique for assessing the ageing of solid propellant.

# 1. Introduction

TNO is an independent research organization, conducting research in nine different themes. As part of the Defence, Safety and Security focus area, the Energetic Materials department researches a wide range of topics. Theoretical, model-based and experimental research for the development, processing, use and behaviour of energetic materials is conducted at the TNO locations in Rijswijk and Ypenburg.

In this chapter a short introduction on the topic of research is given as well as the research goal and relevant theory for formulating the research question.

# 1.1 Energetic Materials

Energetic materials are substances that store a high amount of chemical energy. Once this energy is released by a chemical reaction, the reaction can sustain itself, without the help of external sources like oxygen. These materials are used in for example pyrotechnics, high explosives and gun and rocket propellants. Characterization of the ageing of the latter will be the main topic of this research project.

Solid propellant missiles are used in every part of the military. Rocket motors propel missiles used by the Air Force, Navy and Army. A lot of the motors in the inventory of the ministry of Defense have been there for quite some time. Making sure that these missiles are safe to keep in storage and are still safe to use is very important. To ensure safety, missile propellants are disassembled and mechanical tests are performed on small parts of the propellant material. This means that frequently a couple of very expensive missiles are dismantled and sacrificed for these tests. As one may notice from this testing procedure, a couple of missiles are taken as a sample from a batch. This sample is assumed to be representative for the state of the batch, but does not show the state of every individual missile. This is even more important considering the different environments (e.g. temperatures, humidity) the missiles are stored in during their lifetime and the differences in operating conditions like hanging under an F16 aircraft compared to missiles in storage. This means the tests are very expensive, and the results applied to all missiles can have a too large safety factor for large parts of a batch.

# **1.2** Solid propellant missiles

In figures 1.1 and 1.2a a schematic representation of a solid propellant missile is shown. It consists of a combustion chamber (fig. 1.2a section C-D) and a nozzle (M-C). In the combustion chamber an igniter is present (O), which can ignite the solid propellant (Kr). The propellant grain is cast, molded or extruded into a cylindrical shape with a hole in the middle. The grain is embedded in a metal or composite material casing. The open end of the missile is the nozzle. When the propellant is ignited, the exposed surface of the material starts to burn. The propellant can sustain the burning without the need of external sources such as oxygen, so the propellant burns up via the free surface. The combustion gases build up in the combustion chamber and when the pressure is high enough, the gases are exhausted via the nozzle. This results in a thrust and a force propelling the missile forward. Once the propellant is ignited it cannot be extinguished and reignited [1,2].



Figure 1.1: Schematic of a guided missile with the solid propellant located in the propulsion section [3]

The force resulting from the pressure build-up inside the missile can be somewhat regulated up front by choosing a specific shape for the propellant. Different grain geometries have different initial burning surfaces and surfaces throughout the burning process as shown in figure 1.2b. This way the amount of combustion gases, thrust and thus the amount of force is regulated by the initial shape of the propellant. There are a couple of different thrust patterns: Neutral, which keeps a constant burning surface and the same amount of thrust along the burn. Progressive, which has an increasing amount of burning surface and thus an ascending thrust curve. Lastly, regressive, which has decreasing amount of burning surface and thus a descending thrust curve. Next to these, there are thrust patterns which have peaks at different moments of the burn. The geometry of the propellant grain can vary throughout the length of the combustion chamber as well as the type of solid propellant. This way, different parts of the rocket motor can have different functions, for example a booster engine and a flight engine [4].



(a) Schematic of a solid propellant missile [1]

(b) Various shapes of solid propellants with corresponding thrust patterns [4]

Figure 1.2: Schematics of interior of solid propellant missiles

### 1.3 Research Plan

To minimize the current issues with assessing the degradation of solid propellant missiles, non-destructive testing (NDT) would be a very good alternative. With nondestructive testing methods, as the name implies, one can evaluate the ageing of a missile without sacrificing one. At the moment the only non-destructive method used for assessing solid propellant rocket motors is X-ray, which is very helpful for finding failures like cracks, holes or delaminations, but it cannot describe degradation of the material properties of the propellant material.

The main goal in this research area is to find a non-destructive method to assess the ageing of solid propellant missiles. The question posed by TNO is therefore 'Which non destructive testing methods are useful for characterizing ageing in solid propellant rocket motors?'

The main research question for this project will be formulated in section 1.9, which is based on this question and will be specified on vibration and propagating wave based methods.

In order to formulate this research question a relevant introduction on solid propellants is given. The remainder of this introduction covers degradation of propellants, loads on propellants, failure modes and inspection methods.

# 1.4 Solid propellants

The two main ingredients of solid propellants are an oxidizer and a fuel. Together with a binder this is mixed and cured as a solid propellant. Other possible ingredients are stabilizers, catalysts to accelerate or decelerate the burning rate or plasticizers. These adjust the physical properties of the solid propellant and can be used as a second type of fuel or curing agents which cross link molecules and thus have an effect on the flexibility of the cured product.

There are a lot of different mixtures for solid propellants, but two main types can be distinguished: homogeneous and heterogeneous solid propellants. In a homogeneous mixture the fuel and oxidizer are generally in the same molecule. The mixture has no molecules larger than macro-level. Homogeneous solid propellants can be categorized as single-base or double-base. In single-base propellants there is one type of propellant base, usually nitrocellulose. In double-base propellants there are two types of molecules in the propellant base, usually nitrocellulose and nitroglycerin.

Heterogeneous, or composite, propellants consist of different substances as fuel and oxidizer. The most common used combination is ammonium perchlorate (AP) as the oxidizer and powdered aluminium as the fuel [2,5].

# 1.5 Degradation of propellants

Ideally, solid propellants that have been mixed and formed into their final shape would show no more chemical or physical changes after they have cured. However, in reality, the propellant will keep changing chemically and thus the mechanical properties keep changing too. This change in mechanical properties is mainly due to the degradation of the binder which in most cases is hydroxyl-terminated polybutadiene (HTPB). The controlling factor in this ageing process is oxidative crosslinking of the HTPB binder molecules, a diffusion process [6]. In this process the polymer chains of the binder link to each other, forming so called cross-links as shown in figure 1.3. This continuous crosslinking hardens the binder and eventually makes the material brittle and thus less flexible. In the case of HTPB the crosslinking is oxidation-induced, which means the chemical reaction is due to the presence of oxygen [7, 8]. Oxygen is present at the inner surface of the propellant as can be seen in figure 1.2. Because the oxidative crosslinking occurs at the inner surface, a growing band of stiffer, brittle propellant is present at the inner surface. While the Young's modulus E increases, the density  $\rho$  does not change considerably during this process. This layer of aged propellant has different mechanical properties than the non-aged propellant and has a higher chance of cracking and damaging of the material because of the higher stiffness and lower ultimate strength.



Figure 1.3: Cross links (red) between polymer chains A, B and C

# 1.6 Loads on propellants

Solid propellant missiles are used in all parts of the armed forces, which means that missiles are subjected to a wide range of handling, storage and deployment conditions. Missiles that are stored in Northen and Central Europe encounter a small amount of temperature changes during the day and during the year, while missiles stored at a base in the Middle East endure large temperature changes (up to more than 65°C). When a missile has been deployed on a jet airplane it has endured temperatures much lower than on the ground (as low as -50°C). These temperature changes cause internal stresses and strains in the material. Next to this different thermal expansion coefficients of the metal casing and the solid propellant can induce debonding between the layers [9]. Temperature is also the main load for the degradation process. The higher the temperature, the faster the degradation process proceeds.

Transport and handling of the missiles cause mechanical loads on the solid propellant in the form of vibrations and shock loads. Missiles transported over rough roads by trucks endure a lot of vibrations which can cause cracks in the propellant material. Missiles that are handled with less care endure shock loads, also causing cracks or deformations [2].

# 1.7 Failure Modes

The two most common failure modes are cracking of the propellant material and debonding between the casing and the propellant material. Cracking can occur as a result of too high stresses and strains, repetitive stresses and strains that weaken the material, (air) pockets due to the fabrication process in the material or other factors that locally weaken the propellant.

Debonding is the process of detaching of two layers. This happens due to the difference in thermal expansion of the two layers, but can also occur due to vibrations, shock loads or air bubbles [9].

Both of these failure modes are undesirable because they both locally increase the free surface to burn. This means that once the fire front has reached this spot, there is a sudden increase in free surface to burn, resulting in more combustion gases and a higher pressure inside the motor. If this pressure is too high, the engine could burst and explode. In reality, these (severe) cracks and debondings are not observed very frequently while assessing the propellant rocket motors of missiles still in use. Without indicators of failed propellant material, visible as cracks or debondings, it is hard to assess the state of the solid propellant material without sacrificing a missile and estimate the remaining lifespan of the missile. This means that ideally the non destructive tests should focus more on the material ageing and the change in material properties rather than look for cracks and debondings if one wants to assess the life expectancy of a propellant rocket motor.

# **1.8** Inspection methods

Inspecting weapon systems to determine the state of the material is very important because of the high risk materials that are present. Various methods to detect flaws in the materials or material properties are used, as described in this section.

#### **1.8.1** Currently used inspection methods

Currently solid propellant rocket motor testing is done with random samples from a batch of motors. As mentioned in section 1.5, the environmental loading can vary a lot from missile to missile. Missiles in storage have a different ageing process than missiles used in (out of area) missions. This means that it is far from ideal to use testing methods which forces one to use random samples from a batch because of time, usage or monetary limitations. Results of multiple tests are combined to come to a substantiated life expectancy for the batch with a large enough safety factor. In this section a few of the at the moment most frequently used techniques are described, after which options for a new technique are discussed.

X-ray is a relatively fast and easy method to make the interior of the test object visible. The missiles can be checked for irregularities in the material. X-rays consist of high energy photons that are either passing through or absorbed in an object or body. The difference in molecule size and material density has influence on the absorption of the photons. The photons that do pass through the matter end up being dark spots on the film and parts of the film that do not catch photons, result in light parts. This makes that (air-filled) cracks, voids and delaminations are visible as dark spots in the material [10]. An example is shown in figure 1.4. However, the precise location in terms of depth cannot be determined. Inconsistencies in the material can be missed and the shape and size can be misinterpreted because of the angle of the image. There are ways to overcome this drawback: in the case of solid propellant motors, multiple images under different angles are made to make sure every flaw is shown at at least one of the images without a possibility that parts of the motor are left uninspected. Besides, X-rays bring along a certain safety hazard regarding radiation. This means the location where the missiles are inspected needs to have the proper safety requirements and the user needs to have the proper knowledge and skills.



Figure 1.4: Example of an X-ray image of an solid propellant rocket motor with a defect shown in the circle.

Another method to detect voids and cracks in a material is the use of ultrasound. Ultrasound uses sound waves in the ultrasonic region (above 20 kHz). There is a wide range in ultrasound techniques and many are used in non destructive testing of (composite) materials [11]. Two setups are mainly used: transmission with transducers on either side measuring the waves that propagate through the whole sample or pulse-echo with one transducer which measures the reflected waves. In the search for voids and cracks the pulse-echo setup is used. Ultrasonic waves reflect on every interface between materials and these reflections are measured as long as the signals is not fully damped. From the measured pattern it can be concluded if there is for example an air-filled void in the material [10]. Ultrasound is mostly used on solid propellant motors for the detection of delaminations between the casing and the inner layers and propellant. This is because it can be difficult for the signal to overcome the metal-propellant boundary and penetrate into the sample material.

Both X-ray and ultrasound are methods that can help discovering voids and delaminations in the engine. However, as mentioned in section 1.5, these failure modes do not occur very often in engines that are still in use. This means that the ageing of the propellant is detectable in the change in material properties, mostly the stiffness of the inner surface of the cylinder. Measuring stiffness can be done with several mechanical tests like a simple tensile test. Tensile specimens are cut from the propellant grain and from the slope of the stress-strain curve (in the linear elastic regime) the Young's modulus E is calculated.

Table 1.1 shows the above described methods with their advantages and disadvantages. It is clear that at the moment none of the used tests can non-destructively assess failures in the material and the change in stiffness of the material at the same time. In the next section vibration and propagating wave based NDT methods are described and their use for solid propellant rocket motors is discussed.

 Table 1.1: Advantages and disadvantages of current testing methods.
 (Delam::Delaminations, Non-dest.:Non destructive)

			Ability to a	assess			
Testing method	Speed	Ease of use	Stiffness	Crack	Delam.	Non-dest.	Sample
X-ray	+	-	-	+	+	+	-
Ultrasound	+	±	-	±	+	+	±
Mechanical	-	-	+	-	-	-	-

#### 1.8.2 Alternative inspection methods

The way that objects respond to (forced) vibrations is specific for every individual object. Specific eigenfrequencies induce mode shapes when the object is driven in this frequency. Normally it is undesirable for objects or structures to be driven in their eigen- or resonance frequencies. This is because the amplitude response is then very high due to resonance as shown in figure 1.5. Objects or structures without appropriate damping can start to oscillate violently and be damaged.

Despite this disadvantage, eigenfrequencies and mode shapes can also provide very helpful information. Because the eigenfrequencies are specific for every individual object or structure, they can be used to detect changes or damages in the structure. The input and response data of a driven vibrating or rotating structure contains a lot of information which can be obtained by analyzing the frequency content of the displacement, velocity or acceleration data. Resonance frequencies and even mode shapes can be made visible by processing the data this way. By comparing the eigenfrequencies of the pristine structure with the (possibly) damaged structure conclusions can be drawn whether there are changes in the object, visible as frequency shifts and differences in mode shapes. Beside these basic classifiers a variety of classifiers in the frequency and modal domain have been developed [12, 13].

A disadvantage of the described methods is that they work very well for relatively simple, linear structures. It is harder to distinguish accurate eigenfrequencies of more complex, combined structures. For relatively simple structures like beams or plates one can predict some mode shapes and attach sensors at sensible locations. However, if these mode shapes are harder to predict, one should use a lot of sensors on the object to avoid the possibility of misinterpreting mode shapes due to spatial aliasing. When the object does not have enough sensors, the vizualization of the mode shape does not approach reality accurately [13,14]. Another difficulty that arises when one would use the above mentioned methods with solid propellant missiles in use, is that any frequency shift or classifier that points to the presence of damage most probably cannot be directly related to a specific type or location failure inside the missile.



Figure 1.5: The effect of the driving frequency on the amplitude response [15]

Next to these methods, which can be named traditional methods, new vibration based methods are in development. These are methods in which artificial intelligence and self-learning networks are used. Artificial Neural Networks (ANNs) are trained with input and output data of vibration tests on objects with structural damage. The data can be from experimental results or from numerical simulations of the structure. When the Neural Network is trained sufficiently, it can supply information about the location and severity of the damage from experimentally measured vibration data [16,17]. The use of ANNs is promising in the field of NDT, but the theory and application of this method are outside the scope of this study.

(Ultra)sound waves are made up of vibrations that can be used for non destructive testing. When using ultrasound, one is not interested in the response of the object as a whole on the input vibrations, but more on the properties of the material that have an influence on the way that vibrations propagate inside the material. Ultrasound can be used to locate delaminations in solid propellant rocket motors, but it may also be used to determine whether the inner ring of the propellant material has aged, as described in section 1.5. The layer of aged propellant has different mechanical properties like stiffness and hardness, which have an effect on the propagation of vibrations through the material.

Besides the conventional use of ultrasonic waves in which the pulse-echo method is used to detect flaws in homogeneous materials, there are other uses of ultrasonic waves. One of those focuses on identifying the stiffness of the material. This method is under development for medical application and is called Ultrasonic Elastography. As the name states, it is a method to identify the elasticity, or stiffness of a material. There is a number of different elastography methods, but generally they consist of two steps: (1) distort the material at a certain depth and (2) measure the response due to the distortion. There are multiple ways to accomplish both steps. The early developed methods, called strain imaging, mechanically compress the material on the surface and ultrasound images made before and after the deformation are compared. The amount of deformation is a measure of the stiffness of the tissue. Another way to distort the material is forming a 'push' inside the material with acoustic radiation force (ARF). This uses high intensity sound waves which distort tissue on a certain depth [18]. By measuring the shear wave velocity  $v_s$  and density  $\rho$  the elasticity modulus E can be calculated:

$$E = 2G(1+\nu) \tag{1.1}$$

$$v_s = \sqrt{\frac{G}{\rho}} \tag{1.2}$$

with shear modulus G, Poisson's ratio  $\nu(0.5 \text{ for incompressible materials})$ .

Ultrasonic Elastography is now widely researched and used for medical applications, but has not been developed for NDT applications yet. In medical applications it is mostly used in cases with tissues having a very different stiffness like a tumor in soft tissue [19–21].

However, the idea of measuring a certain layer of the solid propellant material which has developed different (mechanical) properties than the original material with ultrasound is not new. Applications in the field of inspecting a layer of deteriorating concrete have been proven to be suitable. In this case ultrasonic waves are used to reflect on the surface of the deteriorated material layer. This way three different reflections can be distinguished in the received signal as shown in figure 1.6 [22]. The purple wave is passed on through the interfaces, while the blue arrows indicate the part of the signal energy that is reflected from each interface. The same technique may work for inspecting a deteriorating layer in solid propellants. Assuming there is a sharp enough interface between non-aged and aged solid propellant material, ultrasonic waves that propagate inside the material and reach the interface of the pristine and the aged material give a reflection visible in a pulse-echo measurement.



Figure 1.6: Three reflection interfaces. First reflection: Surrounding material-Undamaged material(1). Second reflection: Undamaged material(1)-Deteriorated material(2). Third reflection: Deteriorated material(2)-Surrounding material.

#### **1.9** Research question

The vibration based NDT techniques mentioned in this chapter could all be useful for characterizing the ageing of solid propellant rocket motors. However, the use of traditional (frequency and mode shape shift based) methods have some difficulties when used for the subject of solid propellant rocket motors. More complex objects consisting of multiple parts make it difficult to measure (at) the right data (points) and the specificity of the damage data is low.

It can be concluded that the use of ultrasound is promising for characterizing the

ageing of solid propellant rocket motors provided that the ultrasonic waves can penetrate the material far enough and reflect off the surface of the deteriorated material layer. Therefore, the remainder of this research will try to answer the question:

# Can ultrasonic signals be used to characterize ageing in solid propellant rocket motors?

As already mentioned in section 1.8.1, there are a number of theoretical and practical problems such as the damping inside the material and the metal-propellant transition. In order to give a substantiated answer to the main research question the following sub questions will be discussed:

How are ultrasonic signals affected by damping in solid propellant material?

How do ultrasonic signals propagate through pristine and aged solid propellant material?

How are ultrasonic signals affected by the transition over the metal-solid propellant interface?

# 2. Theory of ultrasonic wave propagation

This chapter discusses the theory of generation of ultrasonic waves, wave propagation and attenuation of ultrasonic waves in solid propellant material as a foundation for an experimental design.

# 2.1 Generation of ultrasonic waves

Ultrasonic (US) waves can be generated and collected by piezoelectric transducers. Piezoelectric materials generate an electric charge in response to a mechanical stress applied on the material and vice versa. Piezoelectric materials have a crystalline structure, an example is shown in figure 2.1. The atoms with different charges ensure a stable situation when no pressure is applied. When pressure is applied to the material, the structure deforms, changes shape and both sides of the crystalline structure are charged. This ensures the flow of an electric current. When the pressure is applied in the other direction, i.e. compression instead of tension, the charges and corresponding current flow change direction. In this manner an alternating current is generated by alternating the strain applied on the material.



Figure 2.1: Piezoelectric material example. Green arrow in direction of the current flowing [23]

The opposite is also true: A mechanical strain is generated in the material when an electric field is applied across the material. This results in a vibrating motion of the element and the generation of (ultra)sound waves due to the oscillating pressure changes. When short pulses are desired, the element should be excited in its natural frequency. This way a short pulse with maximum amplitude is generated. Damping backing material in the transducer makes sure the pulse is damped out shortly after generation [11, 24].

(Unfocused) transducers do not have a single point source of the ultrasound waves, the transducers commonly have a circular surface the waves originates from. Because the waves originate from multiple points on the transducers surface, the pressure waves amplify or reduce in intensity due to interference when crossing paths. This results in large intensity fluctuations near the transducers face. The region where these fluctuations are present is called the near field. As shown in figure 2.2, behind the near field, the far field starts, in which the beam also starts to spread and the intensity decreases gradually. Due to the intensity changes in the near field, it can be very hard to accurately detect flaws in this region. The point at which the near field has ended and the far field starts is the point with the highest intensity, also called the natural focus point. Flaws that are at the depth N (m), the natural focus point, will have optimal detectability due to the maximum strength of the sound waves at

depth N [10, 23, 25]. The length N of the near field is defined by:

$$N = \frac{D^2}{4\lambda} \tag{2.1}$$

in which D is the diameter of the transducer and  $\lambda$  the wavelength.



Figure 2.2: Intensity fluctuations in the near field of a transducer [25]

# 2.2 Wave propagation in solid propellant material

Sound waves propagate in air through the compression and rarefaction of particles, called longitudinal waves. In longitudinal waves, particles vibrate in the same direction as the wave propagation. Molecules of solid materials are capable of vibrating in other directions, resulting in various other waveforms. In the case of ultrasonic applications, the two most used waveforms are longitudinal and shear (transverse) waves. In the latter, particles vibrate perpendicular to the wave direction. Both waves are shown in figure 2.3 [26].



Figure 2.3: Shear (transverse) waves and longitudinal waves with the particle motion relative to the propagation direction

Shear and longitudinal waves have different wave velocities  $v_s$  and  $v_l$  defined by:

$$v_s = \sqrt{\frac{G}{\rho}} \tag{2.2}$$

$$v_l = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} \approx \sqrt{\frac{E}{\rho}}$$
(2.3)

with G the shear modulus, K the bulk modulus, E the elasticity modulus and  $\rho$  the density.

As shown in equation (2.3)  $v_l$  depends on both the bulk and shear modulus, so the materials response to (uniform) pressure and the materials response to shear stress. However, the shear and bulk modulus are related to the elasticity modulus, it can be approximated by replacing the numerator by E.  $v_s$  only depends on the shear modulus. The shear wave velocity  $v_s$  is generally lower than longitudinal velocity  $v_l$  [27]. Every material has its own sound velocity and changing material properties like stiffness and density directly influence the sound velocity. Degraded solid propellant material has a higher stiffness than pristine material, causing the sound velocity  $v_l$  to be higher. Sound velocity can be calculated from the time between two back reflections (time of flight) and the thickness of the sample.

Next to the longitudinal and transverse waveforms other more complex forms are possible, for example due to elliptical vibrations of particles. This study focuses on the longitudinal waveform as shown in figure 2.3 to create an understanding of the propagation of ultrasonic signals in solid propellant material, so these more complex waveforms are not considered.

### 2.3 Mode conversion

As mentioned and shown in figure 1.6 ultrasonic waves partly reflect when crossing an interface of two materials with different acoustic properties (acoustic impedance mismatch). In addition, the waves refract when the surface is hit at an angle. Refraction is the change of the angle of a wave when passing on to a next material having a different sound velocity. The part of the wave in the second material is moving at a different speed than the part of the wave in the first material, causing the wave to proceed at a different angle.

Another energy conversion can take place when a wave hits an interface of two materials at an angle. Waves are based on particle movement and if a longitudinal wave hits the interface at an angle, particle movement may also occur in the transverse direction, causing shear waves. The wave separates in a faster traveling longitudinal wave and a slower traveling shear wave inside the material, this is shown in figure 2.4.



Figure 2.4: Snell's Law for refraction of waves when crossing an interface with different sound velocities [11]

In this figure also Snell's Law for refraction of waves is illustrated. Snell's Law is defined by:

$$\frac{\sin \theta_1}{v_{L_1}} = \frac{\sin \theta_2}{v_{L_2}} = \frac{\sin \theta_3}{v_{S_1}} = \frac{\sin \theta_4}{v_{S_2}}$$
(2.4)

where  $v_{L_1}$  and  $v_{L_2}$  are the longitudinal wave velocities in material 1 and 2 and  $v_{S_1}$ and  $v_{S_2}$  the shear wave velocities in material 1 and 2. When this mode conversion happens to waves at every interface in a (small) sample, the resulting waves are added and the signal can become complicated [11].

#### 2.4 Attenuation

Ultrasonic waves decrease in intensity while traveling through material and this decreasing intensity is visible as a loss of wave amplitude. This phenomenon is known as attenuation and is besides spreading of the beam due to various mechanisms, including absorption, scattering and dispersion. Of these, absorption is the most significant cause. The ultrasound energy is absorbed by the material and converted to other forms of energy, mainly heat.

Attenuation of ultrasonic signals is a function of frequency. Higher frequency signals are generally damped in less distance than lower frequency signals. Vibrating particles at a higher rate (higher frequency) require more energy. More vibration may also cause more energy to be lost due to heat generation. The amplitude of ultrasonic signals typically shows an exponential decay defined by:

$$A = A_0 e^{-\alpha(f)z} \tag{2.5}$$

with A the amplitude,  $A_0$  the initial amplitude, f the frequency and z the distance traveled.  $\alpha(f)$  is normally fitted to attenuation data as a linear, quadratic or power law function. For viscoelastic materials, the power law function is used most often as defined by:

$$\alpha\left(f\right) = \alpha_0 + \alpha_1 |f|^y \tag{2.6}$$

with constants  $\alpha_0$  and  $\alpha_1$ .  $\alpha_0$  is often set to 0 and y between 0 and 2 for most materials (empirically found) [28].

When specifically interested in the contribution of dispersion an imaginary term  $\beta(f)$  can be added to the exponent of equation (2.5) [28–31]. Deriving the frequency dependent attenuation and dispersion terms from attenuation data can be done in several ways. Two of them are elaborated on in appendix B.

#### 2.5 Reflection

When an ultrasonic wave comes across an interface it reflects off these interfaces as shown in figure 1.6. In doing so, part of the energy is reflected and the remainder propagates through the other material. The part of the energy that is reflected can be calculated with the reflection coefficient, defined by:

$$R = \left(\frac{Z_2 - Z_1}{Z_2 + Z_1}\right)^2 \cdot 100\% \tag{2.7}$$

$$Z = \rho v \tag{2.8}$$

with  $Z_1$  the acoustic impedance of the first material and  $Z_2$  the acoustic impedance of the second material. Acoustic impedance is a material property dependent on density  $\rho$  and acoustic velocity  $v_l$ . R multiplied by 100% yields the reflected energy as a percentage of the initial wave energy [10]. The remainder of the energy is transmitted to the next material as shown in figure 2.5. Water and steel differ a lot in acoustic impedance. From this figure it is clear that most of the energy is reflected at each water-steel interface. In the end, the back reflection of the steel consist of only 1.3% of the initial energy and can be collected by the transducer. Measurements are done submerged in water or with a coupling liquid between the transducer and the sample, because the low acoustic impedance of air makes it virtually impossible to transmit the waves from and to liquid or solid materials. Even when a transducer is pressed onto the sample, air will be trapped between the transducer and the sample. Water and coupling liquid will provide an (air)tight coupling and have an acoustic impedance more in the region of a solid material, making sure more energy will be transmitted from the (metal) transducer into the material. Figure 2.5 shows a setup in which the transitions from one material to another are very well defined and sharp. When a transition is not as well defined and more diffuse, the ultrasonic signal may not reflect.



Figure 2.5: Example of energy division between reflection and transmission [32]

Besides these reflections, scattering causes the sound to be reflected in other directions than the original direction of the propagating wave. This occurs when the wave comes across particles smaller than the wavelength. The ultrasound scatters in all directions creating multiple echoes with smaller amplitudes from the particle.

# 2.6 Viscoelasticity and dispersion

Solid propellants are viscoelastic materials. This means that the material exhibits both viscous as well as elastic material behaviour. Viscous materials have a time dependent strain rate, they resist strain linearly with time. Water has a relatively low viscosity, resulting in a high flow. Honey has a relatively high viscosity, resisting flow (deformation).

Elasticity is a measure of the ability of a material to resist deforming due to a force on the body and to return to its original shape and size when the force is removed. Viscoelastic materials exhibit material behaviour of both viscous as elastic material types. The viscous component of the viscoelasticty could result in a temperature and time dependent strain rate. Hysteresis, stress relaxation and creep are all typically observed in viscoelastic materials. These phenomena have the time dependent stress-strain behaviour as shown in figure 2.6. A loading and unloading cycle due to hysteresis is shown in figure 2.6a. In this stress-strain curve it is shown that the loading and unloading cycle are not, as in elastic materials, the same. A viscoelastic material loses energy when a load is applied and the removed. The area within the loop is the energy that is dissipated in one cycle. Figure 2.6b shows that a viscoelastic material experiences a decrease in the amount of stress while subjected to a constant strain known as stress relaxation. Figure 2.6c shows that these materials experience a time dependent increase in strain. When the constant stress is removed, the material reforms the amount of initially gained strain ( $\varepsilon_0$ ), which is elastic material behaviour, and then resumes to decrease in a nonlinear way to a residual strain [2,5,27]. Some non-Newtonian fluids also exhibit viscoelastic properties. They behave like fluids (flow) or solids (bounce or break) depending on strain rate.



Figure 2.6: behaviour commonly present in viscoelastic materials,  $\sigma$ =stress,  $\varepsilon$ =strain

In summary, viscoelastic materials are materials with a 'memory'. Due to this time dependent behaviour, these materials may show acoustic dispersion when being subjected to (ultra)sonic waves. Dispersion means that a pulse, which is made up of a center frequency component and some (smaller) side frequency components, is separated into its different frequency components. This is because the velocities of the different wave components change while propagating through the material, with lower frequencies traveling faster than the higher frequencies. As shown in figure 2.3, acoustic waves are carried by vibrating particles. When an acoustic wave is put on a material, a force vibrates the particles. In a viscoelastic material the time dependent strain behaviour may alter the vibrations, resulting in a non-elastic response and a change in speed. When the speed of the vibrations is altered depending on the frequency of the vibrations, it means that the material is dispersive. Dispersion is also present in light waves, visible as a light bundle separating into a spectrum of light waves with different frequencies after passing through a dispersive material.

# 3. Experimental Setup

In the previous chapters a theoretical background is given on ultrasound and its applications in the field of non destructive testing. It is expected that ultrasound is able to help characterize ageing in solid propellant materials. Before conducting the follow-up experiments, feasibility experiments are done to test some variables. The follow-up experiments are designed and tuned with the results of the feasibility experiments. The feasibility experiments will be pulse-echo measurements and test the following variables:

1. Which frequency range is optimal to use so the attenuation of the US signal is minimum?

Attenuation is frequency dependent, finding the optimal frequency range makes sure that back reflections are well defined and distinguishable.

2. Which sample thickness is useful in the current set-up?

Attenuation is traveling depth dependent. It is expected that the solid propellant material damps the ultrasonic signal a lot, so it is examined which thickness still gives a usable number of back reflections.

3. Do the inert samples exhibit the same acoustic behaviour as active solid propellant material?

Inert propellant samples are used in the experiments for safety reasons. This means that some reactive ingredients are substituted for inert ingredients which may alter the acoustic behaviour. This is done by comparing empirically conceived acoustic material properties of inert samples with values found in literature of active propellant material.

4. Do the samples within one batch exhibit the same acoustic behaviour?

The mixing process is a manual process with its accompanying risks of differences within a batch of samples.

Because it was expected that the inert propellant material damps the ultrasonic signal considerably, samples with a small thickness (5-30 mm) were created. The setup of all experiments will be a pulse-echo setup. This setup is chosen because in the desired application of assessing solid propellant rocket motors, pulse-echo measurements would also be used. It is not possible to place transducers on the inside of the motor for a transmission measurement and transmission measurements over the full diameter of the engine are impossible due to the cavity (bore hole) in the middle of the engine.

The feasibility experiments were used to test which frequency range is best to use and if the thicknesses used provide enough back reflections for further analysis. Based on the experience of the first mixing process and the results of the feasibility experiments a second batch of samples have been produced for the follow-up experiments.

# 3.1 Inert solid propellant samples

Samples of inert propellant material were produced for the feasibility and follow-up experiments. Inert material is used because safety regulations prohibit non-certified

persons to work with reactive samples or transport them.

In the absence of a standard recipe, an experimental method is conceived and modifications are made during the production process if needed. The full method can be found in Appendix A, a summary addressing important issues is described here.

Two batches of samples were produced. The first batch includes samples without a container and were used in the feasibility experiments. The second batch includes samples with a container and were used in the follow-up experiments. The samples for the follow-up experiments were aged in a stove to mimic years of natural ageing.

To mimic the composition of hydroxyl-terminated polybutadiene (HTPB) based propellant material the reactive (solid) particles that are bound by HTPB are substituted by inert solid particles, in this case potassium sulfate. The binder, HTPB and auxiliary substances, and potassium sulfate are mixed in a ratio of 85:15. This ratio ensures that the mixture cures properly and the solid particles do not migrate and collect at the bottom, which results in non-homogeneous samples.

The ingredients are mixed in a Resonant Acoustic Mixer (RAM). This mixer uses the natural frequency of the mixing pot and its content so that the content is mixed to a homogeneous mixture. The RAM can also put the contents of the pot under vacuum, in order to remove air from the mixture to reduce or prevent the occurrence of bubbles. Due to the vibrations of the mixer, the mixture heats up. In this case a beneficial side effect, because the final mixture is very viscous. Heating up the mixture makes it less viscous and easier to pour into the final containers or molds. It is hard to pour the mixture in the containers without causing air bubbles to be trapped in the mixture. However, during curing at 60°C the bubbles migrate to the surface of the samples and burst before the sample is fully set.

Table 3.1 shows the samples that were used in the feasibility experiments. Because there were doubts if the samples with a thickness more than  $\pm 15$  mm cured properly in the this batch, these were not used in the experiments.

Sample ID	Thickness
1.1	8.4mm
1.2	8.6mm
1.3	11.4mm
1.4	13.0mm
1.5	13.3mm

Table 3.1: Samples produced for feasibility experiments

Table 3.2 includes the samples of the second batch, produced after the feasibility experiments were done. The containers, as shown in figure 3.1, in which the samples were cured were made by the workshop of TNO Rijswijk and can be closed air tight by a lid. This was done because the samples can now be sealed when not in use, which makes sure there is no air pollution around the samples. With the sample material in a container, all samples have one surface exposed to air, so the oxygen induced ageing process will proceed from this surface only. Also, the ultrasonic measurements can now be done through the bottom of the container. This resembles the setup in a solid propellant rocket motor: the ageing proceeds from one surface exposed to air and pulse-echo measurements have to be done through a casing layer.

Reference samples were produced to be used in hardness measurements, because the containers do not fit in the setup used for these measurements. These reference samples have a mold of thick aluminum foil. The ultrasonic measurements were done from the free surface of the reference samples and not through the bottom layer of aluminum foil. Figure 3.2 shows the setup for the ultrasonic measurements for both

types of samples.

Sample	Thickness (mm)	Container	Aging temp.
P1	17.05	Plastic	$60^{\circ}\mathrm{C}$
P2	17.90	Plastic	$70^{\circ}\mathrm{C}$
P3	16.65	Plastic	$60^{\circ}\mathrm{C}$
M1	9.30	Stainless steel	$60^{\circ}\mathrm{C}$
M2	15.70	Stainless steel	$60^{\circ}\mathrm{C}$
M3	20.40	Stainless steel	$70^{\circ}\mathrm{C}$
R1	12.00	Aluminum foil 1mm	$60^{\circ}\mathrm{C}$
R2	14.25	Aluminum foil 1mm	$70^{\circ}\mathrm{C}$
S1	24.80	Aluminum foil 1mm	$60^{\circ}\mathrm{C}$
S2	22.95	Aluminum foil 1mm	70°C

Table 3.2: Samples produced for the experiments in batch 2



Figure 3.1: Containers for the second batch of samples. Red arrow shows the direction of the ultrasonic signal



Figure 3.2: Setup for ultrasonic measurements, left: reference samples with aluminum foil mold, right: samples in containers of plastic or metal

#### 3.1.1 Accelerated ageing

The ageing of the inert propellant samples for the follow-up experiments (batch 2) is accelerated in a stove at 60°C and 70°C. At these temperatures ageing is relatively fast, but still safe for the sample material. Any higher temperature would increase the chance of other, possibly dangerous, processes to start. To convert the storage time

at high temperatures to the storage time at 18°C the Arrhenius equation is used [33]:

$$t = t_{ref} \cdot e^{\frac{E_{act}}{R} \left(\frac{1}{T_{cal}} - \frac{1}{T_{ref}}\right)}$$
(3.1)

with t the ageing time in weeks,  $t_{ref}$  the corresponding time in weeks at 18°C, E the activation energy which is 70 kJ/mol in this case, R the universal gas constant,  $T_{cal}$  the temperature for which the ageing time is calculated and  $T_{ref}$  the reference temperature 18°C.

When equation (3.1) is applied to a number of different reference temperatures and reference ageing times a simple graph shows the accelerated ageing. Figures 3.3a and 3.3b show the accelerated ageing. It is clear that the accelerated ageing time (weeks in stove) plotted against the natural ageing time (years at  $18^{\circ}$ C) has a linear relation. As a rule of thumb, every  $10^{\circ}$ C increase in temperature means that the ageing is progressing twice as fast. Part of the inert propellant samples are aged at  $60^{\circ}$ C and the remaining samples at  $70^{\circ}$ C. The samples have been aged in stoves for 6 weeks. This means that the corresponding ageing for the  $60^{\circ}$ C samples is equivalent to storage for 4.4 years and for the  $70^{\circ}$ C 9.3 years.



(a) Accelerated ageing time at different reference times



(b) Accelerated ageing time at different reference temperatures

Figure 3.3: Arrhenius equation applied to different reference temperatures and ageing times at  $18^{\circ}\mathrm{C}$ 

To monitor the accelerated ageing of the samples, twice a week the hardness of the reference samples is measured. Hardness measurements are non invasive and non destructive and although there is no analytic relation between the indentation hardness and for example the Young's modulus, an approximate relation between the Shore hardness and the Young's modulus has been established [34]. An increasing Shore hardness reading indicates an increasing Young's modulus. Hardness readings are only compared within the same sample, so it is assumed that when the hardness readings increase the ageing process is making the sample material stiffer.

#### **3.2** Experimental setup and instrumentation

The instruments used are a ITE Ultimo 2000 pulser-receiver (fig. 3.4) and Panametrics transducers. Based on expert opinion, 1 MHz and 500 kHz transducers are used on the samples in the feasibility experiments. This is chosen because the material has mechanical properties comparable to rubbers and plastics. For these types of materials transducers with a frequency range around 500kHz - 1MHz are normally used [35].



Figure 3.4: ITE Ultimo 2000 pulser-receiver

The input signal can be tuned to two different shapes with the setup as used in these experiments: square wave and spike excitation. The most commonly used shape is a square wave with a length of half the transducers frequency period. With this excitation signal, the piezo element is excited at its resonance frequency. An excitation period shorter than this would result in a lower amplitude than possible and an excitation period longer than this would distort the oscillation. In this case the length of the square input signal is 500ns or 250ns, which is half the wavelength of a 1MHz (1µs) or 500kHz (0.5µs) wave respectively. The spike excitation signal has a very fast rise and an exponential decay. It generates a broadband pulse and the duration does not have to be tuned to the transducer. Because the square wave input signal can be tuned to have optimal amplitude, these signals generally have a greater energy output. Square wave input signals are used in the feasibility experiments.

The samples from batch 1 have various thicknesses between 8 mm and 14 mm (see table 3.1) and are used for the feasibility experiments. They are used to examine the uniformity and homogeneity. In addition, propagation speed and attenuation in samples of different thickness are examined. The experiments are all done at 21°C. A coupling liquid is used to transfer the ultrasonic pulse in the material.

Setups in which a transmission signal with a sending transducer on one side and a receiving transducer on the other side will have less attenuation of the signal than a pulse-echo setup. Pulse-echo setups work with one transducer that alternates sending a pulse and receiving the signal that reflects off of the interfaces within a sample. For applications where the objective is to find for example the sound velocity in the material, transmission measurements are preferred. When the ultrasound is used to find the thickness of a sample or flaws in the material, reflections are needed and the pulse-echo measurements are preferred. When the setup prohibits a transmission measurement, a pulse-echo setup can also be used to examine properties like the sound velocity. In pulse-echo setups the intensity of the signal should be increased, because of the longer distance the signal has to travel. Although transmission measurements are preferred because of the shorter distance the signal has to travel, pulse-echo measurements are done to resemble the set-up in a actual solid propellant rocket motor where the transducer must be used on the outside of the casing. In the setup with an rocket motor the ultrasonic signal reflects off the propellant-air interface at the inside surface of the propellant material, which can be seen in figure 3.5. In the followup experiments measurements are carried out by sending ultrasonic signals through the bottom of the containers, which can be difficult because the casing and sample material have very different acoustic impedances.



Figure 3.5: Schematic of a solid propellant missile with air filled bore hole (yellow) in the middle of solid propellant material and a transducer (blue) and ultrasonic signals (red). Adapted from [1]

The hardness measurements are done with a Zwick Roell Shore A analog hardness tester as shown in figure 3.6. Three measurements are done per sample and the values are averaged. For proper readings the measurement is filmed and the Shore A value is read at 1, 3, 5 and 10 seconds after the probe touches the sample material.



Figure 3.6: Zwick Roell Shore A analog hardness tester [36]

# 3.3 Results and conclusions feasibility experiments

Figure 3.7 shows the ultrasonic signals of a pulse-echo signal of sample 1.1. Notice that the signal in the first  $0.1 \cdot 10^{-4}$  seconds is not a back reflection received by the transducer, but a transducer-dependent signal that is always present even when measuring in air. Five back reflections, with the first around  $0.15 \cdot 10^{-4}$  seconds, are indicated by red arrows. It can be seen that in the 1MHz signal, five back reflections are nicely separated, while in the 500kHz signal, there is a lot of noise and the back reflections are not always clearly distinguishable. For the experiments, it will be important to distinguish the back reflections, so therefore the experiments will be done with the 1 MHz transducer.



Figure 3.7: Ultrasonic signals of sample 1.1 with 1 MHz and 500 kHz, back reflections are indicated with a red arrow.

Figure 3.8a shows the envelope (in blue) around the ultrasonic signal (in red) of figure 3.7a. It is important to pinpoint the maximum magnitude of the signal. With the envelope this peak is found and the attenuation in the material can be fitted by fitting an exponential curve through the peaks, as shown in figure 3.8b. The first peak is the signal that is sent into the material and is not taken into account for the fit, because it was cut off by the window (peak to peak) in the measurements. It is now clear that the samples fit an exponential decay as described in section 2.4. Besides, it can now be checked if the acoustic behaviour (in terms of attenuation) of ultrasound is the same in all samples to check the homogeneity of the batch. Figure 3.9a shows the mean and standard deviation of the exponential fits of the ultrasonic signals of all 5 samples at 1MHz and 500kHz. Figure 3.9b shows an exponential fit through all back reflection peaks. The fit for 1MHz has an  $\mathbb{R}^2$  of 0.9311. An  $\mathbb{R}^2$  close to 1 indicates that the data points are close to the fit, so it is assumed that the acoustic behaviour in samples of the same batch is comparable.



Figure 3.8: Envelope (blue) and exponential fit (red), sample 1.1, 1 MHz



(a) Mean and standard deviations of the fits through back (b) Fit through all back reflection peaks of all five samples reflection peaks of all five samples

Figure 3.9: Average curve of all fits through back reflection peaks of five samples

The sound velocity, density and acoustic impedance of the material can be calculated with:

$$v = \frac{2d}{t_r} \tag{3.2}$$

$$\rho = \frac{m}{V} \tag{3.3}$$

$$Z = \rho v \tag{3.4}$$

with d the thickness of the sample,  $t_r$  the time between two back reflections (also known as time of flight), m the mass of the sample and V the volume of the sample. Table 3.3 shows the sound velocity, calculated density and calculated acoustic impedance of the samples of batch 1. These are calculated with measurements of dimensions and weight taken with a digital caliper and digital scale. The mean  $\mu$ and standard deviation  $\sigma$  are calculated with MATLAB, the coefficient of variation is defined by:

$$CV = \frac{\sigma}{\mu} \tag{3.5}$$

The coefficients of variation are below 5%, which confirms the homogeneity within the batch.

One remark on table 3.3 is that although the sound velocity v is in the expected range of 1510 to 1650 m/s, the same as active solid propellant [35], the mean density  $\rho$  of the inert HTPB based propellant material is not in the same range as active solid

propellant. The binder of this material is the same as in active propellant material as is the ratio in which the binder and solid particles are mixed. However, the solid particles used are not alike. This results in different densities, the density is 528 kg/m<sup>3</sup> while the density of active HTPB based propellant is around 1700 kg/m<sup>3</sup> [37]. Consequently, there is a difference in density related material properties like the Young's modulus E (equation (2.3)) and acoustic impedance Z (equation (3.4)).  $E_i$  of the inert material is about 1.3GPa compared to  $E_a$  of active material of 4.4GPa. This is in line with Young's moduli reported in literature [38, 39].

The acoustic impedance Z is also directly related to the density of the material. Knowing that the sound velocity is alike in inert and active propellant material [35], this means there is a difference in Z between inert and active propellant.  $Z_i$  of inert material is approximately  $8.53 \cdot 10^5$  Rayl, while  $Z_a$  of active material is approximately  $27 \cdot 10^5$  Rayl. This will play a role when trying to reflect off of a internal interface between aged and non-aged propellant material because the amount of energy reflected is dependent on the difference in value for Z of both layers. However, it is assumed that the difference in Z in the aged and non-aged inert material is not much different than in active material. This is because the change in material properties is due to the degrading binder HTPB and not a change in the solid particles. This would mean that the same kind of degradation is present in both materials and the change in the value of Z would most probably be comparable. This means that the amount of reflected energy R is also comparable, because R mainly relies on the difference between  $Z_1$  and  $Z_2$ .

	v (m/s)	$\rho ~(\mathrm{kg/m^3})$	$Z (\cdot 10^5 \text{Rayl})$
1.1	1518	531.3	8.06
1.2	1684	523.6	8.82
1.3	1566	519.6	8.13
1.4	1672	524.4	8.77
1.5	1637	541.3	8.86
$\mu$	1615	528.0	8.53
σ	63.95	7.621	0.35
CV	3.96%	1.44%	4.14%

Table 3.3: Sound velocity v, density  $\rho$  and acoustic impedance Z of the samples in batch 1.  $\mu$ : mean,  $\sigma$ : standard deviation, CV: coefficient of variation  $\frac{\sigma}{\mu}$ 

A couple of conclusions can be drawn from the feasibility experiments. The frequency best to use is in this setup is 1MHz, because the back reflections are nicely separated. Samples with a thickness smaller than 15mm give good results, enough back reflections are received for further analysis. The inert propellant samples have a sound velocity in the same range as active solid propellant and the samples are homogeneous throughout the batch.

#### 3.4 Follow-up experiments

The feasibility experiments were carried out successfully. The goal of the follow-up experiments is to detect ageing in solid propellant material with ultrasound. Ageing is a change of the material properties of the surface exposed to oxygen as described in section 1.5. It is expected that ultrasound behaves differently in aged material in a number of ways.

1. An additional surface reflection from the added interface between non-aged and aged material.

As mentioned in section 2.4, ultrasonic waves do not reflect on interfaces that are too diffuse. Because the degradation process of solid propellant material is a diffusion process, this may be the case. If the interface is too diffuse, no extra reflection will be visible in the signal.

2. A change in reflection time.

A change in reflection time indicates a change in sound velocity in the material, which points to a change in material properties. It is expected that the elasticity modulus E will increase over time with ageing, so this would mean that the sound velocity v defined by:

$$v = \sqrt{\frac{E}{\rho}} \tag{3.6}$$

will also increase.

3. A change in frequency content of the back surface reflection.

Due to dispersion (see section 4.2.2) the pulse is separated into its different frequency components and the resulting pulse will therefore have a different frequency content. Because of the viscoelastic material, it is expected that dispersion will contribute to the attenuation of the ultrasonic signal in this case.

The experiment designed to examine if the mentioned changes will be visible in the ultrasound data are elaborated on in this section.

# 4. Experimental Results and Interpretation

This chapter discusses the results of the follow-up experiments, showing the hardness evolution over time and testing the hypotheses about the ultrasonic signals posed in the previous chapter. The first measurements were done on January  $11^{\text{th}}$  (week 0) and the experiments were continued until February  $22^{\text{nd}}$  (week 6).

#### 4.1 Hardness

Shore A hardness is measured two times a week. Figures 4.1a and 4.1b show the evolution of the Shore A hardness values. Looking at thin reference samples (R1 and R2), it can be observed that they have had an relatively fast increase in hardness value in the first days, whereafter the hardness value decreases again to increase at a slower rate. The same can be seen in the thick reference samples (S1 and S2), but the increasing of the hardness value takes a little longer. The increase is again followed by a decrease, after which the hardness values start increasing again. This peak in the beginning of the graphs may be explained by a phenomenon called post-curing, a process in which the material hardness rises fast after which it settles again. It can be observed that the two thinner samples (R1 and R2) and the two thicker samples (S1 and S2) both show the same beginning of the curve (post-curing process). However, after this initial peak the two samples that are aged at 60°C (R1 and S1) and the two samples that are aged at 70°C (R2 and S2) show the same behaviour. This is shown in figures 4.2a and 4.2b, in which a linear curve is fitted through the data after the initial post-curing process. The linear regressions are as follows:

$R1(60^{\circ}C):$	y = 0.76x + 24.42,	$R^2 = 0.8909$
$R2(70^{\circ}C)$ :	y = 1.60x + 26.31,	$R^2 = 0.9116$
$S1(60^\circ C)$ :	y = <b>0.94</b> x + 23.64,	$R^2 = 0.8664$
$S2(70^{\circ}C):$	y = 1.62x + 29.71,	$R^2 = 0.9024$

It is clear that the slopes of the R1 and S1 curve are similar and the slopes of the R2 and S2 curve are almost identical. The rule of thumb, that every  $10^{\circ}$ C increase results in a twice as fast ageing also holds when looking at the mean slopes of the linear regressions of the samples aged at  $60^{\circ}$ C and  $70^{\circ}$ C, i.e. 0.85 vs. 1.61 /wk.

It can be concluded that the post-curing process takes longer for the thicker samples, but after this process has settled, the thickness difference of the samples does not influence the hardness value as much as the difference in temperature does.

It must be noted that these measurements are surface indentation measurements. This means that the hardness is measured only at the surface, which shows a linear increase in hardness. The way that the ageing process, and with that the hardness increase, progresses into the material will most probably not be a linear process. This means that with these hardness measurements only the ageing at the surface is monitored, but no conclusions on the depth of the ageing process can be drawn from these measurements.

The samples are cut after the 6<sup>th</sup> week of measurements. Hardness measurements are done on the cross section to gain a rough insight on the thickness of the degraded layer.



(a) Shore A hardness values of reference sample R1 and R2

(b) Shore A hardness values of reference sample S1 and S2

Figure 4.1: Shore A hardness values of the reference samples at 60°C and 70°C



(a) Reference sample R1 and R2

(b) Reference sample S1 and S2

Figure 4.2: Linear regression fits through Shore A hardness values of the reference samples at  $60^{\circ}C(a)$  and  $70^{\circ}C(b)$  from moment post-curing has ended.

#### 4.2 Ultrasonic measurements

An ultrasonic measurement of sample R1 is shown as an example in figure 4.3. The beginning of the signal, till  $1.3 \cdot 10^{-5}$ s, is a transducer and input signal specific part. It is the direct reaction of the transducer on the input signal that it sends. The first back reflection is visible around  $1.9 \cdot 10^{-5}$ s (marked in green). Two more back reflections are visible around  $3.8 \cdot 10^{-5}$ s and  $5.7 \cdot 10^{-5}$ s. Around  $2.9 \cdot 10^{-5}$ s and  $4.6 \cdot 10^{-5}$ s a small reflection is also noticeable (marked in yellow). This could be due to a small air bubble or another pollution in the material.

A remark on the comparison of the signals of one sample between different weeks is that the amplitude should not be compared. A contact layer between the transducer and the sample should be formed with the use of a coupling liquid, so no air is trapped between the transducer and sample and the ultrasonic signal is passed on through the sample. The position of the transducer on the sample is optimized with a real-time ultrasonic signal and the contact layer is produced by applying pressure to the transducer. When sufficient amplitude (comparable to preceding weeks) of the back reflections is reached on the real-time signal, the pressure is lifted off the transducer and after 30 seconds without pressure 200 measurements are taken. This means the measurements are comparable on shape and reflection time, but not directly comparable based on amplitude.

In the remaining subsections, the changes in the signals will be studied, focusing on respectively extra reflections, change in sound velocity and changes in frequency content. Also the effect of the metal casing on the signals will be studied.



Figure 4.3: Ultrasonic signal of reference sample R2 in week 0, with red the transducer and input signal specific part, in green the back reflections and in yellow the unexpected reflection of presumably a pollution in the material

The following sections discuss the results of the ultrasonic signals of the follow-up experiments. As hypothesized in section 3.4, three phenomena will be discussed: an additional surface reflection, a change in reflection time and a change in frequency content. Lastly the influence of a metal casing layer on the ultrasonic signal is discussed.

#### 4.2.1 Extra surface reflection

An extra surface reflection should be detected by inspection of the shape of the ultrasonic signal. An extra reflection, caused by a possibly present interface between pristine and degraded material, should be visible as a reflection with a higher frequency (but lower amplitude) than the back reflections. Figure 4.4 shows the signals of week 0 and week 6. However, it can be observed that there is no demonstrable difference in shape between week 0 and week 6. This may be because the ageing process of solid propellant materials is a diffusion process. The aged material is visible as an individual layer, but on microscopic level, the transition may be too diffuse. The ultrasonic waves will not experience the transition as such because the transition is 'smeared out' over a longer distance and the changes in the acoustic properties will be gradual along this distance. Another explanation is that the transition is sharp enough, but the acoustic properties of the non-aged and aged propellant material are too similar. If the acoustic impedance Z of both layers is very similar, the amount of energy that is reflected off of the interface is very low and the reflection will be non-detectable in the signals measured.



Figure 4.4: Ultrasonic signal of reference sample R2 in week 0 and week 6

#### 4.2.2 Change in velocity

An envelope of the measured signal is created and the time between peaks ( $t_r$  or time of flight) in this envelope is calculated to detect a change in velocity of the signal in the material. The signal of reference sample R2 is taken as an example. The measured signal of week 0 and its envelope are shown in figure 4.5. Peaks are located with the findpeaks function in MATLAB. Per signal the back reflections of the sample material are located and it is determined how many back reflections are usable. In the case of sample R2, the first three back reflections are included for calculating the velocity. As shown in figure 4.5, four back reflections are indicated by the blue arrows, the fourth is omitted due to low signal to noise ratio.



Figure 4.5: Ultrasonic signals of reference sample R2 and its envelope in week 0

Table 4.1: Location on time-axis ( $\cdot 10^{-5}$ s) of peaks as shown in figure 4.5 and time between peaks:  $\Delta t_i = t_{i+1} - t_i$ 

	week 0	week 1	week 2	week 3	week 4	week 5	week 6
$t_1$	1.16	1.14	1.13	1.12	1.11	1.10	1.08
$t_2$	2.94	2.90	2.88	2.85	2.83	2.81	2.78
$t_3$	4.74	4.67	4.65	4.60	4.57	4.52	4.48
$t_4$	6.57	6.45	6.43	6.31	6.30	6.17	6.09
$\Delta t_1$	1.78	1.76	1.75	1.73	1.73	1.72	1.71
$\Delta t_2$	1.80	1.77	1.77	1.76	1.71	1.71	1.70
$\Delta t_3$	1.83	1.78	1.78	1.71	1.74	1.65	1.61
mean difference	1.80	1.77	1.77	1.73	1.73	1.69	1.67

The locations on the time-axis of the peaks  $t_1$  to  $t_4$  and amount of time between two peaks  $\Delta t_1$  to  $\Delta t_3$  are shown in table 4.1 for week 0 to week 6, as is the mean difference. It can be seen that the mean difference between the peaks, representing the average time of flight, decreases over time. This trend of a decreasing  $\Delta t_i$ , or time of flight (tof) between back reflections, and thus an increasing velocity, is also seen in figures 4.6 to 4.8. These show the mean time of flight between back reflections for the samples in plastic containers (P1,P2 and P3) and the reference samples (R1,R2,S1 and S2), respectively. It is visible that every sample shows an decreasing trend in the time of flight between back reflections over (ageing) time. The sound velocity  $v_l$  is approximated by:

$$v_l = \sqrt{\frac{E}{\rho}} \tag{4.1}$$

An increase in  $v_l$  indicates an increase in elasticity modulus E or a decrease in density  $\rho$  or a combination. The ageing of solid propellant material is due to oxidative crosslinking of binder molecules. In this process  $\rho$  does not change considerably, so this means that the value for E must increase in order to have an increase in  $v_l$  as shown in .



Figure 4.6: Mean time of flight of samples in plastic container over 6 weeks



Figure 4.7: Mean time of flight of thin reference samples over 6 weeks



Figure 4.8: Mean time of flight of thick reference samples over 6 weeks

The slopes of the linear regression and corresponding  $\mathbb{R}^2$  values are in table 4.2. It is shown that although every linear regression has a negative slope a, not every linear regression has a good fit ( $\mathbb{R}^2$ ). The samples in plastic containers show a relatively high  $\mathbb{R}^2$  value in comparison with the reference samples, which have an outer layer of aluminum foil. This is with an exception of sample R2, which actually shows the highest slope value as well as the highest  $R^2$  value. An explanation for the lower  $R^2$  values of the reference samples could be that in these the pulse-echo measurement is done on the sample material surface. The hardness measurements are also done at this surface and this creates small distortions on the surface of the sample. Measuring through these distortions may result in changes in the ultrasonic signals.

Another observation from table 4.2 is that the slope value a of the samples aged at 60°C are between the values of -0.0029 and -0.0038, whereas the slope value a of the samples aged at 70°C are much higher, with the exception of sample S2. This is logical because the higher temperature causes more material degradation (increase of E), causing the sound velocity to increase more.

The actual change in propagation velocity of the signal can be calculated using the time of flight when the thickness of the samples is measured. The samples are cut in half to measure the exact thickness of the samples. These results are also shown in table 4.2. It is shown that in every sample, a measurable difference is found with values between 10.16 m/s and 79.60 m/s. As mentioned samples aged at 70°C have a higher change in velocity than the samples aged at  $60^{\circ}$ C, which is also logical due to the faster ageing at higher temperature. The smallest differences are seen in the thickest samples (S1, S2), which was expected. The change in velocity however is due to the aged part of the material only and the percentage change therefore depends on the thickness of the sample. The overall change in velocity in a thinner sample will be more pronounced than in a thicker sample with the same amount of aged material present. It may be possible to relate the change in overall velocity to the thickness of the aged material if the ageing process into the material is known. For clarification figure 4.9 shows the material condition as function of the depth in a sample, assuming the material degradation follows an exponential function. The change in velocity is only due to the degraded part, shown in red on the x-axis.

Sample	Temp.	Slope a	$R^2$	Thickness	$v \ge 0 \text{ (m/s)}$	$v \le (m/s)$	v change (m/s)	% change
P1	60°C	-0.0029	0.6667	17.05  mm	1614	1630	15.43	0.96
P2	70°C	-0.0075	0.8820	17.90 mm	1586	1622	35.92	2.26
P3	60°C	-0.0034	0.9401	$16.65 \mathrm{mm}$	1588	1603	15.28	0.96
R1	60°C	-0.0038	0.2708	12.00 mm	1514	1558	44.25	2.92
R2	70°C	-0.0137	0.9842	14.25  mm	1594	1674	79.60	4.99
S1	60°C	-0.0036	0.1812	24.80 mm	1582	1592	10.16	0.64
S2	70°C	-0.0029	0.3516	22.98 mm	1574	1584	10.85	0.69

Table 4.2: Slope  $(tof = \underline{\mathbf{a}}x(\text{ageing time in weeks})+b)$  and  $\mathbf{R}^2$  values of trendlines as shown in figures 4.6 to 4.8 at different temperatures

Hardness measurements were done on the cut section to gain a rough insight on the thickness of the degraded layer. It was expected that the hardness would increase with thickness (bottom up) because of the stiffer layer that would form at the free surface. However, the hardness values are inconclusive and it is not possible to derive a thickness of a degraded layer from the hardness measurements. A visual inspection does also not give insight in the thickness of the degraded layer. Small amounts of spilled material are brittle and show a color change. In the sample no color change is visible. The samples aged at 70°C do have a darker color than the samples aged at 60°C, but this is throughout the whole sample. This suggests that the degraded part does not have a sharp transition and the material properties doe not change very much.



Figure 4.9: Material condition assuming an exponential ageing shape as function of the depth in the sample

#### 4.2.3 Change in frequency content

Dispersive media change the velocity of waves traveling through the material, in other words change the frequency content of the signal. The aged propellant material is expected to be a dispersive medium. It may be the case that the aged material is more or less dispersive than non-aged material. To create smooth fast Fourier transforms (FFT's), only the first back reflection is taken from the signals. Using the FFT method on the complete signal does not give good results and the multiples of the back reflections have been damped too much resulting in sparsity of information in the back reflections. The multiples would provide more information on how the material changes the frequency content of the signal, because these reflections are the result of the signal that has traveled through the material for a longer period.

The main contributing frequency in the back reflection is between 0.5-1MHz. Because the FFT is done on a very short time window (101 points  $\cdot 5 \cdot 10^{-8}$ s, sampling frequency  $2 \cdot 10^7$ Hz), the frequency spacing is very high, 156kHz. To create a better frequency resolution zero padding is applied to the signal. A frequency resolution of 153Hz is achieved by zero padding the signal to 990 times the signal length. This will give sufficiently specific results for determining differences. Differences that could appear are a change in frequency of the main peak(s), a change in the number of peaks in the FFT or a change in the full bandwidth of the FFT.

Figure 4.10 shows the cut-outs of the first back reflections and their FFT's. There is a difference of 11.14kHz between the peaks in the FFT's. This is a considerable difference and suggests that aged material indeed has a different frequency content than non-aged material. The number of peaks stays the same and the bandwidth of the FFT's is very similar.



Figure 4.10: Left: first back reflection of US signals of sample R2 in week 0 and week 6. Right: FFT's of first back reflections with maximum frequency values indicated.

The change in frequency content cannot be directly attributed to dispersion, since only a small part of the signal is used. Cutting the signal at a specific location leads to different in- or exclusion of information. It is sub optimal to manually cut back reflection from the signal, because it is hard to pinpoint the exact beginning and ending of the reflection. In appendix B a method is discussed for assessing the frequency dependent damping of ultrasonic signals in a material and for characterizing frequency changes and dispersion.

#### 4.2.4 Influence of metal casing

The most realistic setup for ultrasonic measurements on solid propellant rocket motors would be pulse-echo measurements from the outside of the casing to the bore hole in the middle and back, see figure 3.5. However, the metal casing and solid propellant have a large difference in acoustic impedance Z. Stainless steel has a value  $Z_s$  of  $46 \cdot 10^6$  Rayl, where solid propellant has a value  $Z_p$  of  $8.53 \cdot 10^5$  Rayl (see table 3.3). This acoustic impedance mismatch results in a large amount of energy that is reflected at the interface between metal and propellant:

$$R = \left(\frac{Z_p - Z_s}{Z_p + Z_s}\right)^2 \cdot 100\% = 92.85\%$$

This means only 7.15% is passed on to the inert solid propellant material to propagate through. When the wave reaches the propellant-metal boundary for the second time, in opposite direction, again only 7.15% of what is left of the signal after propagating through the sample material is passed on to the metal and then back to the transducer. Though the reflected energy is 92.85% at the metal-inert propellant interface, the acoustic impedance mismatch between metal and active solid propellant will be less due to the higher density of active propellant material. The calculated  $Z_a$  was approximately 27.10<sup>5</sup> Rayl, which results in a R of 78.74%, passing 21.26% of the signal through the interface. The result is that when doing these experiments with active propellant material, the signal will improve.

Besides the energy loss at the metal-propellant interface, a high frequency 'noise' is present in the signal because of the high sound velocity  $v_{steel}$  in steel (5800 m/s). These signals are the reflections of the ultrasound signal in the metal bottom of the container and are visible in figure 4.11. Sample M1 and M3 show the same behaviour, with an increase in intensity between  $0.2 \cdot 0.3 \cdot 10^{-4}$  s and between  $0.5 \cdot 0.6 \cdot 10^{-4}$  s. These are exactly the locations where a back reflection of the sample material is expected and at the same position where samples with a plastic casing show back reflections as shown in figure 4.12. Sample M2 does not show the same behaviour. It can be concluded that for two of the three samples with a metal casing, the back reflections are visible. However, for determining the time of flight, it is necessary that the same moment of the peak is located on every back reflection, e.g. the origin, the maximum or the end of the pulse. Using an envelope gives the opportunity to get the t related to the maximum of the pulse. In the signals of M1 and M3, an envelope would not be able to locate this maximum accurately and consequently. Different envelope methods or settings give different values for the t location of the maximum of the pulse(back reflection).



Figure 4.11: US signals of samples in metal containers in week 0



Figure 4.12: Comparison of location of back reflections in samples with the same thickness with plastic(P2) and metal(M3) casing in week 0. Small difference explained by small thickness difference and difference in sound velocity in the casing materials.

Processing the signal with for example a low pass filter would remove the high fre-

quency contributor, but would again result in a signal where the actual peak of the back reflection cannot be determined accurately enough for further analysis, an example is shown in figure 4.13. The high frequency signal is partly removed, but the signal to noise ratio drops, which makes the back reflections hard to distinguish.



Figure 4.13: Raw data and (low-pass) filtered signal of sample M1, week 0

# 4.3 Implications for ultrasonic signals due to hardness measurements

The hardness measurements done to monitor the ageing of the samples are Shore A indentation measurements. This means that a small probe is pushed in the material and the resistance the material has to this indentation is measured. In this process the material is slightly damaged on the surface. This means that measurements cannot be done in the exact same position every time. Besides, this means that the reference samples, for which is measured on the surface have small defects on the same surface as where the ultrasonic measurements are done. This can have an influence on the results and the comparison of signals over the weeks. It was observed that as the weeks passed it got harder to get the same amplitude as the previous week. This was especially the case for the reference samples. This could be due to the damage present on the surface as a result of the indentation hardness measurements. But it could also be as a result of the increased stiffness. The increased stiffness makes it harder to achieve a good contact layer between the transducer and the sample.

#### 4.4 Summary experimental results

The results of the hardness measurements for monitoring the ageing process show an expected increase in surface indentation hardness. This can be related to an increase in Young's modulus. In addition, the rule of thumb: every 10°C increase of ageing temperature corresponds with twice the ageing rate, is confirmed by the hardness values.

None of the ultrasonic measurements show an extra surface reflection, which can be related to an aged layer of propellant material. However, an increase in propagation velocity of the ultrasound is observed in every sample. A higher velocity relates to an increase in Young's modulus. Although it does not provide information on the thickness or exact value of material properties of the degraded layer yet, the results give reason for further research. Although the frequency contents of the first back reflections hint to a change in frequency content of the signal, conclusions cannot be drawn from this. The signal as obtained by these experiments was not sufficient for analyzing the frequency content in detail, but it gives reason for further research on this topic.

The metal container causes a large loss of signal that propagates through the sample material and results in a high frequent signal caused by reflections in the metal layer. However, back reflections are recognizable in the pulse-echo signal.

# 5. Conclusions

To conclude this research project the sub questions and research question as posed in section 1.9 are answered below.

#### How are ultrasonic signals affected by damping in solid propellant material?

Solid propellant is a highly damping material. A decent amount of back reflections is visible when using thin (15mm) samples. However, this may give rise to challenges when using ultrasonic signals in the desired application of the larger solid propellant rocket motors, which generally have a thickness larger than 100mm. The largest sample in this thesis had a thickness of 24.8mm, which gave two useful back reflections. Since one back reflection is needed to calculate the time of flight (given the input signal is well defined) the thickness could be increased while maintaining sufficient information.

# How do ultrasonic signals propagate through pristine and aged solid propellant material?

Aged solid propellant has a higher Young's modulus than pristine material, which causes the ultrasonic signals to propagate with higher velocity in aged solid propellant material. The increase in velocity was especially visible in the samples accelerated aged at 70°C, which is comparable to 9.3 years of natural aging at 18°C. Samples aged at 60°C (4.4 years) also show an increase in sound velocity, but not as decisive. This means that there is a considerable difference in propagation (velocity) of ultrasonic signals between pristine and aged solid propellant material.

# How are ultrasonic signals affected by the transition over the metal/solid propellant boundary?

The metal-propellant boundary results in a major reflected signal intensity ( $\sim 93\%$ ) at the interface. A high frequent signal is present in the signal because of the high sound velocity in metal. However, in two of the three samples used, the back reflections are distinguishable. These back reflections are not yet accurate enough to calculate the same change in velocity as in the samples with no container or plastic container. Since the acoustic impedance mismatch of the metal-propellant interface is less in the case of active propellant material, it is expected that the signal will improve considerably in measurements with active material. This could make it possible to accurately calculate a time of flight and thus a sound velocity (increase) in solid propellant rocket motors.

# Can ultrasonic signals be used to characterize ageing in solid propellant rocket motors?

The whole of this research project serves as a feasibility study on using ultrasound for characterizing ageing in solid propellant rocket motors. Ageing is characterized by an increase in Young's modulus of the material exposed to oxygen, which is reflected in a higher sound velocity. A change in sound velocity between pristine and aged sample material is directly related to a change in Young's modulus. This change is measurable in the sample material used in this thesis. Although there are some practical limitations to implement the method on solid propellant rocket motors, this thesis shows that ultrasonic measurements are a promising method to pursue for further research.

# 6. Recommendations

From the results and conclusions follow some recommendations for further research. These include recommendations on how to improve ultrasonic results, recommendations on which aspects should be revisited and a future outlook for practical implementation of the method on solid propellant rocket motors.

### Method changes to improve ultrasonic signal

It is assumed that the expected extra reflection of the interface between aged and non-aged material will be fairly low in amplitude to the relatively small change in acoustic impedance Z between the two layers. It is therefore important to optimize the ultrasonic signal as much as possible to be able to observe this extra reflection. In the setup that was used the backwall reflections were actually in the near field of the transducer, which makes it likely that the amplitude of the pulse is not at its maximum at the location of the expected interface between the non-aged and aged layer. This can be improved by placing a stand-off pad or block with the same acoustic impedance as the coupling liquid. This ensures that the near field intensity changes are inside this block instead of in the aimed depth of the sample.

In this study square input signals are used in the measurements. Other input signals, for example sine waves, might improve the quality of the signal. When it is clear which frequency (transducer) gives the optimal results for the material, the input signal can be tuned to this frequency and less noise is present in the measurements, which makes observing extra surface reflections easier.

It can also be that different wave forms, like shear waves with particle movement perpendicular to the wave direction or waves with elliptical vibration patterns of particles improve the signal quality for the desired application.

### In depth analysis of attenuation

The general fit for the amplitude decay data of ultrasonic signals in (visco-elastic) materials is given in section 2.4 as:

$$A = A_0 e^{-\alpha(f)z} \tag{6.1}$$

with A the amplitude,  $A_0$  the initial amplitude, z the distance traveled and  $\alpha(f)$  fitted to a power law function defined by:

$$\alpha\left(f\right) = \alpha_0 + \alpha_1 |f|^y \tag{6.2}$$

with  $\alpha_0$  often 0 and y between 0 and 2 for most materials.

In this study, equation (6.1) is used to fit attenuation data with  $\alpha$  constant for the frequency of the transducer used to determine the homogeneity of the batch. However, an in depth analysis of the frequency dependent attenuation behaviour would be helpful to understand which ultrasonic methods are best to use and at which frequency the attenuation is minimal. It is possible to research the contribution of dispersion by adding an imaginary term  $i\beta(f)$  to the exponent of equation (6.1). Raisutis' method explains how to characterize the ultrasonic attenuation and the phase velocity dispersion assumed that the phase velocity and attenuation coefficients are not independent, but are interrelated and each can be determined according to the other [40].

The Acoustics and Sonar department of TNO has also developed a method for analyzing the frequency dependent attenuation of materials. Initially it was developed for small clay and rubber samples, but it could be used with solid propellant material as well. Both methods are elaborated on in appendix B. Both methods are limited by the frequencies of the transducers, so broadband transducers should be used for optimal results. With these frequency sweep input signals can be used to cover a large bandwidth. For further research on using ultrasound for characterizing ageing in solid propellant rocket motors it would be helpful to first analyze and understand more of the mechanisms that contribute to the attenuation of the ultrasonic signals.

#### Insight in degradation process

Neither hardness measurements on the cut section nor visible inspection on color change gives insight in the degradation process in the samples. It was expected that a degraded layer would be visible and hardness measurements would confirm those visual changes. However, this is not the case and suggests that the ageing may have not progressed as expected. Gaining more insight on the ageing process is essential for interpreting results of ultrasonic testing. Measuring stiffness at different depths in degraded material can give insight in the ageing process and help with interpreting results.

### Correlation with other tests

Assuming ultrasonic testing will be developed in the future to be a useful NDT technique for characterizing ageing in solid propellant rocket motors, it would be important to correlate the outcomes of ultrasonic testing with other data. For validation, the data should first be correlated with the tests that are in use for characterizing ageing and lifetime assessment right now: (destructive) mechanical tests that assess the material properties.

# Future outlook: Possible setup in solid propellant rocket motors

The measurements that were done in this research were on small samples. Solid propellant material is a highly attenuating medium. The samples used in this research all have a very small thickness compared to actual solid propellant rocket motors. Pulseecho measurements in the samples with a plastic casing gave two or three workable back reflection multiples. This means that in thicker material, in which the distance the signal travels is much larger, it is quite possible that the signal will be damped out completely and no back reflection can be observed in the received signal.

It was shown that a plastic casing does not pose large problems, however metal casings are more problematic. rocket motors are cylindrical and have a metal casing and an air filled void in the middle. This means that the ultrasonic techniques are optimized to propagate through a metal-solid propellant interface, pulse-echo measurements from outside the casing to the middle of the rocket motor would be the simplest setup as shown in figure 6.1a.

However, it is more likely that the metal-propellant barrier will remain a challenge. This means that it would be more logical to place small ultrasonic transducers inside the casing, in direct contact with the propellant material, for transmission measurements as shown in figure 6.1b. Using ultrasonic techniques that assess material properties, the results of signals that propagate near the middle of the material can be compared to signals that have propagated more superficially to characterize the ageing, as shown by the blue pathways in figure 6.1b. Another option would be to place a transducer on the surface of the propellant material in the air filled cylinder to do pulse-echo measurement from there directly on the propellant material. Looking at the fabrication process and use of the rocket motor, it may be more logical to put the ultrasonic elements at the inside of the casing rather than in the middle void. During the fabrication process the propellant material is poured into the casing and is cured inside the casing, which would make it easy to attach the elements on the inside of the casing before pouring the propellant material in. This way there is also a very small chance of the elements detaching or moving. With the elements immersed in the propellant material, no coupling material has to be used to make sure there is an airtight fit. During the ignition of the propellant material, the material starts to burn on the free surface on the inside of the propellant material. It seems logical that any possible pollution or decelerator of the burn pattern is more critical at this early stage of the ignition than in the last stage, when the burn surface has reached the casing.



Figure 6.1: Different setups for ultrasonic experiments on a cylindrical solid propellant rocket motor

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# A. Method: mixing inert solid propellant material

Appendix A describes the method that was developed to mix, pour and cure a small batch of inert solid propellant samples. This method is applicable for a mixture of  $\pm$  350 gram total weight, which is the maximum volume for one large RAM container.

# Ingredients

Binder ingredients		
HTPB (Hydroxyl-terminated polybutadiene)	Prepolymer	69.000%
IDP (Isodecyl Pelargonate)	Plasticizer	25.000%
IPDI (Isophorone diisocyanate)	Harder	5.320%
Flexzone 6H	Antioxidant	0.670%
FeAA	Catalyst	0.001%
Binder (above)	Binder	15.00%
Potassium sulfate	Solid particles	85.00%

### Method

- 1. Sieve potassium sulfate with a 1 mm sieve, removing clumps from the powder
- 2. Prepare molds with thick aluminum foil when the samples will not be kept in their containers afterwards
- 3. Mix HTPB and IDP in a seperate container
- 4. Add potassium sulfate to the RAM container and indent the middle for the HTPB/IDP mixture
- 5. Add HTPB/IDP in the indenture in the potassium sulfate
- 6. Add IDPI, Flexzone and FeAA
- 7. RAM in intervals with increasing intensity, see table A.1
- 8. RAM at 100% intensity until homogeneous and the container starts to feel warm
- 9. RAM with vacuum at 100% intensity until air bubbles disappear
- 10. When mixture is warm enough to be poured out of container, pour into molds in a fume cupboard
- 11. Leave in a  $60^{\circ}$ C stove to cure for one week
- 12. When cured, aluminum foil can be peeled away

Step	Time(s)	% Intensity	
1-4	30	50-70-90-100	Each step 30 seconds
5	120	100	
6	300	100	
7	120	100	Vacuum alternating on/off
8	300	100	Vacuum on

Table A.1: RAM steps for a large container with 350 gram ingredients

# B. Methods for analyzing frequency dependent attenuation

# **B.1** Frequency dependent attenuation

The method described below is taken from a method created by A.W.F. Volker for TNO [41]. Most of the explanation is taken from this document and some changes and additions in the form of text and figures are made for further clarification.

To characterize frequency dependent attenuation in clay and rubber samples, a method has been developed to to this with a setup with two transducers and two identical PMMA walls. The setup is shown in figure B.1. The sample is placed between the two parallel walls and transducers are placed on opposite sites on the walls. This way the transducers can be used for pulse-echo as well as transmission measurements. By doing all four measurements the transducer specific parts of the signal (transmit and receive transfer functions) can be filtered from the signals and only the actual attenuation by the sample material remains.



Figure B.1: Setup with the sample clamped between two PMMA walls

The signals of transmission and pulse-echo experiments can be represented in the frequency domain as a multiplication of transfer functions. A transmission experiment where transducer 1 transmits and transducer 2 receives can be described by:

$$V_2^T = D_2 \cdot W_2 \cdot T_{1L \to 2} \cdot W_L \cdot T_{1 \to L} \cdot W_1 \cdot S_1 \tag{B.1}$$

Where  $V_2^T$  is the signal measured at transducer 2 (in the frequency domain),  $D_2$  is the receive transfer function of transducer 2,  $W_2$  describes the propagation through wall 2,  $T_{L\rightarrow 2}$  is the transmission coefficient belonging to the interface between the sample and wall 2,  $W_L$  describes the propagation through the sample over distance L and is the frequency dependent variable that helps characterizing the frequency dependent attenuation,  $T_{1\rightarrow L}$  is the transmission coefficient belonging to the interface between wall 1 and the sample,  $W_1$  describes the propagation through wall 1 and  $S_1$  is the transmit transfer function of transducer 1.

In the same way the transmission experiment where transducer 2 transmits and transducer 1 receives is described by:

$$V_1^T = D_1 \cdot W_1 \cdot T_{L \to 1} \cdot W_L \cdot T_{2 \to L} \cdot W_2 \cdot S_2 \tag{B.2}$$

where  $V_1^T$  is the signal measured by transducer 1(in the frequency domain),  $D_1$  the receive transfer function of transducer 1,  $T_{L\to 1}$  is the transmission coefficient belonging to the interface between the sample and wall 1,  $T_{2\to L}$  is the transmission coefficient

belonging to the interface between wall 2 and the sample and  $S_2$  is the transmit transfer function of transducer 2.

A pulse-echo experiment with transducer 1 transmitting and receiving the reflection of the interface between wall 1 and sample is described by:

$$V_1^{Pe} = D_1 \cdot W_1 \cdot R_{1 \to L} \cdot W_1 \cdot S_1 \tag{B.3}$$

where  $V_1^{Pe}$  is the signal measured by transducer 1 (in the frequency domain), and  $R_{1\to L}$  is the reflection coefficient between wall 1 and sample.

The pulse-echo measurement with transducer 2 is described by:

$$V_2^{Pe} = D_2 \cdot W_2 \cdot R_{2 \to L} \cdot W_2 \cdot S_2 \tag{B.4}$$

where  $V_2^{Pe}$  is the signal measured by transducer 2 (in the frequency domain), and  $R_{2\to L}$  is the reflection coefficient between wall 2 and the sample.

By multiplying equations (B.1) and (B.2) and dividing by equations (B.3) and (B.4) the following is obtained:

$$\frac{V_2^T \cdot V_1^T}{V_2^{Pe} \cdot V_1^{Pe}} = \frac{T_{L \to 1} \cdot T_{L \to 2} \cdot T_{1 \to L} \cdot T_{2 \to L}}{R_{1 \to L} \cdot R_{2 \to L}} \cdot W_L^2 \tag{B.5}$$

by eliminating  $D_1$ ,  $D_2$ ,  $S_1$ ,  $S_2$ ,  $W_1$  and  $W_2$  from the equation. The influence of both the transducers and the walls are eliminated from the equation. Equation (B.5) only consists of the received signals and reflection and transmission coefficients, which can be calculated and are frequency independent. The only unknown left is  $W_L^2$ , which describes the propagation through the sample.

One sent pulse is used in the method. The ultrasound pulses, either the signal that had passed through the setup or the first back reflection of the wall-sample interface, must be cut from the measured signal in the time domain with a window, for example a rectangle or Hamming window. Figure B.2 shows an (ideal) example of a pulse-echo measurement and a Hamming window around the pulse. Because convolution in the time domain is the same as multiplication in the frequency domain, the left hand side of equation (B.5) can be done by convolution in the time domain before conversion to the frequency domain by Fourier transform.



Time

Figure B.2: Hamming window (red) around received pulse signal (black)

The difference in sound attenuation  $(\alpha_{dif})$  can be calculated as follows from the signals measured:

$$\alpha_{dif} = \frac{20 \log_{10} \left( |W_L^2| \right)}{L} \tag{B.6}$$

The attenuation difference can be plotted against frequency and the graph will give an idea about which frequencies will damp the signal maximally and minimally.

# B.2 Attenuation and phase velocity dispersion estimation

The method described here is a short summary of a method described by Raisutis et al. [40]. It is created to predict back surface reflections of highly attenuating plastics. Solid propellant material has similar properties as plastics, so is expected this method could be applied to solid propellant material too.

Figure B.3 shows the setup for this method. It is a pulse-echo setup immersed in water with air behind the sample. This way the ultrasonic signal will reflect off of two surfaces resulting in an ultrasonic signal  $u_r(t)$  reflected by the back surface and  $u_0(t)$  reflected by the front surface of the sample.  $u_0(t)$  is the reference signal, which has not traveled through the sample and  $u_r(t)$  is the signal that has changed due to attenuation and dispersion after propagating through the sample material.



Figure B.3: Submerged pulse-echo setup

Prediction of the signal  $u_r(t)$  can be done if the complex transfer function  $H(i\omega, x)$  of the sample is known:

$$u_r(t) = iFFT[U_0(i\omega) H(i\omega, x)]$$
(B.7)

where  $H(i\omega, x)$  is the complex transfer function in a pulse-echo mode of the object with an arbitrary thickness x and  $U_0(i\omega)$  the Fourier transform of the reference signal  $u_0(t)$ . iFFT denotes the inverse Fourier transform. The complex transfer function can be found from pulse-echo measurements using a sample of thickness  $x_0$ :

$$H(i\omega, x) = \frac{U_r(i\omega, x)}{U_0(i\omega)}$$
(B.8)

with  $U_r(i\omega, x)$  the Fourier transform of the reflected signal  $u_r(t)$ . The complex transfer function  $H(i\omega, x)$  can be presented in terms of real part  $R(\omega)$  and imaginary part  $X(\omega)$ :

$$H(\omega, x) = K(R(\omega) + iX(\omega))$$
(B.9)

$$= H_{att}(\omega, x) H_{disp}(i\omega, x) \tag{B.10}$$

with

$$H_{att}(\omega, x) = K_0 e^{-\alpha(\omega)x} \tag{B.11}$$

$$H_{disp}\left(i\omega,x\right) = e^{i\beta(\omega)x} \tag{B.12}$$

K takes into account signal losses and distortions caused by interfaces of the test object and the surrounding medium,  $K = 1/K_0$ ,  $K_0$  is the reflectivity coefficient,

 $\alpha(\omega)$  is the attenuation coefficient,  $\beta(\omega)$  is the propagation constant which is related to the phase velocity  $v_p$  by  $\beta(\omega) = \omega/v_p(\omega)$ .

In general the phase velocity dispersion and attenuation are interrelated. This means that the attenuation of the material is known, the phase velocity dispersion could be determined from that. The full elaboration of the method to do this with the help of the Kramers-Kronig relation connecting the real and imaginary parts of complex functions is described in [40].