Ultrasonic Non-Collinear shear wave mixing for the detection of ageing in PVC pipes

by

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Abstract

Physical degradation in pipelines made of PVC is caused by a naturally occurring phenomenon called ageing. Physical ageing makes the pipeline brittle, which ultimately leads to its failure. Detection of physical ageing in PVC pipelines is a topic of on-going research as there is no unique method to determine the age of pipelines. Water companies do not know the current state of pipelines in terms of its age and investigations to determine the age of PVC pipelines were made using an ultrasonic inspection technique called non-collinear wave mixing. The non-collinear wave mixing technique involved the interaction between a shear wave and a longitudinal wave under certain resonant conditions, that generated a response longitudinal wave. This thesis reports on the application of the non-collinear wave mixing technique using a different wave interaction, to detect ageing in PVC pipelines. The wave mixing used, involves the interaction between two shear waves that generates a response longitudinal wave. The change in an ultrasonic parameter with respect to ageing time is investigated. The ultrasonic parameter of interest is the difference in amplitude of the generated longitudinal wave at a certain ageing time, with respect to its amplitude at pristine state.

In the previous research, the configuration used for the non-collinear wave mixing technique comprised of a receiver placed on the opposite side as that of the transducers sending the pump waves. Both sides of the material had to be accessed and this configuration is called the double-sided access configuration. This configuration was chosen because the ageing-induced changes in the non-linear elastic properties of PVC are small and hence it is difficult to detect these changes only if single-sided access to the material is possible. However, in industries, the material to be inspected is usually embedded and only single-sided access to the structure is possible. Therefore, a configuration in which the receiver is placed on the same side as that of the transducers sending the pump waves is investigated in this research. The extracted amplitudes of the shear pump waves and the generated longitudinal wave are compared in both the configurations.

Based on the results obtained, it is found that the amplitude of the shear pump waves and the generated wave changes with ageing time in both the configurations. Therefore, it is concluded that the non-

collinear ultrasonic wave mixing technique is sensitive to the phenomenon of physical ageing in PVC. As known from the previous research, it is also concluded here, that the double sided access configuration can be used to detect ageing in PVC. However, it is also found that the single-sided access configuration is sensitive to the phenomenon of ageing and can also be used for its detection in PVC.

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1. Introduction and motivation

Water distribution systems make use of pipelines to transmit waste water for treatment and subsequent reuse. Pipelines are also used for the distribution of drinking water from water treatment plants to the point of use. Materials used in the construction of pipelines are selected based on its application. Commonly used materials for the transmission of drinking water include cast iron, copper, steel, concrete and polyvinyl chloride (PVC) [1]. The benefits and drawbacks of these pipe materials used in drinking water transportation applications, are discussed in the following section.

Pipelines made of steel are the strongest and the most durable of all materials used in the water distribution system as they can withstand high pressures during the flow of water. Steel pipelines can be used in water distribution systems for long distance water transportation applications [2]. Another commonly used pipeline material is galvanised iron, although its popularity is decreasing due to corrosion caused by high pressures of water during slow or static flow. To withstand high water pressures, pipelines made of cast iron are used. However, cast iron pipelines are bulky, making them heavy and causing difficulty in transportation [3]. Due to the corrosive nature of pipelines, water transported through galvanised iron/steel pipes, is found to have unpleasant odour and taste [4]. Cement based pipes are non-corrosive in nature which make them strong and durable. However, cement based pipes are also bulky, making it difficult to handle, install and transport [5]. Pipelines made of asbestos cement (AC) were extensively used in the potable water distribution network in the mid 1900's. AC pipes undergo gradual degradation in the form of corrosion due to internal calcium leaching which occurs over time [6-7]. Leaching causes reduction in effective cross-sectional area of the pipe which consequently results in the loss of its mechanical strength. The use of asbestos have reported to cause health related issues that arise when its fibres are inhaled. The lungs cannot expel them due to their large size and thus can cause a lung disease called Asbestosis. The use of asbestos also lead to cancer of the mesothelial lining of the lungs called Mesothelioma [8-9]. Such disadvantages in metals and cement based pipeline material led to research and investigations on materials that could overcome these drawbacks. This led to the development of pipeline materials made of plastics, which started in the mid-thirties [10].

Development of plastic pipes made of materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly vinyl chloride (PVC) brought revolutionary changes in pipeline industry. PVC is a predominant material used in the Dutch drinking water distribution network. Almost 50% of the pipelines transporting drinking water are made of PVC in the Netherlands [11]. PVC offers advantages over commercially used piping materials in terms of its durability and cost effectiveness and thus, used in the transportation of potable water and waste water in agricultural and industrial applications [12]. The advantages offered by PVC pipes over other commercially used piping material, led to their extensive usage during the expansion of water and gas distribution systems in the mid-sixties [11]. The demand for PVC pipes increased substantially throughout the years among water and gas distribution companies, which is one of the main reasons why such companies are interested in the study of this material.

Due to extensive usage of PVC as a piping material, failure prevention of pipelines made of PVC became an important subject of study in the recent years. Researches were conducted to examine the factors that cause degradation in PVC pipes [13-15]. Degradation of PVC can be caused by physical, chemical or mechanical factors [15]. An external agent such as chlorine, causes chemical degradation in PVC which makes the pipeline material brittle. UV-degradation is the most well-known aspect of degradation in PVC. The latter happens only in pipes that are stored in open air [16]. In practice, UV-degradation is of no importance for drinking water pipelines since they are buried under the ground. Mechanical stresses act on pipes during its service from its surrounding environment. This causes mechanical degradation of PVC pipes. As the pipeline material is susceptible to degradation during its service, physical degradation takes place in the pipeline materials with the course of time and this phenomenon is called ageing. Physical ageing makes the pipeline brittle, which ultimately leads to its brittle failure.

Understanding the manner in which failure in a pipe takes place is very important since there are two main differences between a ductile and brittle failure. Firstly, more energy is absorbed before ductile failure occurs when compared to brittle failure. A ductile PVC pipe can therefore withstand stronger impact forces than a pipe which is aged. Secondly, it is easier to stop the gas or water flow in a ductile rupture than in a brittle rupture. This is attributed to the fact that sharp and irregular fracture surfaces are formed after the occurrence of a brittle fracture [17].Therefore, pipelines have to be inspected to detect their current state so that they can be replaced before failure occurs.

The consequences of pipeline failure include direct costs i.e. cost of repair, cost of water loss, cost of damage to surrounding property, indirect costs i.e. cost of water supply interruption, cost of potential increase in the deterioration rate of surrounding property, and social costs i.e. cost of water quality degradation due to certain levels of contamination and the cost of decrease in public trust in the quality of water supply [18].

In order to inspect the current state of pipes, the pipelines have to be dug out and examined individually. This mode of evaluation will intervene in the operation of the pipeline since the pipelines are taken out of service when this evaluation is performed. In contrast to destructive testing, non-destructive evaluation (NDE) of the current state of pipelines is performed without intervening in its operation [19]. NDE techniques should be able to provide insights on defects, if present inside the structure, when the pipelines are in service in the distribution network.

The commonly used NDE techniques for the inspection of water mains and waste water network include electromagnetic methods such as eddy current, ground penetrating radar, and magnetic flux leakage, mechanical methods such as acoustic emission, ultrasonic testing, impact-echo, acoustic leak detection, sonar, and visual inspection methods based on the use of closed-circuit cameras [20]. However, there is a lack of commercially available systems for the inspection of pipelines made of plastic materials such as PVC [21-22]. Ultrasonic testing is the current best practice used in the inspection of pipelines in the metal industry [23]. Plastic materials such as PVC, are difficult to inspect using ultrasonic testing due to its acoustic property of high attenuation of sound [24]. Attenuation depends on the frequency of the ultrasonic wave. Due to frequency-dependent attenuation, the higher frequency components of the ultrasonic signal are attenuated more than the lower frequency components. Therefore, detection and characterization of defects of a similar size at different distances in the pipe becomes a strenuous task.

Several studies have been conducted to develop reliable NDE methods for the inspection of plastic pipelines [25-27]. Ultrasonic transducers are currently being used in the inspection of two commonly used plastic pipeline materials, i.e. High-density polyethylene (HDPE) and PVC, using techniques such as pulse-echo, creeping waves and time-of-flight diffraction (TOF). Ultrasonic testing is performed for the detection of grooves and cracks within the pipe [28-30]. Voids present in the ground external to the buried pipe with varying shapes and dimensions can also be detected using ultrasonic testing [31].

Detection of physical ageing in PVC pipelines is a topic of on-going research as there is no unique method to determine the age of pipelines. Therefore, the water companies do not know the current state of pipelines in service. Physical ageing causes change in the mechanical properties of the pipeline material such as its yield stress [32]. Therefore, researches are conducted to detect changes in the mechanical properties of pipelines as a result of ageing using NDE [33]. In this research, an attempt is made to determine the physical ageing in PVC material using the NDE technique of ultrasonic non-collinear wave mixing. The amplitude changes in the pump waves and the generated wave, are extracted and analysed to see if they display a trend with respect to ageing time. If a trend is followed, the ageing phenomenon in PVC pipelines can be characterised by the amplitude changes of the ultrasonic waves recorded from the non-collinear wave mixing technique.

2. Theory

The sections below describe topics such as the production process of PVC and the different additives incorporated into it during its manufacture, chemistry of physical ageing in PVC and the different degradation mechanisms occurring in it due to ageing, influence of temperature changes in PVC which can occur during its time of service, the NDE technique of ultrasonic testing describing pulse-echo, angle beam inspection and the non-collinear wave mixing principle. A brief explanation on signal processing is also included in this section.

2.1. Production process of PVC

PVC pipes are usually manufactured by three polymerisation processes i.e. suspension, bulk and emulsion. However, 80% of the total production of PVC pipes on a commercial scale are produced by suspension polymerisation [33]. A free radical chain reaction mechanism gives rise to addition polymerisation of vinyl chloride monomer which includes steps of initiation, propagation and bimolecular termination. The overall reaction showing the formation of PVC from vinyl chloride monomer is shown in Figure 1.

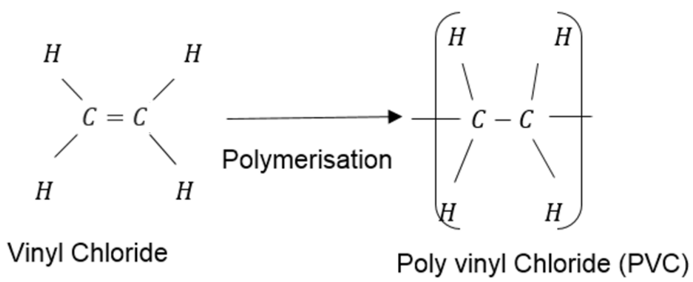


Figure 1: Polymerisation of vinyl chloride monomer [33]

In the manufacturing process of PVC pipes, certain compounds called additives are added to the material to impart either physical or chemical properties to improve its performance. The additives include stabilisers, plasticisers, fillers, colorants, lubricants and antioxidants [34]. Stabilizers are added to PVC pipes during its manufacturing, to impart thermal stability in order to make the final PVC compound resistant to heat, ultraviolet light and oxygen. Fillers such as carbon black are used as screening agents in PVC pipes because it can absorb harmful ultraviolet radiations without causing any change in the chemical structure of the polymer. The most commonly used additive in water distribution pipelines made of PVC are plasticizers such as diisononyl phthalate, which improves the flexibility of the pipeline material [35].

Glassy polymers such as PVC are not in the state of thermodynamic equilibrium and its molecules continuously strive towards attaining that state. The small conformational changes caused by the molecules inside the polymer chain leads to decrease in the thermal stability of the PVC structure and make it susceptible to physical damage. The material tends to soften and consequently deform, when exposed to temperatures over 80ºC [17]. With increase in service time, the pipelines are susceptible to physical damage and consequently, degradation takes place as a result of ageing.

2.2. Chemistry of Physical ageing

Physical ageing occurs due to the fact that glassy polymers like PVC are not in a state of thermodynamic equilibrium but are continuously striving to attain that state [36]. The small conformational changes taking place due to the change in orientation of molecules inside the material, changes the thermodynamic condition of the polymer which results in an increase in the polymer density [37]. As the polymer density increases, its molecular mobility decreases and consequently its resistance against plastic deformation increases. An increase in the polymer resistance against plastic deformation is a direct consequence of physical ageing which results in reduction of its operational lifetime. Consequently, the yield stress increases gradually with time when the polymer physically ages as shown in Figure 2 [17].

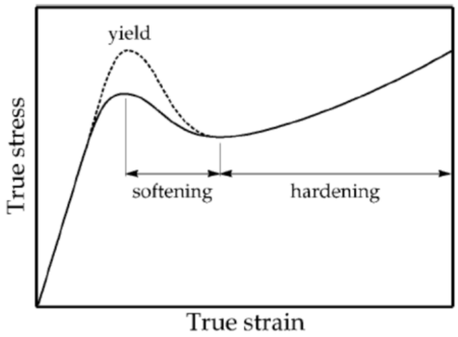


Figure 2: Change in yield stress due to physical ageing [17]

Yield stress is defined as the maximum stress that a material can withstand before deforming from its elastic behaviour to plastic behaviour. Even though increase in yield stress makes the pipe material stronger, it leads to increase in strain softening which results in stronger strain localisation. This has a strong influence on the failure mode of the material [37]. Eventually the plastic zone localises to an extent that cavitation starts to occur and craze is initiated. When the craze breaks down, formation of cracks take place, which explains the consequence of physical ageing. Physical ageing causes PVC pipes to fail in a brittle manner than in a ductile manner [38].

There are several mechanisms by which degradation takes place in PVC pipes as a result of ageing. These mechanisms are discussed in the following section.

2.3. Degradation Mechanisms in PVC due to Physical Ageing

Physical ageing is a phenomenon that occurs gradually with the time of operation in all pipeline materials. As the PVC pipeline continues to be in service, chemicals present in water, such as chlorine, gives rise to a chemical reaction called de-hydro chlorination, causing degradation [39]. De-hydro chlorination is a rapid auto catalytic displacement reaction in which the chlorine atoms displaces hydrogen atoms from the PVC structure in a sequential chain reaction mechanism. Due to the formation of double bonds in the structure, the chemical structure of PVC is altered, making the compound more reactive. The double bond between the two carbon atoms prevent the rotation of atoms, thereby reducing the flexibility of PVC, thus, making it vulnerable to impact loads. This makes the compound instable and consequently lead to degradation. As a result of degradation, drastic changes in the mechanical properties of PVC occur due to chain scission or cross-linking of polymer molecules, resulting in variation in its average molecular weight [39]. Physical ageing also causes accumulation of materials on the inner surface of the pipes such as scales or biofilms [40]. Pipe scaling takes place due to the deposition of calcium or magnesium salts on the walls of the pipe from hard water. Biofilm formation sustains microbial growth on the inner walls of the pipe which will affect the quality of water that is transported through it.

To artificially induce ageing in the PVC material, accelerated method of ageing is performed by increasing the temperature of the PVC material. This method is known as the process of annealing. Section 2.4 describes the changes that take place inside the PVC material when subjected to a rise in temperature.

2.4. Effect of increase in temperature in a PVC material

During the process of annealing, PVC material is subjected to an increase in temperature and strain rate. Plastic polymers are sensitive to temperature and strain rate for a given period of time. These two factors affect the viscoelasticity behaviour of plastics [41].

Plastics such as PVC show a drastic change in their physical properties over a relatively short temperature range [42]. As the temperature increases, the chains of repeating units inside the polymer are positioned further apart. This results in an increase in free volume inside the polymer matrix and thus the kinetic energy of the molecules increases [43]. Consequently, the polymer chains can slide past each other and disentangle easily.

Strain rate refers to the speed at which the impact load is applied on the plastic material. At a particular strain rate, plastics tend to deform from their elastic behaviour to their plastic behaviour and this phenomenon is called yielding. With increase in strain rate, the strain softening phase starts to decrease and at some point no more softening occurs. This is the point where plastic deformation starts to take place. As the strain rate increases, the polymer chains disentangle but do not have enough time to undergo ductile yielding and instead follow brittle failure mechanism. As the application of stress over time is increased, the viscoelastic behaviour of the polymers increases. This leads to an increase in their molecular mobility and thus the polymers exhibit differences in their long and short term properties [39].

2.5. Ultrasonic testing

Ultrasonic testing has been used for a wide variety of applications such as detecting defects in surfaces and sub-surfaces of materials for measuring quantities such as thickness and depth of flaws, wave velocities and attenuation [44]. The inner state of PVC pipes can be monitored in-service and the monitored results can be used to analyse the condition of the pipe, which assist in diagnosis and prevention of potential threats to the pipes [18]. Different ultrasonic testing methods include usage of straight beams, angled beams, immersion testing, phased arrays, through transmissions and time of flight diffraction. However, only straight beam and angled beam inspection methods are used in this research. Therefore, explanation to only these two methods of beam inspection will be mentioned in this context.

2.5.1. *Straight beam inspection*

Figure 3 shows a schematic representation of the straight beam ultrasonic inspection of a material. The straight beam inspection technique is commonly termed as Pulse-echo method in the field of ultrasonic inspection [45].

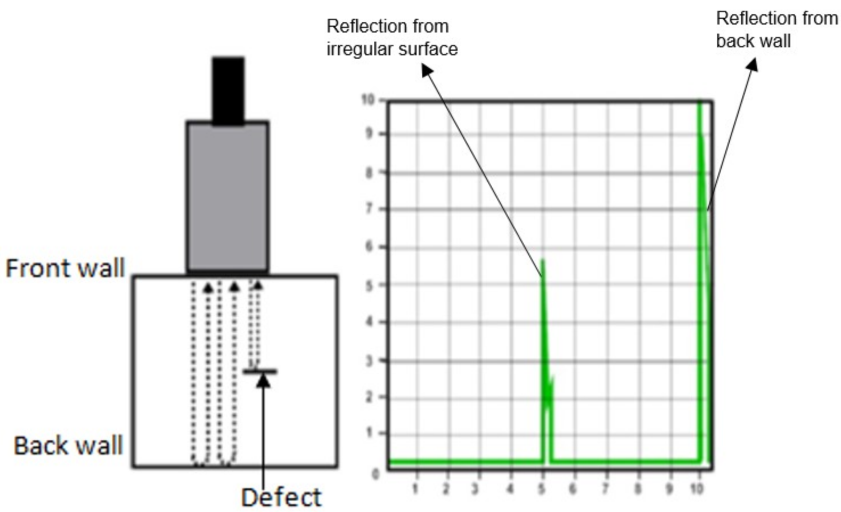


Figure 3: Straight beam inspection (Pulse-echo) [45]

The interface of the material and the surrounding medium on which the ultrasonic beam hits first, is referred to as the front wall of the material. The interface on which the sound beam hits after passing through the front surface, is termed as the back wall of the material.

Ultrasonic inspection follows the principle that when sound beam from a transducer hits a material consisting of an irregular surface, usually found in degraded pipes, it is reflected from the surface before getting reflected from the back wall. This is due to the shorter distance of the irregular surface from the transducer as compared to the back wall. In Figure 3, the reflection from the irregular surface is represented by the first green peak from the left and the reflection from the back wall is represented by the second green peak from the left. The measurement of the distance between the two peaks enables the estimation of the depth at which the irregular surface is located inside the material.

2.5.2. Angle beam inspection

Angle beam inspection comprises of a transducer aligned at a certain angle with respect to the surface of the test specimen. The transducer is oriented to transmit ultrasonic signals to the test sample at a fixed angle. Both pulse-echo and angle beam inspection uses the principle of immersion ultrasonics where a medium such as water or gel is used as a coupling medium between the transducer and the test material [46].

Both reflection and refraction occurs at the boundary between two media that differs in sound velocities and acoustic impedances. If the surface on which the sound beam hits is not smooth, no specular reflections occur but instead the reflection gets diffused into the surface. When sound beam hits on a smooth plane surface, reflection and transmission of the beam takes place. The velocity of sound inside one medium is calculated from Snell's law, equating the ratio of sound velocities V_{L1} and V_{L2} in both media to the ratio of the sine of angle of incidence θ_1 to the angle of refraction θ_2 (see Figure 4).

$$\frac{\sin\theta_1}{V_{L1}} = \frac{\sin\theta_2}{V_{L2}} \tag{2.1}$$

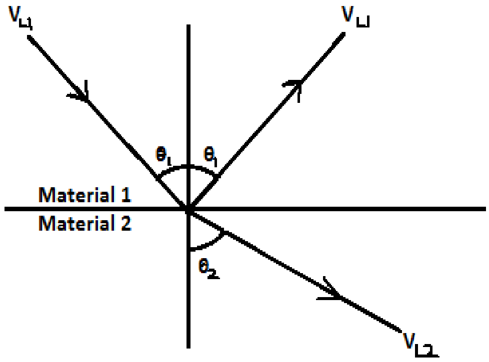


Figure 4: Reflection and refraction of sound waves at the interface of two materials [48]

For a smooth plane surface, the intensity of the incident sound wave is equal to the sum of the intensities of the reflected sound wave and the transmitted sound wave such that energy is conserved. The angle of incidence of the sound wave θ_1 is always equal to the angle of reflection of the sound wave θ_2 according to the law of reflection. For normal incidence angle i.e. $\theta_1 = 0$, the reflected wave and the transmitted wave are also normal to the interface i.e. refraction occurs but at $\theta_2 = 0$, as seen in pulse-echo method.

The most commonly used modes of sound waves in ultrasonic inspection are longitudinal and shear waves (transverse waves). Longitudinal wave propagates through a medium when particle oscillations occur in the direction of the wave propagation. Since they make use of compression and expansion forces and cause changes in the density of the material as they propagate, longitudinal waves can also be called as pressure waves or density waves. Shear wave or transverse wave propagates through a medium when particle oscillations occur at right angles to the direction of propagation of the wave. Shear waves travel slower and are weaker when compared to longitudinal waves. Therefore, in many cases they are generated in the material from a part of the total energy of the longitudinal waves. Shear waves cannot travel in fluids i.e. liquids and gases, but only in solids and other viscous materials [49]. Solid materials have internal shear forces that make them rigid and hold all molecules together, allowing shear waves to propagate through.

Since only longitudinal waves can be generated in a fluid, the refracted and reflected sound wave at the interface of two fluid media should also be longitudinal waves as shown in Figure 5(a). At the interface of a fluid and a solid medium, the transmitted sound wave can be both longitudinal and shear, as shear waves can propagate in a solid material, as shown in the Figure 5(b).

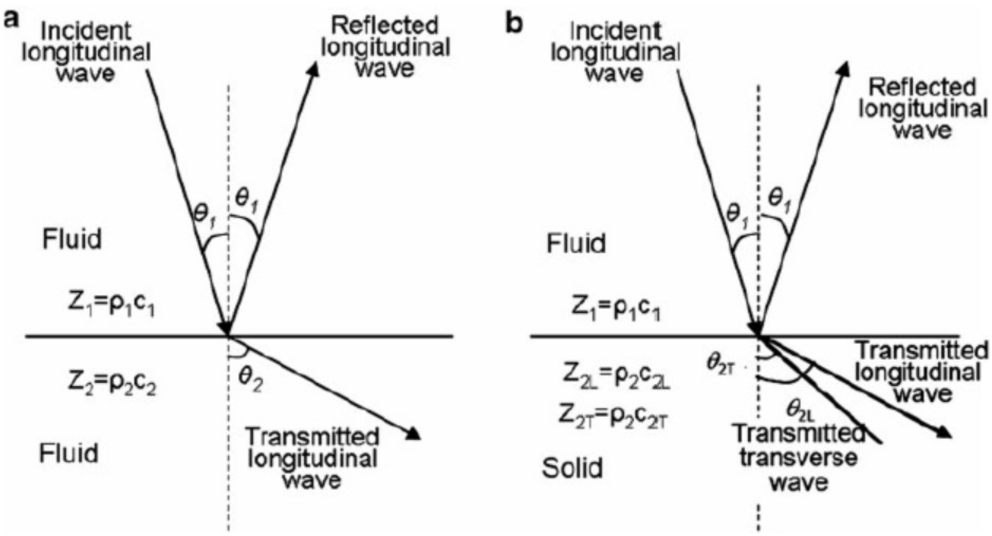


Figure 5: (a) Sound wave propagation at fluid-fluid interface (b) Sound wave propagation at fluid-solid interface [49]

As shown in Figure 5, Z_1 and Z_2 represent the acoustic impedance of medium 1 i.e. fluid and medium 2 i.e. fluid in Figure 5 (a) and solid in Figure 5 (b) respectively. Acoustic impedance is defined as the product of density of the medium and the speed of sound in that medium.

The angle at which the transducer is aligned with respect to the test material determines the mode of ultrasonic beam that is generated inside the material. As the angle of incidence of the ultrasonic beam with respect to the transducer is increased, the angle of the refracted longitudinal wave in the test material increases. As the angle of the refracted longitudinal wave approaches 90^0, a large portion of its wave energy is converted to a shear wave that is refracted at an angle in accordance to the Snell's law (2.1). When the angle of incidence of the ultrasonic beam with respect to the test material is higher than an angle which would create a refracted longitudinal wave of 90^0, the refracted wave inside the test material exists entirely in its shear wave mode. Therefore, if the sound velocity in the test material is higher than in the coupling medium, with increase in the angle of incidence, the refraction of sound will be accompanied by a mode conversion, most commonly from longitudinal wave mode to shear wave mode.

Conventional ultrasonic inspection involves measurements which are based on the hypothesis of linear elasticity theory, where only the changes in linear properties of the material are detected in the measurement results. Change in non-linear properties of materials as a result of its degradation cannot be detected by linear ultrasonic techniques. However, non-linear ultrasonic techniques have a high sensitivity towards micro defects formed due to degradation, such as a fatigue crack. Therefore, non-linear characteristics of material properties have gained prominence in non-destructive testing (NDT) applications [50-51]. These techniques use non-linear components, such as harmonics and modulations, which are generated from the interaction of ultrasonic waves [52]. Therefore, it is necessary to use different ultrasonic measurement methods, such as, the field of non-linear ultrasonics.

It is indicated in literature that the tensile creep compliances for PVC was measured over a wide range of ageing time (10^{-8}-10^{6}s), a part of which was done using linear ultrasonic measurements. The creep compliance loss measurements were made over a wide range of frequencies (0.01Hz-5MHz). It was found that the shape of the measured tensile compliance loss as a function of frequency has a peak which indicated the maximum frequency. However, the shape of the compliance loss curve was almost unaffected by the ageing time. The tensile compliance loss peak was obtained around 30 KHz. The reported low frequency of the peak and low sensitivity of acoustic waves to physical ageing of PVC prove that linear acoustic measurements are not suitable for the determination of physical ageing in PVC [53].

2.6. Non-Linear Effect

As ultrasonic waves propagate in a medium due to localised pressure changes, the medium consists of phases with difference in pressure. Regions of high pressure in the medium will have a high local temperature and regions of low pressure will have a low local temperature [54]. As the speed of sound increases with temperature in a compressible medium, ultrasonic waves travel faster in a high pressure phase when compared to a low pressure phase in a medium.

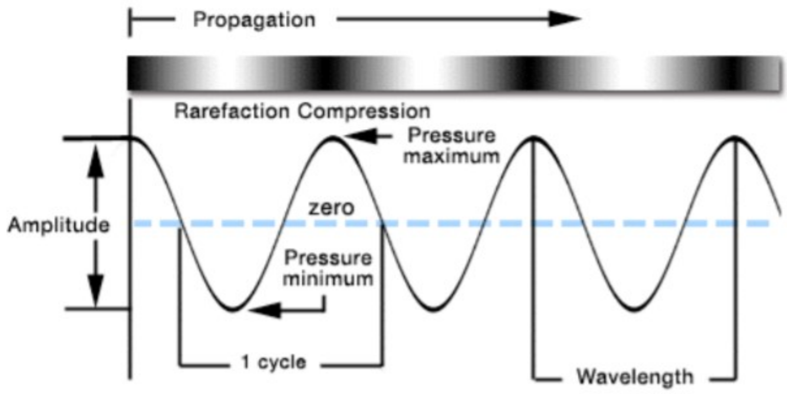


Figure 6: Propagation of sound wave in a compressible medium [55]

Figure 6 shows the propagation of a sound wave in a compressible medium generating a series of compressions and rarefactions due to pressure variations. The point at which is the pressure is minimum is called trough and the point at which the pressure is maximum is the crest. Amplitude of the sound wave is the height difference between a peak and the trough. Wave length is the difference between two successive crests or troughs. The blue line corresponds to zero displacement of the particle. Velocity of sound wave v is the product of its frequency f and wavelength λ.

$$v = f\lambda \tag{2.2}$$

The different speeds of the travelling wave affect the frequency structure of the wave as the crest and trough of the frequency peaks will have non-uniform heights. This effect causes self-distortion of the wave. As a result, other frequency components apart from its primary frequencies are introduced to the wave, which are described by Fourier series [56]. This makes the system non-linear as linear acoustic system responds only to the driving frequencies. The frequency spectra of a non-linear wave comprises of its fundamental frequency and its subsequent harmonics as seen in Figure 7 [57].

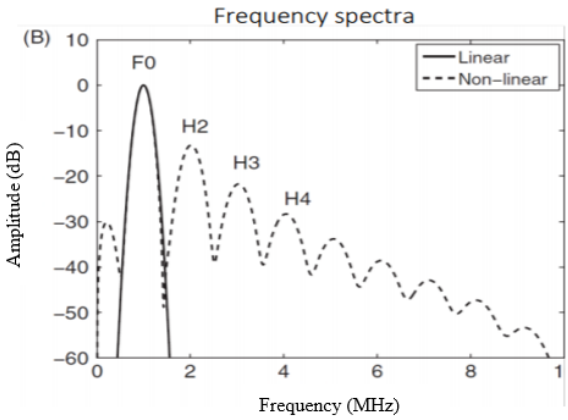


Figure 7: The frequency spectra of a linear (bold line) and non-linear wave (dotted line). Here F0 is the fundamental frequency and H2, H3, H4 are the subsequent harmonics [57]

Ultrasonic waves of higher amplitude will generate more non-linearity in the medium when compared to waves of lower amplitude [58]. The amplitudes of the harmonics H2, H3 and H4 are dependent on the coefficient of non-linearity β of the medium through which the wave propagates. The non-linearity coefficient β is defined below.

$$\beta = 1 + \frac{1}{2}\left(\frac{B}{A}\right) \tag{2.3}$$

Parameters A and B are coefficients of Taylor series expansion used for expressing the change in pressure of a medium with respect to the ambient pressure P_0, when an ultrasonic wave propagates through it. The thermodynamic equation of state relates three sets of quantities describing the thermodynamic behaviour of the medium which are pressure P, mass density ρ and specific entropy s (per unit of mass) or pressure P, mass density ρ and temperature T of the medium. A Taylor series expansion of this relation about the state of equilibrium state is normally used.

$$P - P_0 = \left(\frac{\partial P}{\partial \rho}\right)_s (\rho - \rho_0) + \frac{1}{2!}\left(\frac{\partial^2 P}{\partial \rho^2}\right)_s (\rho - \rho_0)^2 + \frac{1}{3!}\left(\frac{\partial^3 P}{\partial \rho^3}\right)_s \cdots$$

(2.4)

It is to be noted that the pressure change is calculated at constant specific entropy s of the medium. The partial derivatives are taken at ambient values of mass density ρ and specific entropy s.

Replacing $P-P_0$ by P' and $\rho-\rho_0$ by ρ' in (2.4), the following equation is obtained.

$$P' = \rho_0\left(\frac{\partial P}{\partial \rho}\right)_s\left(\frac{\rho'}{\rho_0}\right)+\rho_0^2\left(\frac{\partial^2 P}{\partial \rho^2}\right)_s\frac{1}{2!}\left(\frac{\rho'}{\rho_0}\right)^2+\rho_0^3\left(\frac{\partial^3 P}{\partial \rho^3}\right)_s\frac{1}{3!}\left(\frac{\rho'}{\rho_0}\right)^3 \ldots \tag{2.5}$$

P' and p' are the dynamic pressure and density of the medium which expresses small disturbances relative to the uniform state of rest as the wave propagates through the medium. (2.5) can be re-written as shown below.

$$P' = A\left(\frac{\rho'}{\rho_0}\right)+B\frac{1}{2!}\left(\frac{\rho'}{\rho_0}\right)^2+C\frac{1}{3!}\left(\frac{\rho'}{\rho_0}\right)^3 \ldots \tag{2.6}$$

Where *A, B* and *C* are coefficients of the Taylor expansion.

$$A=\rho_0\left(\frac{\partial P}{\partial \rho}\right)_S,\ B=\rho_0^2\left(\frac{\partial^2 P}{\partial \rho^2}\right)_S,\ C=\rho_0^3\left(\frac{\partial^3 P}{\partial \rho^3}\right)_S \tag{2.7}$$

For the determination of the acoustic non-linearity parameter $\frac{B}{A}$, several methods have been proposed [59-60].The classical thermodynamic method proposed by Beyer [60] relates the $\frac{B}{A}$ parameter with pressure and density during the propagation of sound.

The linearized thermodynamic equation of state is shown below.

$$p' = {c_0}^2 P' \tag{2.8}$$

Therefore, $\left(\frac{\partial P}{\partial \rho}\right)_S$ is written as c_0^2 where c_0 is the speed of sound at equilibrium state. The $\frac{B}{A}$ value of the non-linear coefficient β can be obtained from the (2.7).

$$\frac{B}{A}=\frac{\rho_0^2\left(\frac{\partial^2 P}{\partial\rho^2}\right)_s}{\rho_0\left(\frac{\partial P}{\partial\rho}\right)_s}=\frac{\rho_0}{c_0^2}\left(\frac{\partial^2 P}{\partial\rho^2}\right)_s=\frac{\rho_0}{c_0^2}\left(\frac{\partial}{\partial\rho}\frac{\partial P}{\partial\rho}\right)_s=\frac{\rho_0}{c_0^2}\left(\frac{\partial c^2}{\partial\rho}\right)_s=\frac{\rho_0}{c_0^2}\left(\frac{\partial c^2}{\partial c}\frac{\partial c}{\partial\rho}\right)_s=\frac{\rho_0}{c_0^2}\left(2c\frac{\partial c}{\partial\rho}\right)_s \tag{2.8}$$

Here, the speed of sound is measured during a rapid and smooth pressure change such that the system is considered to be thermodynamically reversible. Non-linearity parameter $\frac{B}{A}$ can be re-written as shown below.

$$\frac{B}{A}=2\mathrm{p}_0 c_0\left(\frac{\partial c}{\partial \mathrm{p}}\right)_s \tag{2.9}$$

The temperature dependency of the $\frac{B}{A}$ parameter can be obtained from the classical thermodynamic method proposed by Beyer [60].

$$\frac{B}{A}=2\rho_0 c_0\left(\frac{\partial c}{\partial P}\right)_T+\frac{2\alpha_T c_0 T_0}{c_P}\left(\frac{\partial c}{\partial T}\right)_P \tag{2.10}$$

T is the temperature, c_p is the isobaric specific heat capacity, α_T is the isobaric thermal expansion coefficient, $\left(\frac{\partial c}{\partial P}\right)_T$ and $\left(\frac{\partial c}{\partial T}\right)_P$ are change in speed of sound with pressure at constant temperature and change in speed of sound with temperature at constant pressure respectively. The first term $2\rho_0 c_0\left(\frac{\partial c}{\partial P}\right)_T$ represents on isothermal pressure changes and the second term $\frac{2\alpha_T c_0 T_0}{c_P}\left(\frac{\partial c}{\partial T}\right)_P$ is based on isobaric temperature changes. As $\frac{B}{A}$ is a function of temperature, the non-linear parameter β is temperature dependent.

2.7. Ultrasonic non-collinear wave mixing

Non-collinear wave mixing is based on the interaction between two or more sound waves which intersect at a certain angle. Elastic waves with different resonant frequencies when propagating through a medium may interact and produce secondary waves of mixed frequencies. The interaction of sound waves can be either longitudinal wave interactions, shear wave interactions or a combination of both. The mixed resonant frequency can be the sum or difference of the frequencies of the interacting waves [61].

The theory of non-collinear wave mixing has been researched upon through years [62]. In the year 1963, Jones and Kobett et al [63] performed an investigation of the principle of scattering of two intersecting plane waves in a homogeneous isotropic medium. This approach was based on the non-linear elasticity theory. In the year 1964, Taylor and Rollins et al [64] investigated the resonance conditions for five different combinations of interactions of sound waves and derived displacement amplitude of the generated wave for each case of interactions. Rollins et al [65] in the same year, produced experimental proof for the proposed theory by observing the generation of a third longitudinal wave from interaction of two planar shear waves under sufficient resonant conditions. He concluded that in some nonlinear wave mixing cases, the amplitude of the generated wave from the interaction of two planar waves can be used to evaluate third order elastic constants of the test material. Therefore, the non-linearity of the material can be examined from the determination of the amplitude of the generated wave from a non-collinear wave mixing interaction. Even though most of the fundamental theories of non-collinear wave interactions were developed in the sixties, Korneev et al [66] recently derived the equations to determine scattering coefficients for all possible nonlinear interactions in a more generalised analytical form for non-destructive evaluation of materials. The equations from Jones and Kobett et al [63] are used in this thesis to explain the analytical theory of non-collinear shear wave mixing.

Two vertically polarized shear waves interact to generate a longitudinal wave under certain resonant conditions. The generated wave has a resonant frequency equal to the sum of the resonant frequencies of the interacting shear waves. Similarly, the wave vector of the generated longitudinal wave is the sum of the wave vectors of the interacting shear waves.

$$\omega_3 = \omega_1 + \omega_2 \tag{2.11}$$

$$\boldsymbol{k}_3 = \boldsymbol{k}_1 + \boldsymbol{k}_2 \tag{2.12}$$

Where ω_i and $\boldsymbol{k}_i$ represent the resonant frequencies and wave vectors of the interacting shear waves i.e. $i = 1, 2$ and of the generated longitudinal wave i.e. $i = 3$. Figure 8 shows the schematic representation of the shear wave interaction taking place, generating a longitudinal wave.

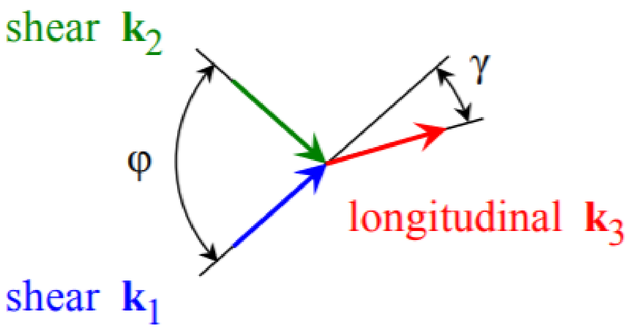


Figure 8: Non-collinear interaction of two shear waves generating a longitudinal wave [60]

φ is the interaction angle between the two incident shear waves and γ is the angle of propagation of the generated wave with respect to the incident shear wave. The numerical value of the interaction angle φ can be found as shown.

$$\left(\frac{\omega_3}{V_L}\right)^2 = \left(\frac{\omega_1}{V_S}\right)^2 + \left(\frac{\omega_2}{V_S}\right)^2 \pm \frac{2\omega_1\omega_2}{(V_S)^2}\cos\varphi \tag{2.13}$$

V_L and V_S represent longitudinal wave and shear wave velocity in the medium respectively. The condition $-1 \le \cos\varphi \le 1$ along with (2.11) and (2.12) must be satisfied such that the non collinear wave interaction occurs. The angle of propagatioin γ of generated longitudinal wave with respect to incident shear wave is defined below.

$$\tan \gamma = \pm \frac{\frac{v_S}{v_S} a \sin \varphi}{1 + \frac{v_S}{v_S} a \cos \varphi} \quad (2.14)$$

The ratio of the two resonant frequencies of the interaction waves $\frac{\omega_2}{\omega_1}$ is denoted by a. The angle of propagation Υ is obtained by simplifying (2.14).

$$\gamma = \tan^{-1}\left(\pm \frac{a \sin \varphi}{1 \pm a \cos \varphi}\right) \quad (2.15)$$

Consider the interaction of two plane waves with wave vectors $\boldsymbol{k_1}$ and $\boldsymbol{k_2}$ in a volume V of a non-linear elastic material (see Figure 9).

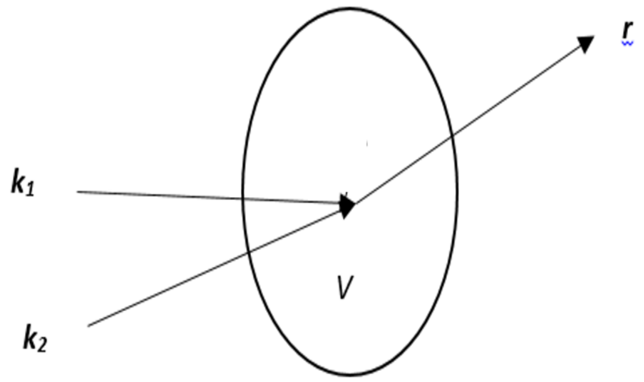


Figure 9: Interaction of two plane waves in a volume V of a non-linear elastic material

The radius vector of the interaction region is denoted by $\boldsymbol{r}$ inside the volume V.

The interaction of two elastic waves in an isotropic solid are represented as the sum of two incident plane waves as shown below [63, 64, 61].

$$\boldsymbol{u} = A_1 \cos(\omega_1 t - \boldsymbol{k_1 r})\, \boldsymbol{a_1} + A_2 \cos(\omega_2 t - \boldsymbol{k_2 r})\boldsymbol{a_2} \quad (2.16)$$

The displacement vector $\boldsymbol{u}$ in an elastic material that is continuous with its spatial derivatives is given below.

$$\boldsymbol{u} = \boldsymbol{u}(x, y, z) = \boldsymbol{u}(x_1, x_2, x_3) = \big(u_1(x_1, x_2, x_3), u_2(x_1, x_2, x_3), u_3(x_1, x_2, x_3)\big) \quad (2.17)$$

The position coordinates are represented by variables x, y, z.

As the non-linear behaviour of the isotropic elastic medium is taken into account during the non-collinear mixing of ultrasonic waves, the addition of third order non-linear elastic constants (TOE) l, m

$$A = n, B = m - \frac{n}{2}, C = l - m + \frac{n}{2} \tag{2.18}$$

Both the linear and non-linear parameters are incorporated in the study of non-collinear wave mixing using constants $C_1,\ C_2, C_3, C_4$ and C_5.

$$C_1 = \mu + \frac{A}{4}, C_2 = \lambda + \mu + \frac{A}{4} + B, C_3 = \frac{A}{4} + B, C_4 = B + 2C, C_5 = \lambda + B \tag{2.19}$$

If the resonant conditions (2.11) and (2.12) are satisfied for the interaction between two elastic planar waves, then the solution of acoustic energy distribution at a distance from the interaction volume (scattered field) is given below.

$$\boldsymbol{u}(r,t) = \boldsymbol{a}_{\boldsymbol{g}}^{\xi} W_g^{\xi} \frac{A_1 A_2}{r} V_g^{\xi} \tag{2.20}$$

$\xi =' + '$indicates the interaction where the pump wave frequencies are summed up and $\xi =' - '$indicates the interaction where the pump wave frequencies are subtracted. The amplitude coefficient of the generated wave W_g^{ξ} is given below

$$W_g^{\xi} = \frac{\left(I^{\xi} \boldsymbol{a}_{\boldsymbol{g}}^{\xi}\right)}{4\pi V_g^{\xi} \mathrm{p}} \tag{2.21}$$

$\boldsymbol{a}_g^{\xi}$ is the unit vector of the natural polarization of a wave, p is the density of the material and V_g^{ξ} is the volume of the material. The value of $\boldsymbol{I}^{\xi}$ is a function of the non-linear parameters A and B defined below.

$$
\begin{aligned}
\boldsymbol{I}^{\pm} = \frac{1}{2}C_1 & \begin{bmatrix} (\mathbf{a_1 a_2})(k_2^2\mathbf{k_1} \pm k_1^2\mathbf{k_2}) + (\mathbf{a_2 k_1})k_2(k_2 \pm 2k_1\cos\alpha)\mathbf{a_1} \\ +(\mathbf{a_1 k_2})k_1(2k_2\cos\alpha \pm k_1)\mathbf{a_2} \end{bmatrix} \\
& + \frac{1}{2}C_2 k_1 k_2 \cos\alpha[(\mathbf{a_1 a_2})(\mathbf{k_2} \pm \mathbf{k_1}) + (\mathbf{a_2 k_2})\mathbf{a_1} \pm (\mathbf{a_1 k_1})\mathbf{a_2}] \\
& + \frac{1}{2}C_3\big[(\mathbf{a_1 k_2})\big((\mathbf{a_2 k_2}) \pm (\mathbf{a_2 k_1})\big)\mathbf{k}_1 + (\mathbf{a_2 k_1})\big((\mathbf{a_1 k_2}) \pm (\mathbf{a_1 k_2})\big)\mathbf{k_2}\big] \\
& + \frac{1}{2}C_4(\mathbf{a_2 k_2})[(\mathbf{a_1 k_2})\mathbf{k_2} \pm (\mathbf{a_1 k_1})\mathbf{k_1}] \\
& + \frac{1}{2}C_5[(\mathbf{a_1 k_1})k_2^2\mathbf{a_2} \pm (\mathbf{a_2 k_2})k_1^2\mathbf{a_1}] \qquad (2.22)
\end{aligned}
$$

The non-bolded variables denote their scalar value and the variables in bold denote their vectors. From (2.21), it is known that the amplitude of the generated wave is a function of the density of the material, second order linear elastic constants (λ and μ) and the third order non-linear constants (A, B and C).

2.8. Non collinear wave mixing configuration

When sound waves hit the interface of two materials i.e. water and PVC, a fraction of the waves is reflected from the front surface of PVC while some fraction of it passes through, where it can be absorbed into the material or transmitted through the material. The difference in the acoustic impedance of the two materials is the reason why reflection of sound waves at the interface of the two materials, takes place. The difference in sound velocities in the two materials is the reason of transmission of signals through the interface of the two materials [69].

Non-collinear wave mixing in PVC was previously studied in a configuration where the receiver was fixed on the opposite side of the transducers sending the shear pump waves [70]. This configuration was preferred because the signal level of the ultrasonic waves that are transmitted through the back wall of the PVC sample is high. Therefore, the receiver can capture the generated wave that is transmitted through the back wall at high energies. In this context, the configuration is referred to as the double-sided access configuration because access to both sides of the PVC material is required.

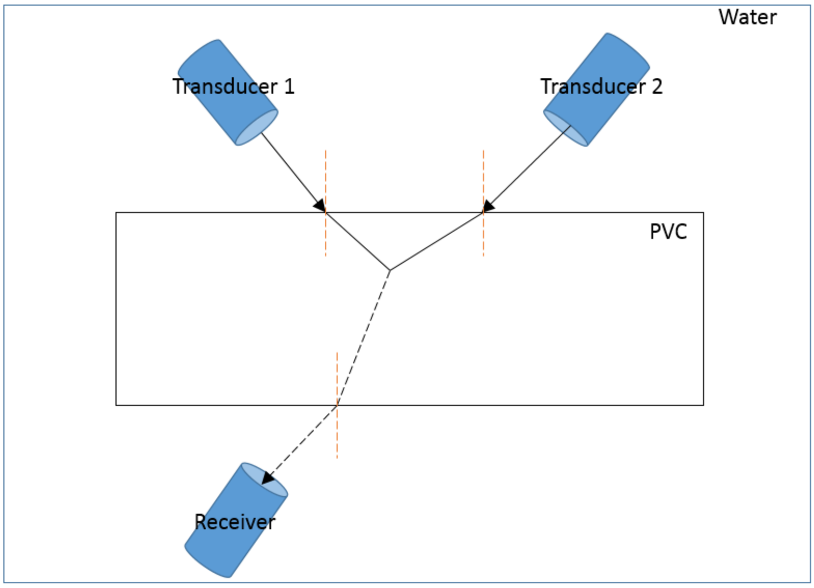


Figure 10: Propagation of signals in double-sided access configuration

Figure 10 shows the pathway of the generated wave in the double-sided access configuration. The shear pump waves (black solid line) interact at a certain depth inside the PVC material to produce the generated wave. The generated wave propagates through the material and hits its back wall. A portion of the generated wave is transmitted through the back wall and recorded by the receiver.

However, only single-sided access of the test material is possible during inspections conducted in industries. Therefore, another configuration in which the receiver is fixed on the same side of the transducers sending the pump waves is examined in this research. In this context, the configuration is referred to as the single-sided access configuration as only one side of the test material need to be accessed.

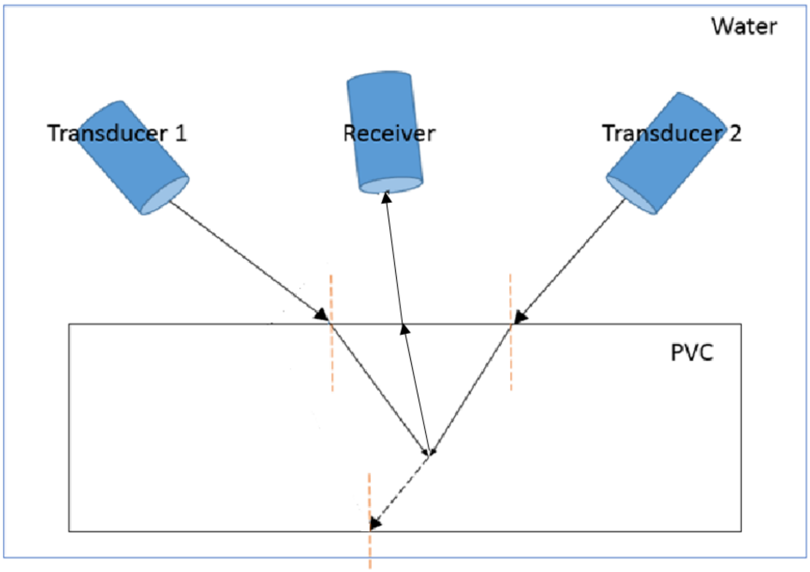


Figure 11: Propagation of signals in single-sided access configuration

Figure 11 shows the pathway of the generated wave in the single-sided access configuration. The shear pump waves interact at a certain depth inside the PVC material to produce the generated wave. The reflected generated wave from the back wall of the material propagates through it and hits its front wall. The portion of the wave that is transmitted through the front wall, is recorded by the receiver. Due to the reflection from the back wall, the amplitude of the generated wave diminishes with distance travelled inside the PVC material until reaching the receiver.

2.9. Signal processing- Frequency and time domain

The analysis of signals is done in two ways, i.e. frequency- domain analysis and time-domain analysis. These forms of analysis are important tools used in signal processing applications. The frequency domain analysis shows how the energy of signals is distributed over a range of frequencies and the time-domain analysis represents the manner in which a signal changes over time [71]. A signal can be converted from the time domain to its frequency domain using a mathematical operator called transform. The transform used in the analysis of the signals obtained is Fourier transform, which decomposes a function with infinite number of sine wave frequency components, into its sum.

When the interacting waves are excited simultaneously with a similar time delay, their wave fronts combine in the interaction zone in the time domain. This is due to the fact that the two primary waves reach and leave the interaction zone at the same time. As the frequencies of the two primary waves are different, the generated wave front exhibits a different shape compared to the response caused by a single frequency component. The amplitudes of both primary signals and the response signal are extracted in MATLAB software.

3. Research Objective

The non-linear behavior of the material have to be take into account during the detection of ageing, as the later phenomenon causes change in its non-linear properties. Linear ultrasonic measurements do not provide any information about the non-linear behavior of the material. The non-collinear wave mixing technique is found to be sensitive towards the phenomenon of ageing, and the wave interaction used is given below.

$$Longitudinal\ wave(\omega_1) + Shear\ wave(\omega_2) = Longitudinal\ wave(\omega_1 + \omega_2)$$

The receiver was placed on the opposite side of the two transducers sending the pump waves due to a high signal to noise ratio of the generated wave. The transducers sending the pump waves have to be inclined at short angles to produce only longitudinal waves inside the test material. If a shear wave has to be generated inside the test material, the transducers sending the pump waves should be inclined at larger angles. For the interaction above, the transducer sending the longitudinal pump wave was inclined at an angle of 32^0 and the transducer sending the shear pump wave was inclined at angle of 53^0 [70]. The distance between the two transducers was 55 mm. Therefore, if the single-sided access configuration is considered for this interaction, it is quite difficult to place the receiver in between the small gap between the two transducers sending the pump waves.

Therefore, the interaction between two shear waves was considered, as the transducers sending the pump waves have to be inclined at larger angles to generate shear waves inside the test material. This would create a larger gap between the transducers such that, the receiver can be placed in between them, on the same side. The interaction used for the detection of ageing is given below.

$$Shear\ wave(\omega_1) + Shear\ wave(\omega_2) = Longitudinal\ wave(\omega_1 + \omega_2)$$

Using the interaction between two shear waves producing a longitudinal wave, the non-collinear wave mixing technique using both double-sided access and single-sided access configuration can be examined. The amplitudes of the shear pump waves and the generated longitudinal wave are compared between both the configurations.

The research objectives can be summarised as follows.

1. Detection of ageing in PVC pipe with the non-collinear wave mixing principle. The interaction chosen is given below.

   $$Shear\ wave(\omega_1) + Shear\ wave(\omega_2) = Longitudinal\ wave(\omega_1 + \omega_2)$$

2. Determination the response of the generated wave at early degradation levels.
3. Determination of the difference in the amplitudes between single-sided access configuration and double-sided access configuration.

The PVC samples used for the non-collinear wave mixing experiments were assumed to be from a healthy pipe at pristine state conditions. Later on, there was an ambiguity about the fact that if the samples were from a healthy pipe. Therefore, another set of PVC samples were rejuvenated to erase any previously built stresses inside the material. The rejuvenated samples were used to examine the response of the generated wave with temperature, to see if they exhibit a trend. The rejuvenated samples should have been used to examine the ageing phenomenon in PVC, however, this could not be performed due to time limitations. Therefore, a fourth objective was created.

4. Examination of the temperature dependency of the generated longitudinal wave after rejuvenation.

4. Materials and methods

In order to physically age the PVC samples, accelerated method of ageing of PVC was performed by annealing the samples. PVC samples were annealed at a temperature of 65^0C below its glass transition temperature (80ºC) at different time intervals. However, these samples were not rejuvenated before annealing, as the samples were assumed to be healthy in its pristine conditions. Later, when there was ambiguity about the fact that if the samples were healthy, another set of PVC samples were rejuvenated by heat treatment above glass transition temperature and immediately quenching in antifreeze (-10ºC) .The two methods of annealing and rejuvenation have been described in detail in the following sections.

4.1. Accelerated ageing of PVC by annealing

As the procedure followed contains a series of steps starting from sample preparation to measuring amplitude variations, it is explained in the following sections, each representing a step followed.

4.1.1. Sample Preparation

An off-white cylindrical pipe made of PVC of approximately 5mm thickness, was taken and cut into small rectangular pieces. The length and width of all the samples were not exactly the same due to certain irregularities formed while being cut. The average length and width of all samples was 105 mm and 55 mm respectively. The PVC pipe used may contain certain amount of plasticizers since the manufacturing details of the pipe are unknown. It was observed that the thickness of each PVC sample had small variations compared to each other. This can be due to the non-uniform thickness of the cylindrical pipe from which the samples were cut. The non-uniformity in the thickness of the pipe can be due to its manufacturing inaccuracies.

As the non-collinear wave mixing technique involves the propagation of shear and longitudinal waves within the PVC material, the shear and longitudinal speeds of sound inside the PVC samples were determined. The longitudinal and shear speeds were measured in nine PVC samples. To determine the two wave velocities inside the PVC material, the technique of immersion ultrasonics was used. The transducer along with the test piece was kept inside a water bath at room temperature (22ºC). Water was used as coupling medium between the transducer and PVC due to a small difference in acoustic impedances between the piezoelectric material of the transducer and water. Since there is a large difference in acoustic impedances between the piezoelectric material of the transducer and air, higher fraction of the acoustic waves gets reflected than getting transmitted through air. Therefore, the acoustic waves hitting the interface of the PVC material and air will be of low energies. Even if the face of the transducer is kept on the surface of the PVC material, there is still some air in between them. Therefore, a medium which has an acoustic impedance close to that of the transducer is used to transmit acoustic waves of high energy through it, such as water or gel [72].

4.1.2. Measurement of longitudinal wave velocity

Longitudinal wave velocity was estimated using an immersion pulse-echo setup which makes use of the reflections from the surface of the test sample. A transducer of 1MHz central frequency is fixed perpendicular to the surface of the sample. The amplitude peaks of the front wall and back wall were extracted and the time difference of recording the peaks was measured. As the thickness d of the sample is known, the longitudinal wave velocity v was calculated using (4.1).

$$v = \frac{2d}{t_b - t_f} \tag{4.1}$$

Where t_b and t_f are the time intervals at which the back wall and front wall peaks were obtained, respectively.

4.1.3. Measurement of shear wave velocity

The shear speed of sound was calculated using a setup that included two transducers of central frequency 1MHz each. One transducer was used to generate the shear pump wave inside the PVC material and the second transducer was used to record the reflections of the shear pump wave from the back wall of the PVC sample. The procedure followed is explained and illustrated below.

A broadband transducer of 1MHz central frequency was kept at a fixed height of 22.75 mm from the PVC sample (see Figure 11). The transducer was aligned to surface of the sample at an angle of 45^0 such that only the shear component of the wave propagates through the material. The transducer was driven by a burst of 2 cycles of pulses with a frequency f_1 of 1MHz and an amplitude of 100 mV (before amplification). The shear wave component travelling along the sample was reflected by the back wall of the sample. The reflections were recorded by a second transducer, of similar central frequency, positioned at the same angle and height from the sample as that of the transducer sending the pump wave. The distance of the receiver from the transducer sending the shear pump wave was fixed such that it records maximum amplitude of the reflected shear wave.

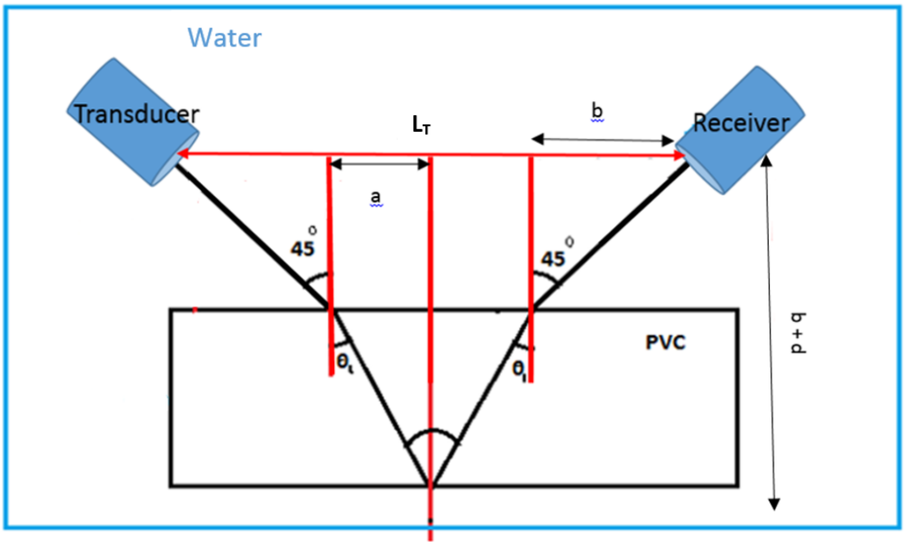


Figure 11: Measurement of shear velocity of sound waves in a PVC sample

Speed of sound in water at room temperature is taken as $v_1 = 1490$ m/s [73]. Shear speed of sound in the PVC sample which is to be estimated is denoted by v_2. In Figure 11, θ_1 is the angle of refraction of sound waves inside the PVC material. The thickness of the sample is d. The distance between the two transducers is L_T. The calculation steps of the shear wave velocity in PVC is shown below.

1) The distance between the transducers L_T is measured.
2) The height of the sensors from the sample is fixed. As the angle of incidence is 45^0, the height of the sensors is equal to the distance b.
3) The distance a is calculated from the geometry as shown.

$$a = \frac{L_T - 2b}{2} \tag{4.2}$$

4) The refraction angle θ_1 is calculated as shown.

$$\theta_1 = \tan^{-1}\left(\frac{a}{d}\right) \tag{4.3}$$

5) As the speed of sound in water v_1 at 22^{0}C is known, along with the angle of incidence 45^0 and refraction θ_1, the speed of sound in PVC is calculated using Snell's law (2.1).

Using similar procedure, longitudinal and shear speeds of sound of 6 specimens were calculated and tabulated in Table 2 (Appendix). After averaging, the longitudinal wave velocity in PVC is 2302.57 m/s with a standard deviation of 30.3 m/s and the shear wave velocity is 1456.66 m/s with a standard deviation of 77.23 m/s.

4.1.4. Non-collinear wave mixing for shear-shear wave interaction

The wave interaction used is $S(\omega_1) + S(\omega_2) = L(\omega_1 + \omega_2)$ where S represents shear pump waves, L represents the generated longitudinal waves, ω_1 and ω_2 are the resonant frequencies of the shear pump waves. Amplitude coefficient of the generated wave W_g^{ξ} along with the interaction φ and scattering γ angle for the shear wave interaction is shown in Figure 12, as functions of the frequency ratio a [70]. It is seen that the amplitude of the generated wave has a peak corresponding to a frequency ratio of 1.5. Therefore, the frequency ratio of the shear pump waves was taken as 1.5 for obtaining maximum amplitude of generated longitudinal signal.

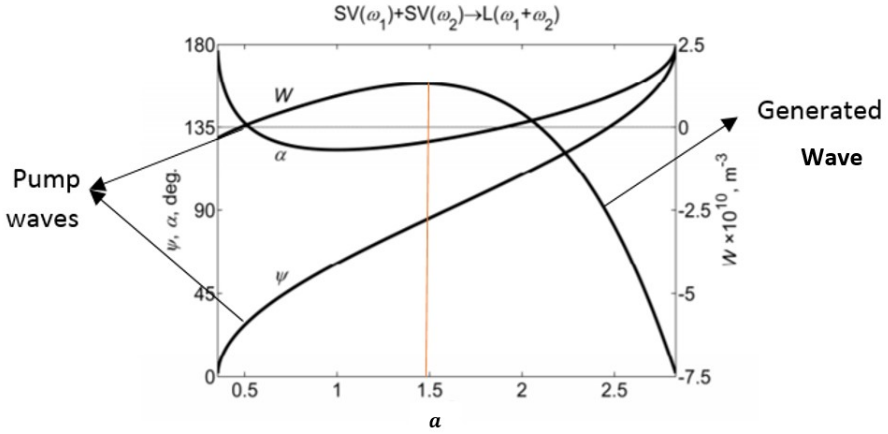


Figure 12: a value for the interaction SV(w1)+SV(w2)=L(w1+w2) [70]

Two broadband transducers of 1MHz central frequency each, driven by a burst of 30 cycles of pulses of frequencies f_1 and f_2 1.110 MHz and 0.74 MHz respectively, and 80 mV amplitude (before amplification), were used. The frequencies f_1 and f_2 were chosen such that, the frequency ratio a equals 1.5. The transducers were kept at a fixed height of 42.4 mm such that acoustic waves (sine waves) were incident at an angle of 45° on the front surface of the sample such that only shear waves propagated through the PVC material. The receiver used was a broadband transducer of 2.25 MHz central frequency as this frequency is close to the sum of the central frequencies of the transducers sending the shear pump waves. The three transducers along with the sample were kept inside a water bath at room temperature (22°C).

The transducers were kept at a height h from the sample surface. The refracted angles of sound waves within the PVC material from each transducer were taken as θ_{R1} and θ_{R2} respectively. The shear component of sound interacted at a certain point inside the sample of thickness d. It was assumed that the interaction took place at a depth p inside the sample (see Figure 13).

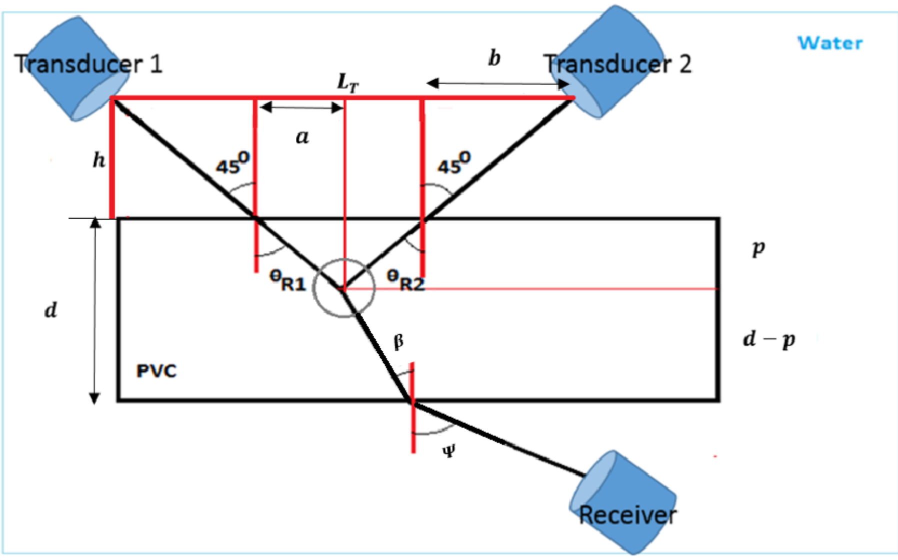


Figure 13: Experimental set up for non-collinear shear wave mixing

The following steps demonstrate the calculation of the distance and the angle at which the receiver has to be fixed with respect to the PVC sample in the non-collinear wave mixing setup.

1) In order to calculate the interaction angle of the two shear waves, the excitation frequencies of the transducers f_1 and f_2 in Hertz were converted to radians per second, ω_1 and ω_2 using (4.4).

$$\omega = 2\pi f$$

(4.4)

2) As per the interaction, the resonant frequency of the generated longitudinal signal is the sum of the resonant frequencies of the incident shear waves.

$$\omega_g = \omega_1 + \omega_2 \tag{4.5}$$

3) Using the resonant frequency of the generated longitudinal wave (4.5) along with the longitudinal and shear speeds of sound, the interaction angle φ of the shear pump waves was calculated using (2.13).

4) The propagation angle γ of the generated wave was calculated using (2.15).

5) Since the angle of incidence of the shear pump waves were known along with the shear wave velocity, the refraction angles θ_{R1} and θ_{R2} in the PVC sample were calculated using Snell's law (2.1).

6) From Figure 13, the interaction angle φ is the sum of refraction angles θ_{R1} and θ_{R2}.

7) Using the values of θ_{R1}, θ_{R2}, the distance a is calculated from (4.6).

$$\theta_{R1} = \tan^{-1}\left(\frac{a}{p}\right) \quad , \theta_{R2} = \tan^{-1}\left(\frac{a}{p}\right) \tag{4.6}$$

8) Since the incidence angle is 45^0, the distance b is the height h of transducers from the PVC sample.

9) The distance between the transducers sending the shear pump waves can be estimated using (4.7).

$$L_T = 2a + 2b \tag{4.7}$$

10) From the calculated values of θ_{R1}, θ_{R2} and the propagation angle Υ, the angle β at which the generated longitudinal wave hits the back wall of the sample was estimated using (4.8).

$$\beta = \theta_{R1} - \Upsilon \tag{4.8}$$

11) Using Snell's law, the angle Ψ at which the generated longitudinal wave is transmitted through the back wall of the sample was calculated.

Figure 14 demonstrates the experimental set up in which the receiver is fixed on the opposite side of the two transducers sending the shear pump waves with respect to the PVC sample. Since acoustic waves are transmitted through both the sides of the PVC sample, this type of configuration is called double sided access configuration.

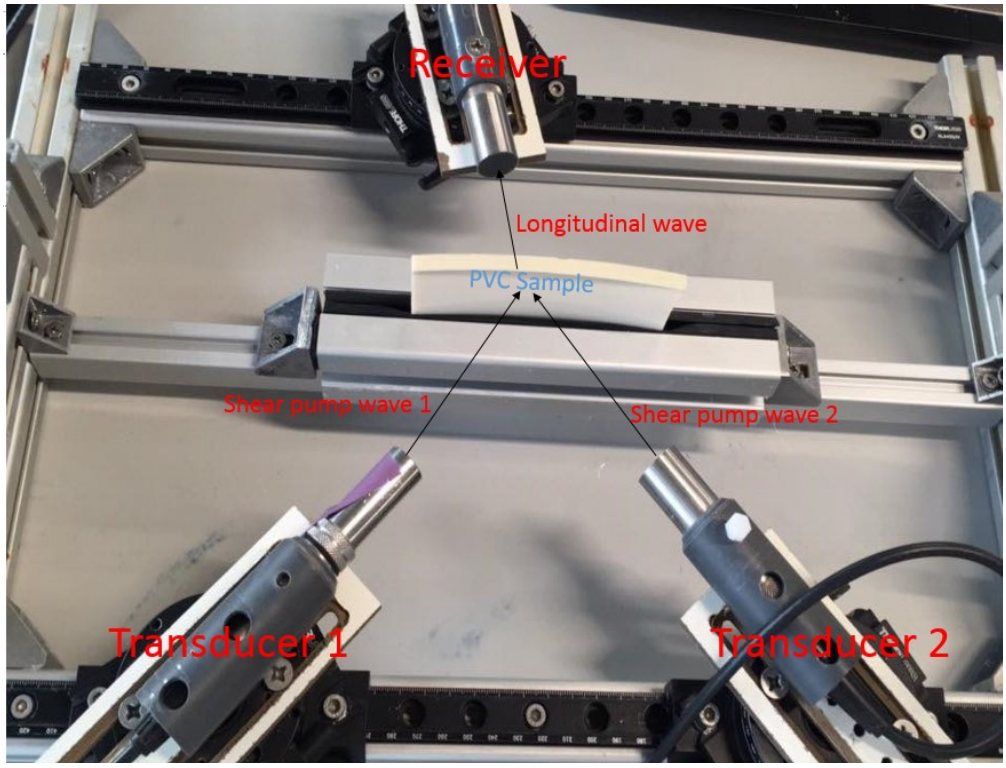


Figure 14: Configuration in which receiver is placed in the opposite side of the transducers sending shear pump waves(Double sided access)

Figure 15 demonstrates the experimental set up in which the receiver is fixed on the same side of the transducers sending the shear pump waves with respect to the PVC sample. Since acoustic waves are transmitted through only one side of the PVC sample, this type of configuration is called single sided access configuration.

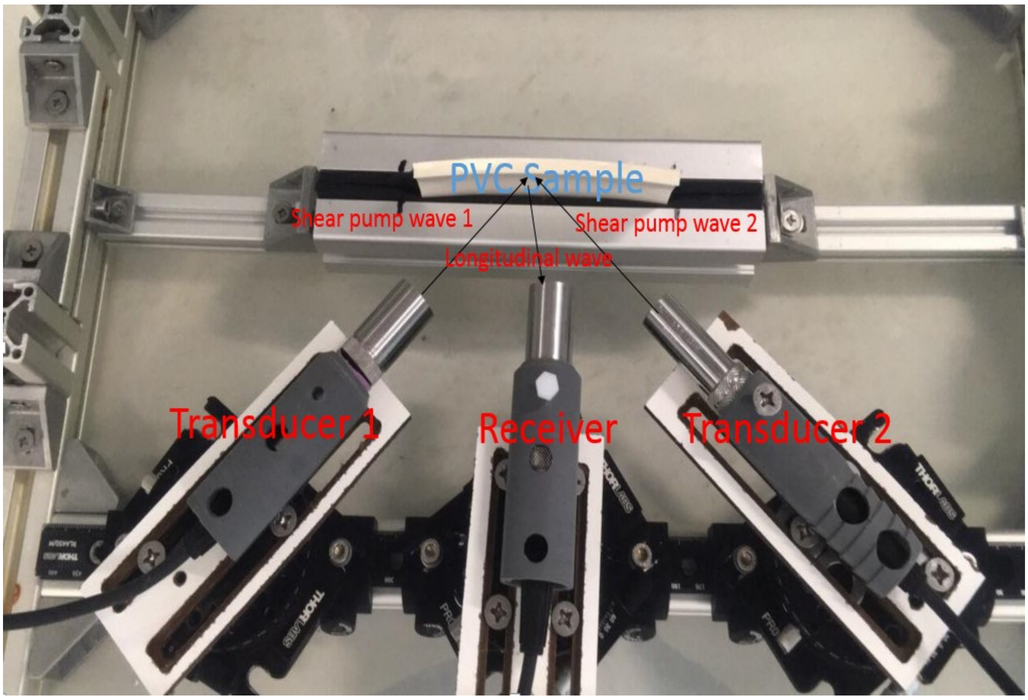


Figure 15: Configuration in which receiver is placed on the same side of the transducers sending pump waves (Single sided access)

It is to be noted that the angle Ψ at which the generated longitudinal wave is transmitted through the sample remains the same at both the front wall and the back wall. Therefore, the angle of inclination of the receiver with respect to the surface of the PVC sample is the same in both configurations.

Table 1 summarises the test parameters used for non-collinear shear wave mixing experiments.

Table 1: Ultrasonic wave parameters

f_1 (MHz)	N_1 (cycles)	f_2 (KHz)	N_2 (cycles)	f_R (MHz)	Θ_1 (deg.)	Θ_2 (deg.)	$z_1 \pm \Delta z_1$ (mm)	$z_2 \pm \Delta z_2$ (mm)	$z \pm \Delta z$ (mm)	$x \pm \Delta x$ (mm)
0.74	40	1.11	40	1.85	45	45	42.4±0.46	42.4±0.46	60.0±1.72	92.45±0.56

f_1 and f_2 are excitation frequencies of the pump waves by sensors S_1 and S_2 respectively. N_1 and N_2 are the number of cycles used for pump wave generation. Inclination angles of the transducers producing shear pump waves are θ_1 and θ_2 and the vertical height of the transducers from the sample are z_1 and z_2 respectively. Δz_1 and Δz_2 represent their respective standard deviations. The distance of the receiver from the sample is denoted by z and the distance between two transducers producing the pump waves is denoted by x. Their respective standard deviations are represented by Δz and Δx respectively. Non-collinear shear wave mixing was performed on the twelve PVC samples and the amplitudes of shear wave 1, shear wave 2 and that of the generated longitudinal wave were recorded in time.

4.1.5. Non-collinear shear wave mixing- Experimental Procedure

The steps below describe the procedure followed for carrying out the non-collinear wave mixing experiment of the PVC samples.

1) A set of twelve samples of PVC are taken for the non-collinear wave mixing experiments to study the interaction of two shear waves. These twelve samples are used for experiments in both single sided and double sided access configurations.
2) The non-collinear wave mixing experiment is carried out for the twelve samples at five different points per sample. Each point recorded in a sample had 32 amplitude measurements which were averaged. Then the five averaged amplitude values recorded at five points were further averaged. The three amplitudes i.e. amplitudes of shear pump wave 1, shear pump wave 2 and that of the generated longitudinal wave were recorded in time.
3) To anneal the samples, they were put in oven UNB-200 (see Figure 16) at a temperature of 65^{o}C for a time interval of eight hours. The samples were expected to be uniformly heated due to circulation of hot air inside the oven by the air turbine.

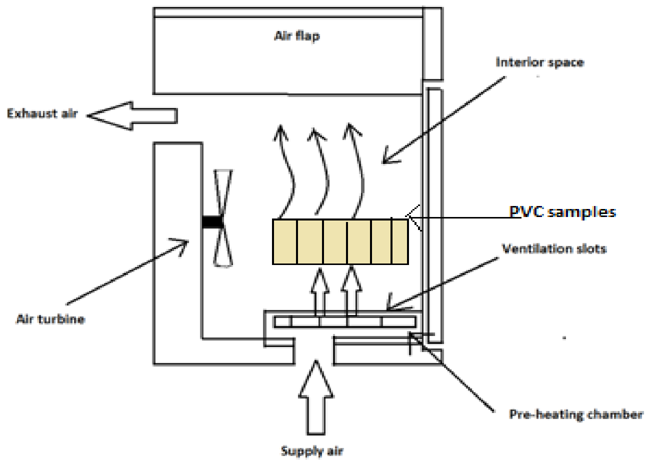


Figure 16: Oven (UNB-200) used for annealing samples

4) After annealing, the samples were taken out and kept aside so that they cool down to room temperature. Ultrasonic non-collinear wave mixing technique was performed on each of the samples at five different points per sample. The three amplitudes i.e. amplitudes of shear wave 1, shear wave 2 and that of the generated longitudinal wave were recorded in time.
5) One sample from the set of twelve is not annealed further since it is used as a benchmark for samples annealed for eight hours. The remaining eleven samples were annealed for another time interval of sixteen hours. After annealing, the samples were kept aside until they cool down to room temperature and the three above mentioned amplitudes were measured at five different points per sample and averaged.
6) This process was repeated for annealing time intervals of twenty-four hours, thirty-two hours and forty hours. The three amplitudes were measured at each time of annealing and the amplitude difference at each time of annealing with respect to the amplitude before annealing, was plotted against annealing time.

4.2. Rejuvenation of PVC by heat treatment and quenching

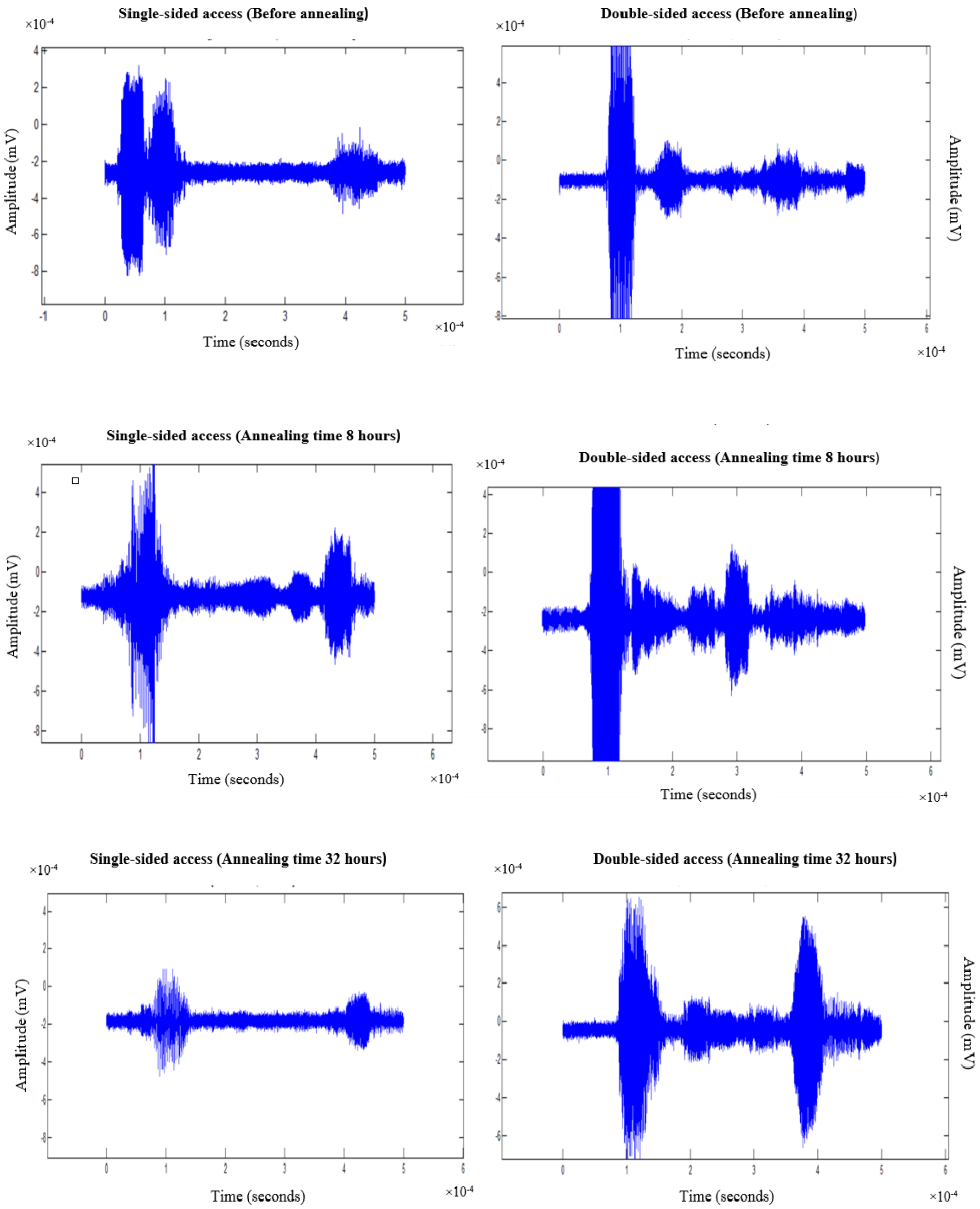
As there was ambiguity about the fact that if the samples used before annealing were at their pristine state or not, the samples were subjected to rejuvenation. Due to time limitations, only two PVC samples were rejuvenated. The samples were rejuvenated by first heating them at a temperature of 100^0C and then immediately quenching them in an anti-freeze solution at a temperature of -10^{o}C. The heating above glass transition temperature (80^{0}C) erases the previously built stresses inside the PVC material [74]. It was then placed in a water bath at room temperature (22^{o}C), where the non-collinear wave mixing technique was performed. The configuration used for the experiments was one in which the receiver along with the two transducers sending the pump waves are all placed on the same side of the PVC sample (single-sided access) . The amplitudes of the generated longitudinal wave was recorded at one point in the sample, with a sampling rate of two minutes. A short time interval was chosen in order to observe how the amplitude of the generated wave changes with temperature within a short period of time after rejuvenation. The ultrasonic test parameters used in this experiment were the same parameters used in the annealing experiment (Table 1 in Section 1).

5. Results and discussion

This section describes the results obtained from the non-collinear wave mixing tests for two sets of PVC samples, i.e. after annealing and rejuvenation. Section 5.1 describes the time domain and frequency domain signals of the amplitudes of the reflections of the two shear pump waves and the generated longitudinal wave for both the double sided access and single sided access configurations. The amplitude difference of the shear pump wave reflections from the PVC samples at a particular annealing time with respect to its amplitude before annealing, is plotted against the time intervals of annealing for both the configurations. The amplitude difference of the generated longitudinal wave reflection at a particular annealing time with respect to its amplitude before annealing is also plotted against the time intervals of annealing. A comparison is made between the three amplitude differences with respect to annealing time for both the configurations. Section 5.2 describes the plot that shows the change in amplitude of the generated wave reflection with respect to time, immediately after rejuvenation of the PVC sample.

5.1. Accelerated ageing of PVC by annealing

A typical ultrasonic signal is composed of multiple modes and reflections with different frequencies. From the results of the non-collinear wave mixing tests of PVC, the reflections of the two shear pump waves and the generated longitudinal wave, from the front wall and back wall are rarely well separated in time (see Figure 17). Therefore, it becomes highly problematic to extract their respective amplitudes.



Single-sided access (Before annealing)
Double-sided access (Before annealing)
Single-sided access (Annealing time 8 hours)
Double-sided access (Annealing time 8 hours)
Single-sided access (Annealing time 32 hours)
Double-sided access (Annealing time 32 hours)
Amplitude (mV)
Time (seconds)
×10-4

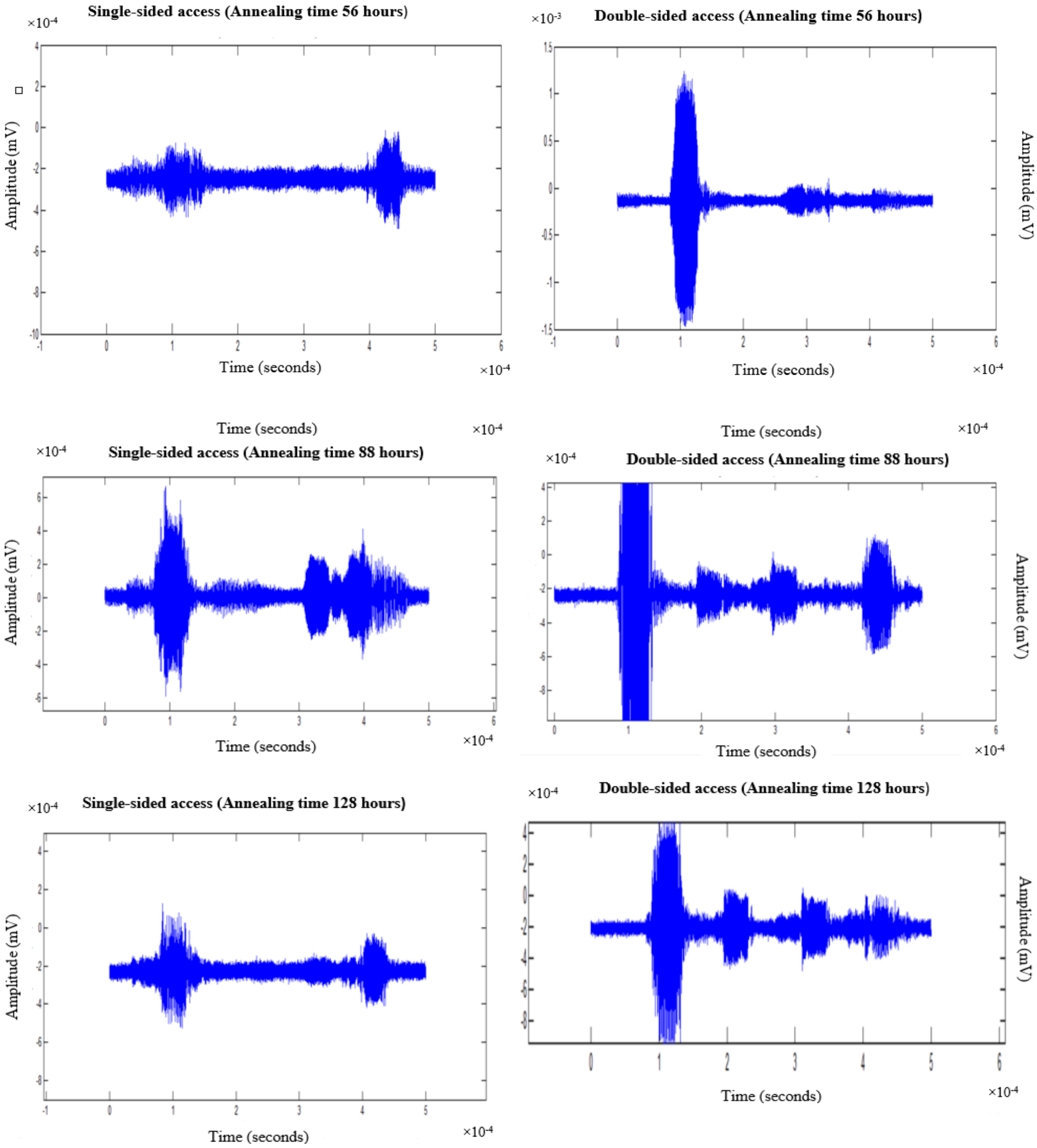
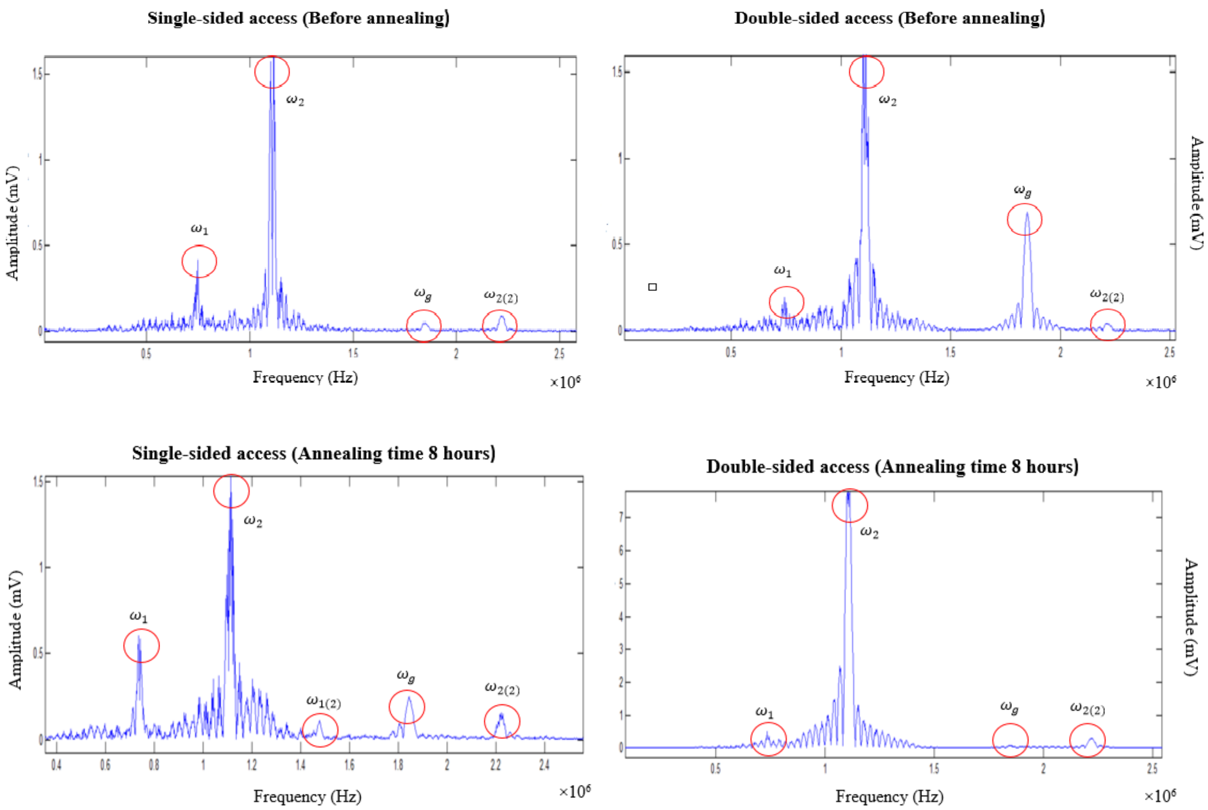


Figure 17: Time domain signals of one PVC sample in both single sided access and double sided access configuration

Figure 17 represents the time domain signals of one PVC sample at each time interval of annealing in both single sided access and double sided access configurations .The x-axis shows the time in seconds and y-axis shows the amplitudes in millivolts. The plots show certain time intervals in which the amplitudes show an increase. However, it is not possible to detect the separate amplitudes i.e. amplitude of the two shear pump waves and the generated wave, from the time domain plot. The reflections of the two shear pump waves and the generated wave superimpose each other and create an interference in the recorded signal because the signals are not well separated in time. The presence of noise in the recorded signals makes the extraction of the amplitudes of pump waves and the generated wave even more complex.

The amplitudes of the shear pump waves and the generated wave exists in their distinct frequencies and has to be filtered to extract them from the time domain. The fast Fourier transform (FFT) filter was used to extract the three amplitudes in their distinct frequencies.



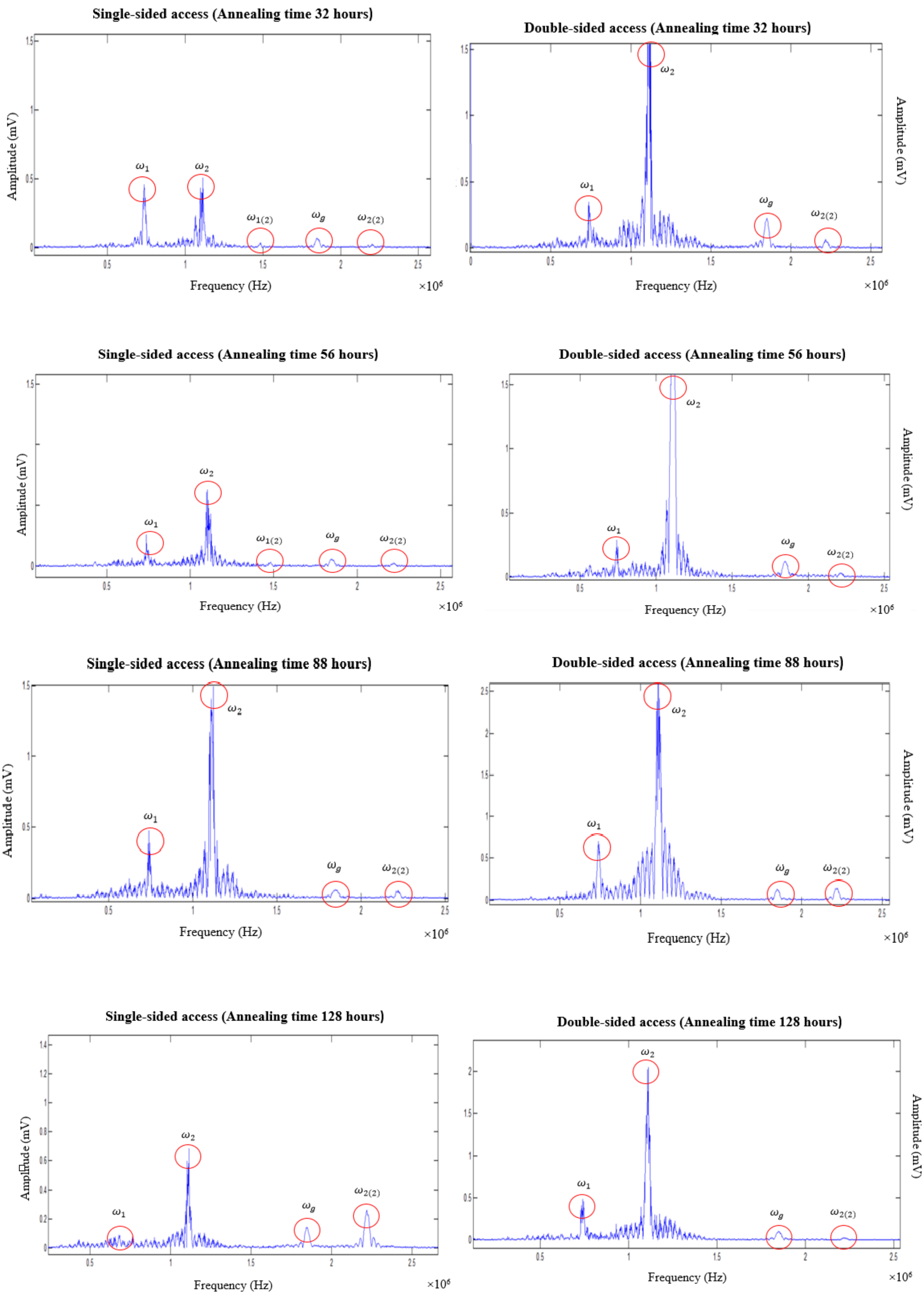


Figure 18: Frequency domain signals of one PVC sample for Single-sided access and double sided access configuration

Figure 18 shows the amplitude peaks of the reflections of shear pump waves 1 and 2 and the generated longitudinal wave at each annealing time, in both single sided and double sided access configurations, at their distinct frequencies. The x-axis shows the frequencies in Hertz and the y-axis shows the amplitudes in millivolts. ω_1 and ω_2 represent the frequencies of shear pump wave 1 and 2 at which their amplitude peaks are obtained where $\omega_1 = 0.74$ MHz and $\omega_2 = 1.11$ MHz respectively. ω_g represents the frequency of the generated longitudinal wave at which its amplitude peak is obtained and $\omega_g = \omega_1 + \omega_2$ = 1.85 MHz. $\omega_{1(2)}$ and $\omega_{2(2)}$ represent the frequencies at which the second harmonic of shear pump wave 1 and 2 is obtained. $\omega_{1(2)} = 2(\omega_1)$ = 1.48 MHz and $\omega_{2(2)} = 2(\omega_2)$ = 2.22 MHz.

As observed from the amplitude peaks of the generated wave in both the configurations, the amplitude of the generated wave is higher in the double sided access configuration when compared to its amplitude in the single sided access configuration. This is because the generated wave has to encounter only one interface i.e. the back wall, in the double sided access configuration whereas it has to encounter two interfaces i.e. the back wall and the front wall in the single sided access configuration, before reaching the receiver. The signal attenuates more when it travels a longer distance inside the material as its amplitude diminishes with the distance travelled. Therefore, the amplitude of the generated wave is higher in the double sided access configuration when compared to the single sided access configuration, as the signal travels a longer distance, in the later configuration.

5.1.1. Amplitude of shear pump wave reflections– Double sided and single sided access configurations

The amplitudes of the two shear pump wave reflections are extracted at each time interval of annealing. The change in amplitudes extracted at each time interval of annealing, with respect to its amplitudes extracted before annealing, is tabulated. This section shows the plots for two PVC samples and the general trend seen in all twelve samples are explained using these plots.

Figure 19 and 20 shows the relative amplitudes of the reflections of shear pump wave 1 and 2 with respect to its amplitude before annealing, for both double sided and single sided access configurations. The x-axis corresponds to the annealing time intervals in hours. The y-axis corresponds to the relative amplitudes in decibels (dB). V represents the amplitude of shear pump wave reflections in millivolts (mV) at a particular annealing time and V_0 represents the amplitude of shear pump wave reflections in millivolt (mV) before annealing. The amplitudes (A) in millivolts were converted to decibels as shown below.

$$A = 20log\left(\frac{V}{V_0}\right) \tag{5.1}$$

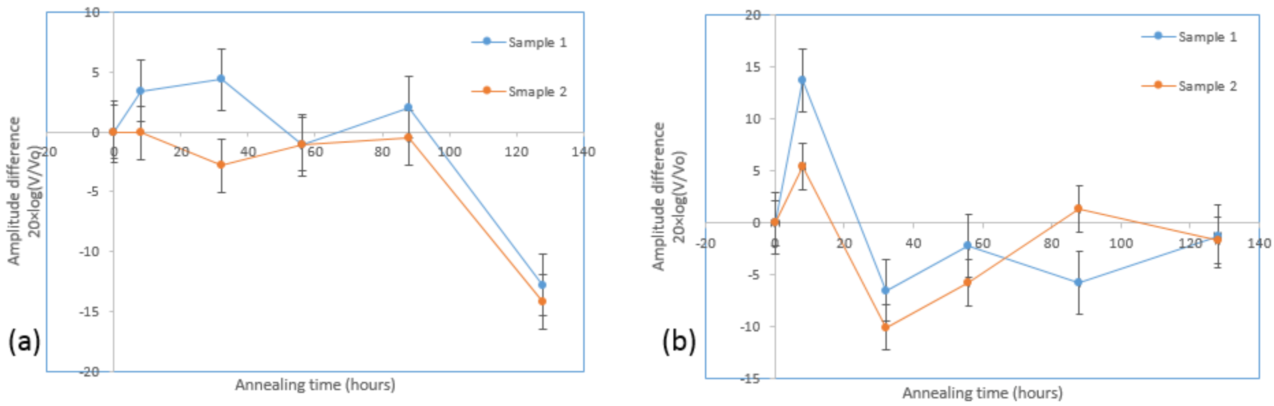


Figure 19: Single-sided configuration: (a) Amplitude change of shear pump wave 1 with respect to annealing time (b) Amplitude change of shear pump wave 2 with respect to annealing time

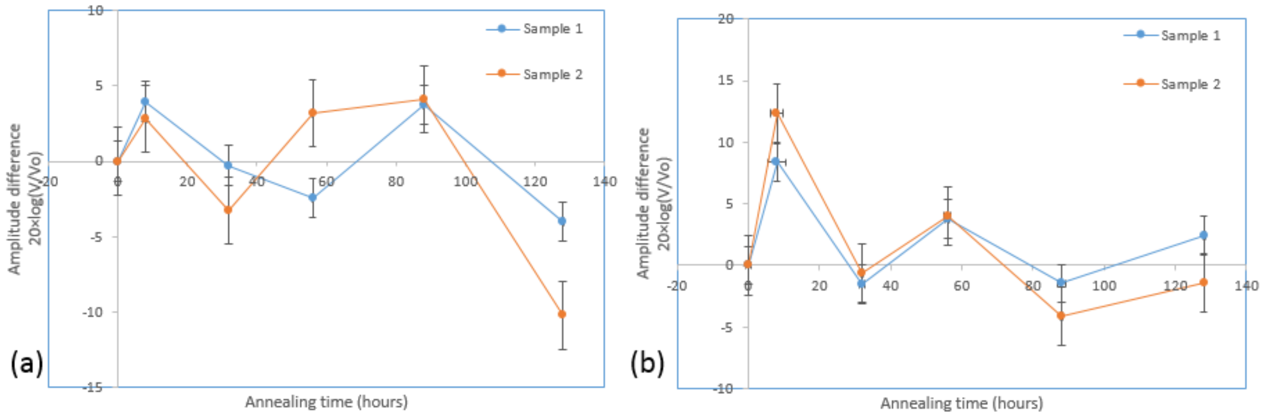


Figure 20: Double-sided configuration: (a) Amplitude change of shear pump wave 1 with respect to annealing time (b) Amplitude change of shear pump wave 2 with respect to annealing time

In Figure 19 and 20, amplitudes (dB) lower than zero implies that the amplitude of the shear pump wave corresponding to that time interval of annealing, is lower than its amplitude before annealing. Similarly, amplitudes (dB) greater than zero implies that the amplitude of the shear pump wave corresponding to that time interval of annealing is higher than its amplitude before annealing. The error bars in Figures

19 and 20 represent the standard deviations of the amplitudes(dB) at five different points per sample, at each time interval of annealing.

As observed in Figures 19 and 20, there is no trend seen in the amplitudes (dB) of the reflections of the shear pump waves with annealing time. The amplitudes of the shear pump waves after each time interval of annealing show either an increase or a decrease with respect to its amplitudes at the previous time interval of annealing, in both single sided and double sided access configuration.

The increase or decrease pattern in the amplitudes of the shear pump wave reflections can be due to the change in acoustic impedance mismatch between PVC and water. The change in density of the PVC material due to annealing, varies its acoustic impedance. Change in the acoustic impedance of PVC increases the acoustic impedance mismatch between PVC and water. Consequently, higher fraction of the signals passing through the material, are reflected at the interface of PVC and water than transmitting through it. The receiver records the signals that transmit through the interface of PVC and water. Due to the change in impedance mismatch of PVC and water at each time interval of annealing, the fraction of signals that are transmitting through the interface also varies. Therefore, the amplitudes of shear pump wave reflections at each time interval of annealing is different compared to its previous annealing time and no specific trend is observed in both the single sided and double sided access configuration.

It is noted that the amplitudes (dB) of the shear pump wave reflections after annealing for a time interval of eight hours show an increase when compared to its amplitude before annealing. However, this is not seen in the case of sample 2 in the single sided access configuration of pump wave 1 (see Figure 19a). In this configuration, the trend seen in the plot is as if the amplitude remains the same after annealing for a time interval of eight hours when compared to its amplitude before annealing.

The amplitudes of the shear pump wave reflections are not recorded from the same points of the sample at each time interval of annealing. This causes variation in the energies of the signals recorded, as some amount of the transmitted signals do not hit the surface of the receiver and will not be recorded. In such cases, the amplitude of the signal recorded will be low when compared to the amplitude at its previous annealing time. This can be the reason why the amplitude of shear pump wave 1 for sample 2, do not increase after annealing for a time interval of eight hours when compared its amplitude before annealing, in the single sided access configuration.

In Figure 19 and 20, it is noted that the final amplitude of the shear pump waves at an annealing time of 128 hours is lower than its amplitude before annealing.

One of the mechanical properties of PVC which show an increase with annealing time, is its hardness, though it is also sensitive to other external factors [75]. As hardness of the PVC material increases, the amount of cross-linking of molecules inside the material increases. This results in increase in the tensile strength of the material. Consequently, the atoms get more concentrated in a given volume in the material. As a result, the density of the material increases. Increase in density leads to increase in the acoustic impedance of the material and consequently, a higher impedance mismatch between PVC and water. This leads to low transmission of the shear pump waves through the water-PVC interface. This explains why the final amplitudes of the shear pump waves are lower compared to their amplitude before annealing.

However, it is noted that the final amplitude of shear pump wave 2 at annealing time of 128 hours is higher than its amplitude before annealing for sample 1 in the double sided access configuration (see Figure 20b).

The reason why the final amplitude of the shear pump wave is higher than its amplitude before annealing is due to the error in the fixture of the samples with respect to the transducers, while the non-collinear wave mixing experiment was carried out. Consequently, the shear pump waves from the transducers would not have hit all the samples exactly at the same point. This is an important factor of consideration as the PVC samples are obtained from a cylindrical pipe which has a curvature. Only the plane at the center of the surface of the sample is flat and this is the plane at which the pump waves should hit the sample such that, the interaction takes place as expected. If the pump waves hit surfaces having a curvature, it scatters in other directions and can be captured by the receiver with different amplitudes. This explanation is also valid for the positioning of the receiver. The receiver should be placed in a position such that it records the response signals from the center of the sample.

This could be one of reasons because of which an increase or decrease pattern is seen in the amplitudes (dB) at each time interval of annealing. However, it is also previously studied that an increase or decrease pattern is observed for the amplitudes (dB) with respect to annealing time of PVC [74]. It could be that there is actually no direct trend followed by the amplitudes (dB) with annealing time of PVC. However, this cannot be concluded at the moment as further investigations are needed.

5.1.2. Comparison of amplitudes (dB) of shear pump waves in single sided and double sided access configurations

Due to attenuation of ultrasonic signals inside the PVC material, the signal amplitude diminishes with the distance travelled inside the PVC material until reaching the receiver. The shear pump waves recorded in the single sided configuration are reflected from the back wall of the PVC material and transmitted through its front wall. The shear pump waves recorded in the double sided configuration are only transmitted through its back wall. Therefore, the amplitude of the shear pump waves should be higher in the double sided access configuration than in the single sided access configuration, as the shear pump waves travel a longer distance in the latter configuration.

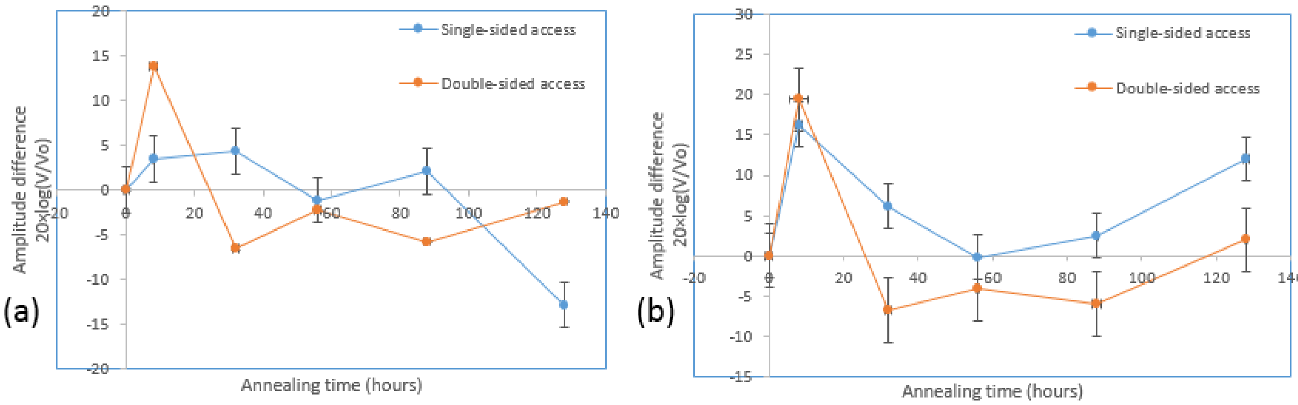


Figure 21: (a) Amplitudes (dB) of shear pump wave 1 in both configurations with annealing time (hours) (b) Amplitudes (dB) of shear pump wave 2 in both configurations with annealing time (hours)

The trends seen in Figure 21a and 21b are plotted for one PVC sample, and the general trend seen in the amplitudes (dB) for all twelve samples are explained using these plots, for the sake of simplicity. All the samples show a trend where either the amplitudes of the shear pump waves at a particular time interval of annealing is higher in the single sided than in the double sided access configuration, or viceversa. This observation does not meet the expectation and it can be due to error in fixture of the samples with respect to the transducers in the double sided access configuration. The fixture of the samples with respect to the transducers sending the pump waves in the single sided access configuration would have been accurate in such a manner that, the pump waves hit exactly at its flat plane. The receiver would have been fixed at the right position with respect to the samples, where it records maximum amplitude of the shear pump waves. The transducers sending the pump waves along with the receiver might not have been fixed at the right position with respect to the samples, where it can record maximum amplitude of the shear pump waves in the double sided configuration. Consequently, the receiver would have recorded reflections of shear pump waves of low energies in the double sided access configuration.

5.1.3. Amplitude of the generated wave reflections- Single sided access and double sided access configurations

The amplitudes of the generated wave reflections are extracted at each time interval of annealing. The change in amplitudes extracted at each time interval of annealing, with respect to its amplitudes extracted before annealing, is tabulated. This section shows the plots for two PVC samples and the general trend seen in all twelve samples are explained using these plots.

Figure 22 and 23 shows the relative amplitudes of the reflections of the generated wave with respect to its amplitude before annealing, for both double sided and single sided access configurations. The x-axis corresponds to the annealing time intervals in hours. The y-axis corresponds to the relative amplitudes in decibels (dB).

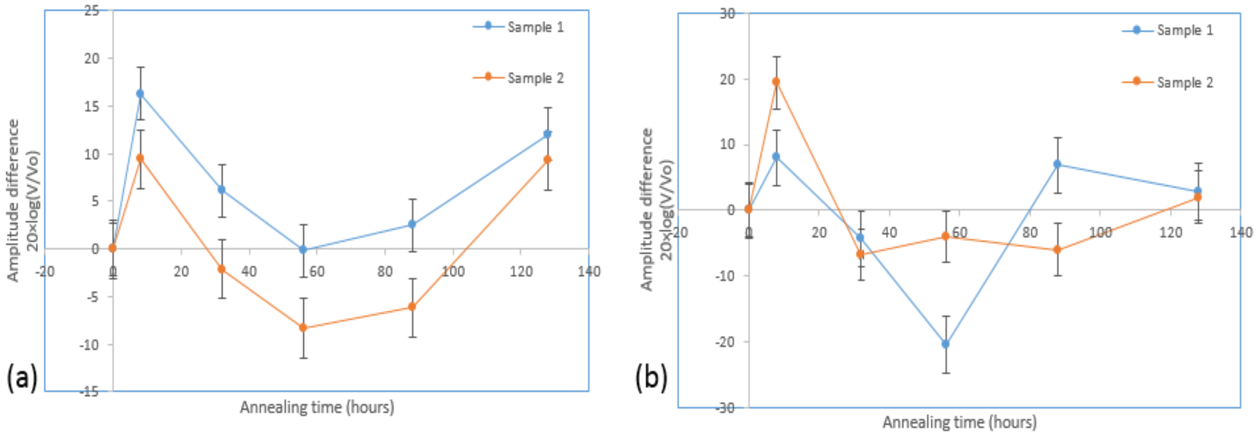


Figure 22: Single sided access Configuration- Amplitudes (dB) of generated wave with respect to annealing time (hours) (a) frequency domain (b) time domain

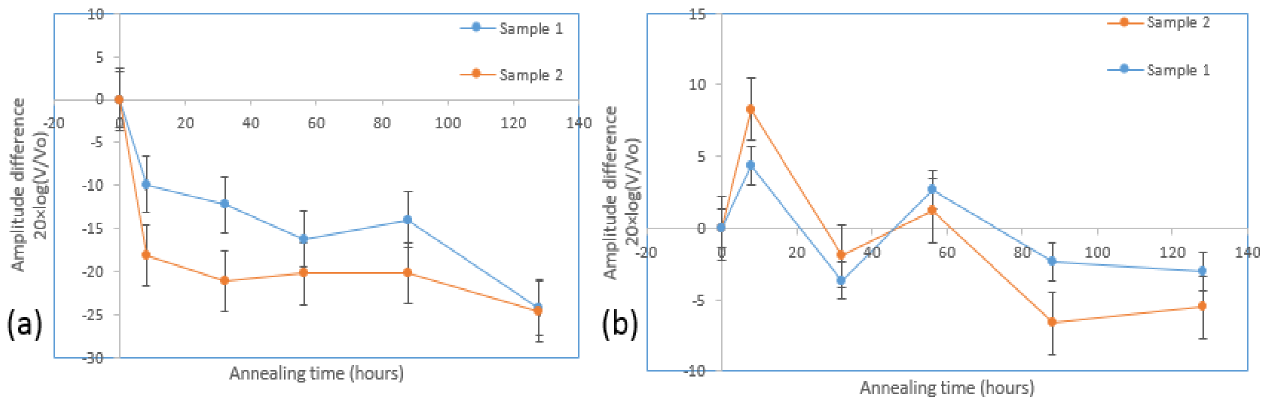


Figure 23: Double sided access configuration-Amplitudes (dB) of generated wave with respect to annealing time (hours) (a) frequency domain (b) time domain

The amplitudes (dB) of the generated wave reflections in both the single sided and double sided access configurations, show an increase or decrease pattern at each time of annealing.

The increase or decrease pattern is due to the variation in the amplitude coefficient of the generated wave (2.21). The variation in the non-linear parameters A and B and the density of PVC due to annealing, are the factors affecting the amplitude coefficient of the generated wave. As the non- linear parameters A and B are temperature dependent (see Section 2.6), they keep varying after each time interval of annealing. The non-linearity of the material is influenced by these elastic parameters and the change in the non-linear behaviour of the material leads to change in its mechanical properties such as its hardness and yield stress, as a result of ageing. Therefore, the value of I^{ξ} is not constant as it a function of the non-linear parameters A and B.

It is studied that after PVC is annealed, the molecular mobility decreases and its specific volume decreases [17]. As a result, the density ρ of the material increases, with annealing. Therefore, due to change in the value of I^{ξ} and ρ, the amplitude coefficient of the generated wave shows variation.

It is noted that the final amplitude (dB) of the generated wave at an annealing time of 128 hours, is lower than its amplitude before annealing in the double sided access configuration (see Figure 23). However, the final amplitude (dB) is higher than its amplitude before annealing in the single sided access configuration (see Figure 22).

As the acoustic impedance mismatch between PVC and water increases after each time interval of annealing, the fraction of signals transmitted through the interface of PVC and water decreases, as more signals get reflected back into the material. As a result the final amplitude (dB) of the reflections of the generated wave is lower than its amplitude before annealing in the double sided access configuration (Figure 23). However, this is not the case in the single sided access configuration as the final amplitude (dB) is higher than the amplitude (dB) before annealing. This could be due to the error in the fixture of the samples with respect to the transducers, while the non-collinear wave mixing experiment was carried out. Consequently, the shear pump waves from the transducers would not have hit all the samples exactly on its flat plane and therefore, the interaction would not have taken place as expected. If the pump waves hit a surface having a curvature, it scatters in other directions and can be captured by the receiver with different amplitudes. This explanation is also valid for the positioning of the receiver. The receiver should be placed in a position such that it records the response signals from the center of the sample.

5.1.4. Comparison of amplitudes (dB) of the generated wave reflections in single sided and double sided access configuration

The generated wave in the single sided access configuration is first reflected at the back wall of the PVC material and then transmitted through its front wall before reaching the receiver. However, the generated wave is only transmitted through the back wall of the PVC material in the double sided access configuration. Therefore, the amplitude of the generated wave reflections in the single sided access configuration should lower than the amplitude of the generated wave reflections in the double sided access configuration, as the signal travels a shorter distance in the later configuration.

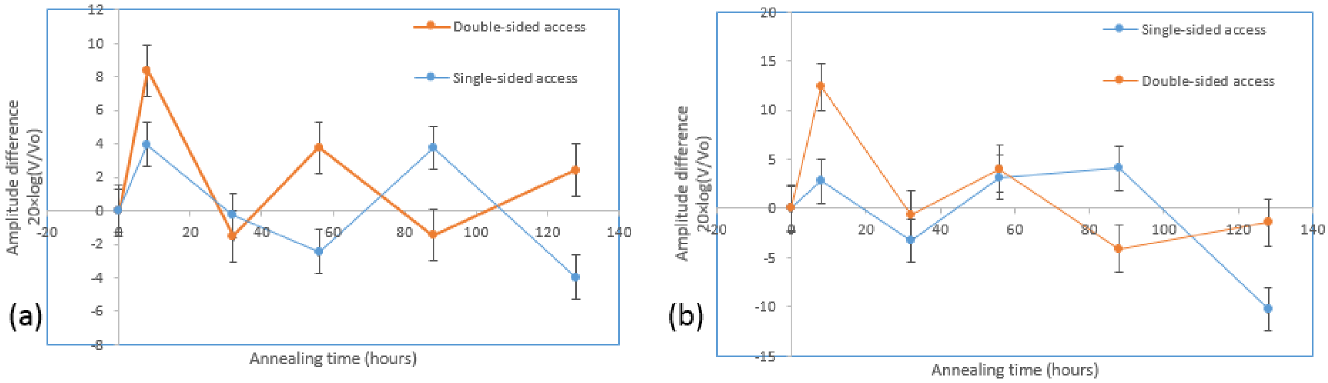


Figure 24: (a) Amplitudes (dB) of the generated wave in both configurations with annealing time (hours) for sample 1 (b) Amplitudes (dB) of the generated wave in both configurations with annealing time (hours) for sample 2

It is noted that the trends plotted in Figure 24a and 24b are for two PVC samples respectively, and the general trend seen in the amplitudes (dB) for all twelve samples are explained using these plots, for the sake of simplicity. All the samples show a trend where the amplitudes of the shear pump waves in the single sided access configuration become higher at certain time interval of annealing than the amplitudes in the double sided access configuration. At a particular time interval of annealing, the receiver was fixed at the right position in the single sided access configuration where it records maximum amplitude (dB) of the shear pump waves. At the same annealing time interval, the receiver might not have been fixed at the right position where it can record maximum amplitude (dB) of the shear pump waves in the double sided configuration. Consequently, the receiver would have recorded reflections of shear pump waves of low energies.

5.2. Rejuvenation by heat treatment and quenching

It is observed that, after heat treatment above glass transition temperature (80^{0}C), the PVC sample deforms into another shape (see Figure 25b).

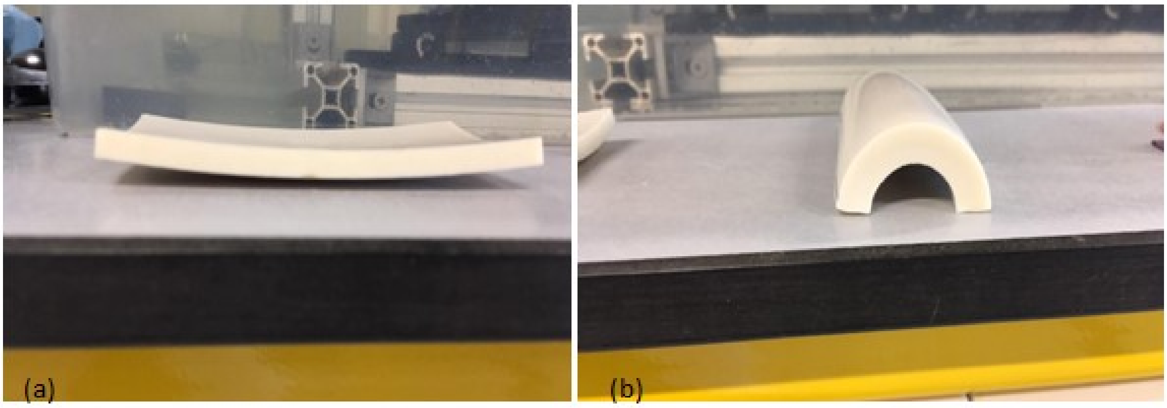


Figure 25: (a) PVC sample before heat treatment (b) PVC sample after heat treatment above glass transition temperature (80^0C)

Figure 26 shows how the sample heats up when the temperature is increased above its glass transition temperature T_g.

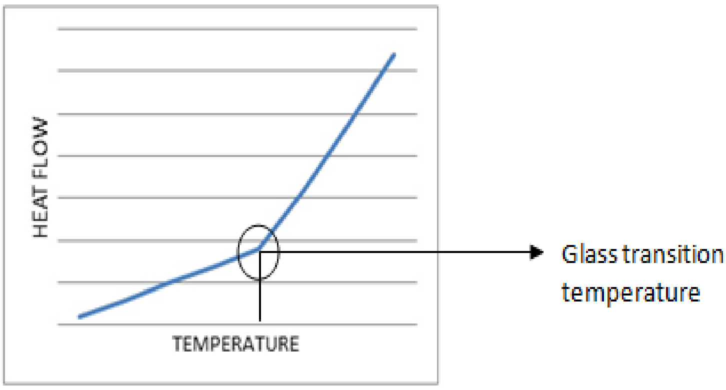


Figure 26: Change in heat flow inside a material as temperature increases above Tg [70]

Increase in the slope of heat flow with rise in temperature above T_g shows that, the heat capacity of the polymer increases above the glass transition temperature.

This increase in heat flow inside the material is the reason why it deforms in to another shape after heating above glass transition temperature, as PVC is a shape-memory polymer [75]. Shape- memory polymers such as PVC are processed by injection or extrusion moulding where the polymer is developed into its permanent/initial shape. In the next process called programming, the polymer sample is deformed into a temporary shape to favour its application. In the context of PVC, the temporary shape is the shape of a cylindrical pipe (Figure 25a). Upon application of an external stimulus such as heat or light, the polymer recovers its permanent/initial shape (Figure 25b).

5.2.1. Amplitude of the reflections of the generated wave after quenching

The non-collinear wave mixing configuration used for the rejuvenated samples was one in which the receiver along with the two transducers sending the pump waves are placed on the same side of the PVC sample (single sided access) . The amplitudes of the generated longitudinal wave was recorded at one point in the sample, with a sampling rate of two minutes. A short time interval was chosen in order to observe how the amplitude of the generated wave changes with temperature within a short period of time after rejuvenation. The amplitude (mV) of the generated wave reflections at each time interval of 2 minutes is plotted in Figure 27.

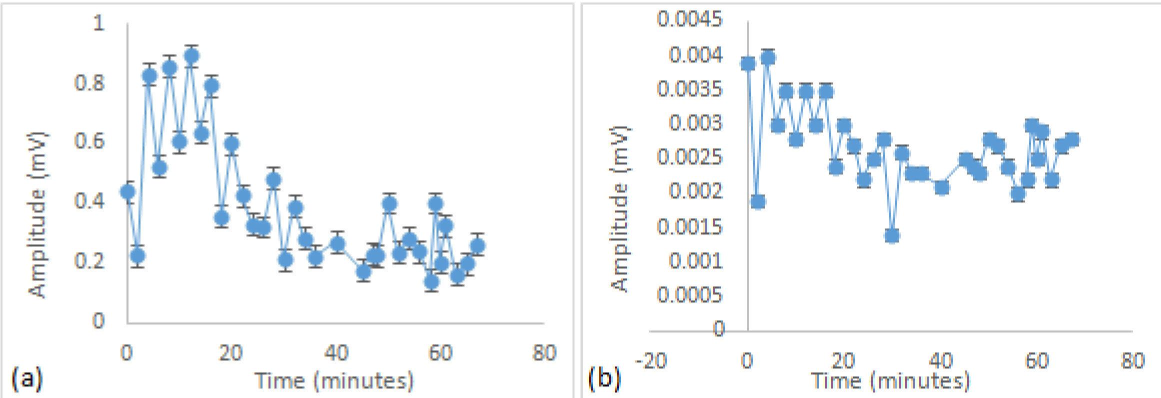


Figure 27: (a) Amplitude (mV) of the generated wave with respect to time in the frequency domain (b) Amplitude (mV) of generated wave with respect to time in the time domain

At time $t = 0$, the amplitude (mV) of the generated wave before rejuvenating, is plotted. After rejuvenation, the temperature of PVC is lower than that of water (room temperature). The amplitude (mV) of the generated wave measured at $t = 2$, decreased compared to its amplitude before rejuvenation. The temperature of PVC starts to increase slowly due to heat exchange between PVC and water. The amplitude at $t = 4$ increased compared to the previous time. After a certain time, the temperature of PVC will be equal to the temperature of water. As the temperature of PVC increases due to heat exchange between PVC and water, the overall trend observed until a time interval of seventy minutes shows that the amplitude of the generated wave reflections decreases, as the temperature increases.

This experiment shows the temperature dependency of the generated wave after rejuvenation of the samples. The trend seen is that the amplitude (mV) of the generated wave decreases with increase in temperature. In order to detect ageing of PVC, the rejuvenated samples have to be annealed as performed in Section 5.1. However, this was not done in this research due to time limitations.

6. Conclusion

Accelerated ageing of PVC was performed by annealing the samples below their glass transition temperature. It can be concluded that the single-sided access configuration can be used to detect ageing of PVC as the amplitudes of the shear pump wave and the generated wave changes at each time interval of annealing. However, as no specific trend was observed in the extracted amplitudes, prediction of the extent of degradation that has occurred in the PVC due to ageing, cannot be done.

It was also found that the amplitude of the generated wave in the single sided access configuration is lower than its amplitude in the double-sided access configuration. However, at certain annealing time intervals, it is higher than the amplitude of the generated wave in the double sided access configuration. This shows that the non-collinear wave mixing setup is very sensitive towards the changes in the fixture of the samples with respect to the transducers. The three transducers have to be perfectly aligned with respect to the sample. Improper positioning of the transducers generate a large variation in the amplitudes of the generated wave. However, the tolerance for this error was not investigated since the error was found only after analysing the amplitude measurements, after the execution of the experiments.

The temperature dependency of the amplitudes of the generated wave was also studied after rejuvenating the PVC samples. Amplitude of the generated wave was found to decrease with time after rejuvenation. However, the extent of degradation due to ageing cannot be predicted from this data alone and further investigation has to be made.

As mentioned earlier, no such remarkable trend was observed in the amplitudes of the generated wave with respect to time. The reasons could be as follows.

1) In order to analyse ageing using non-linear ultrasonic technique effectively, a configuration in which the transducers sending the pump waves, along with the receiver should be fixed such that they do not move while carrying out the experiments. Transmission of ultrasonic signals should be exactly at the flat plane of the sample if it has a curvature. This allows the interaction to take place effectively such that, maximum amplitude of the generated wave is recorded.

2) It is also studied that shear waves attenuates more as compared to longitudinal waves for a same frequency. This means that, for many practical applications, ultrasonic testing is limited to using low frequency longitudinal waves in order to achieve sufficient penetration and sensitivity for a certain thickness of a material. Therefore, ageing of PVC could be more effectively studied using longitudinal wave interactions.

7. Recommendations

1) If the shear-shear interaction could be studied with an accurate experimental set up, and the amplitude changes of the generated longitudinal wave show a remarkable trend, then further investigations can be made to predict the extent of degradation due to ageing in PVC.
2) The shear-shear interaction should also be tested in different thermoplastic polymers to see if there is any trend is observed in amplitude changes with respect to ageing time. If so, it should be compared among different polymers to see if the trend remains the same for all materials.
3) Apart from amplitude changes, other ultrasonic parameters of interest could be investigated to see if they change due to ageing such as energy of the ultrasonic waves.

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9. Appendix

9.1. Longitudinal and shear speeds of sound for nine PVC samples

Table 2: Longitudinal and shear speeds of sound

Specimen position and number		Thickness (mm)	Distance between two sensors (mm)	Height of sensors from specimen (mm)	Angle of refraction	Longitudinal wave velocity (m/s)	Shear wave velocity (m/s)
Upper portion of pipe	G1	5.35	55.91	22.75	44.186^{0}	2296.3	1475.25
	J1	5.3	30.97	11.7	35.53^{0}	2335.8	1224.66
	X1	5.3	41.57	15.75	43.53^{0}	2272.9	1449.95
Middle portion of pipe	G2	5.15	55.30	22.95	42.36^{0}	2272.6	1420.4
	J2	5.4	48.516	19.1	43.68^{0}	2269.1	1455.5
	C2	5.5	42.9	15.98	44.82^{0}	2266.5	1485.53
Lower portion of pipe	H3	5.35	49.7	19.65	44.15^{0}	2311.6	1467.87
	S3	5.5	48.7	19.1	43.65^{0}	2330.0	1454.17
	Q3	5.45	42.69	15.9	44.97^{0}	2348.7	1489.44
Average		5.34				2302.57±30.3	1456.66±77.23

9.2. Amplitude changes of shear pump waves and response waves for twelve PVC samples

9.2.1. Single-sided access configuration

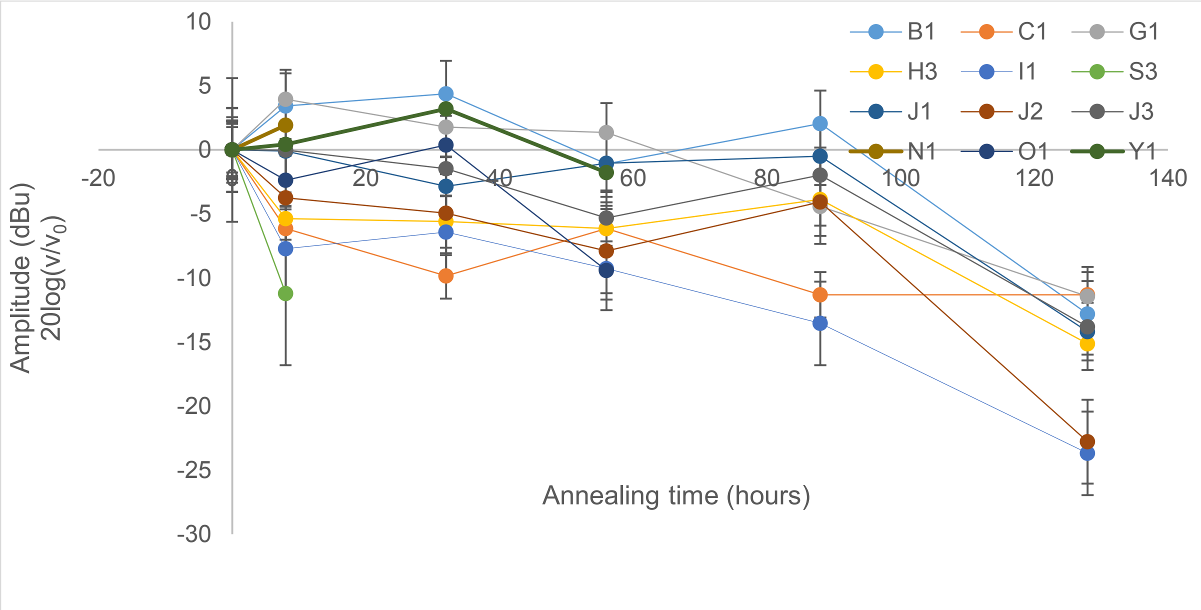

Figure 28: Amplitudes (dB) of shear pump wave 1 with respect to annealing time (hours) (Frequency domain) for twelve samples

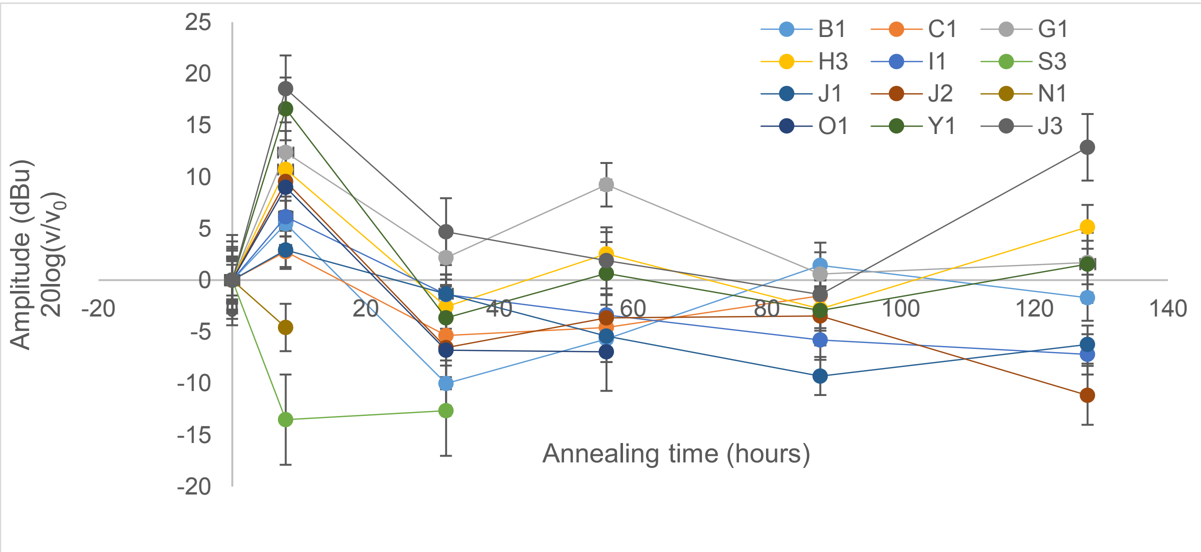

Figure 29: Amplitudes (dB) of shear pump wave 2 with respect to annealing time (hours) (Frequency domain) for twelve samples

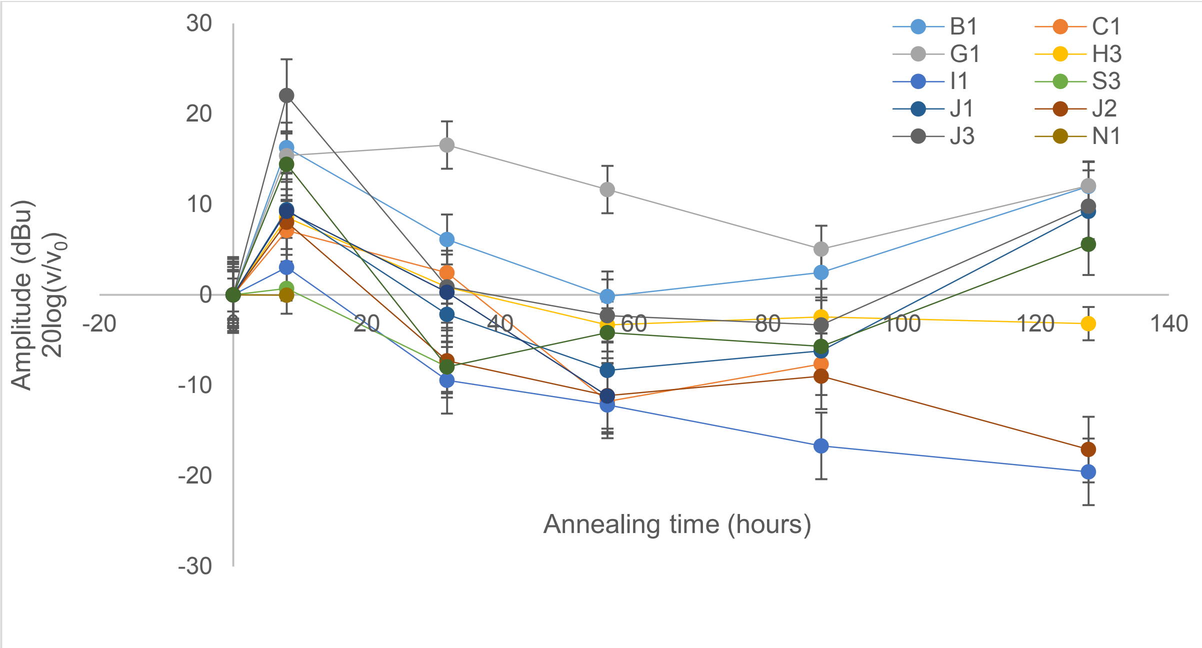

Figure 30: Amplitudes (dB) of generated wave with respect to annealing time (hours) (Frequency domain) for twelve samples

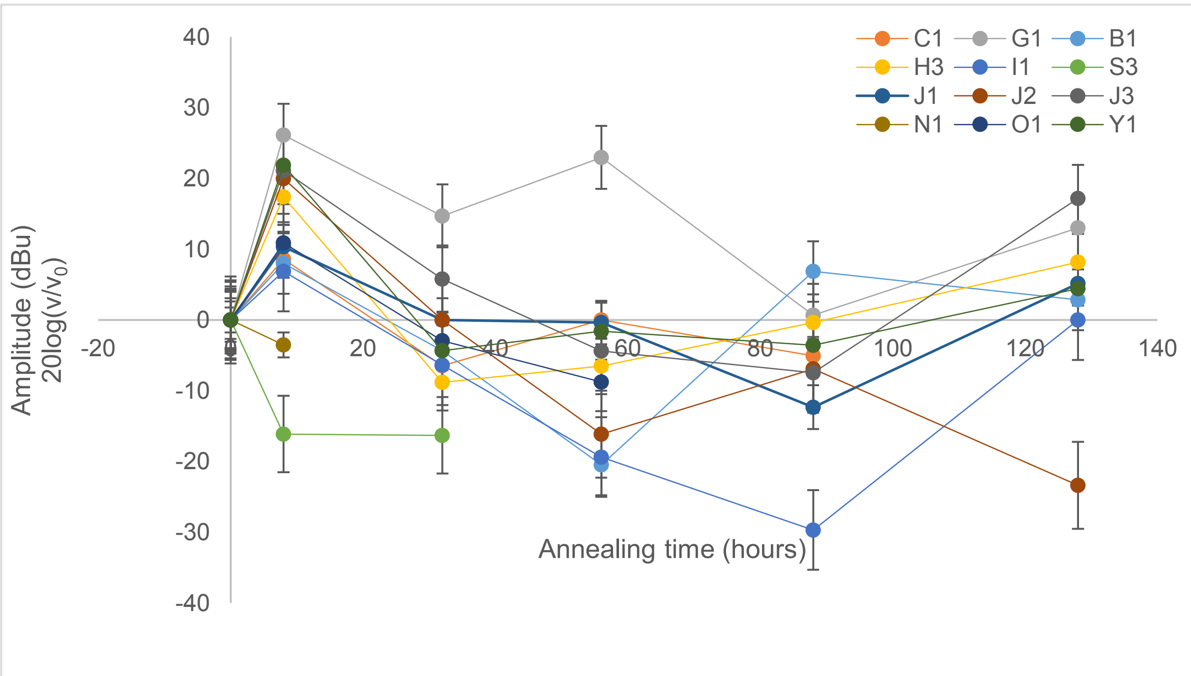

Figure 31: Amplitudes (dB) of generated wave with respect to annealing time (hours) (time domain) for twelve samples

9.2.2. Double-sided access configuration

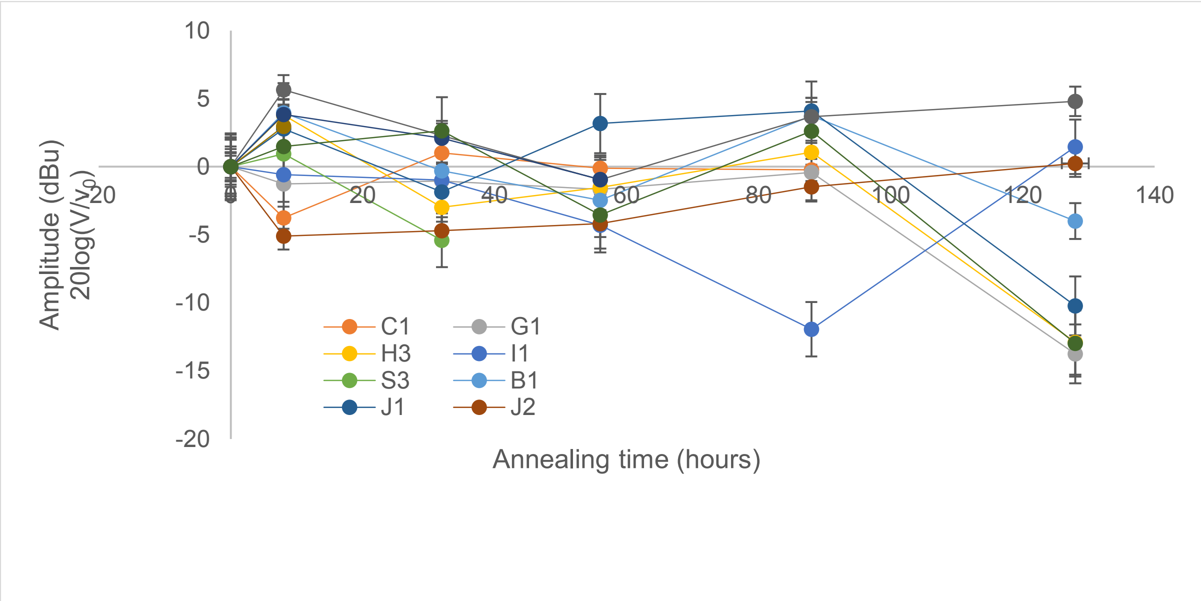

Figure 32: Amplitudes (dB) of shear pump wave 1 with respect to annealing time (hours) (Frequency domain) for twelve samples

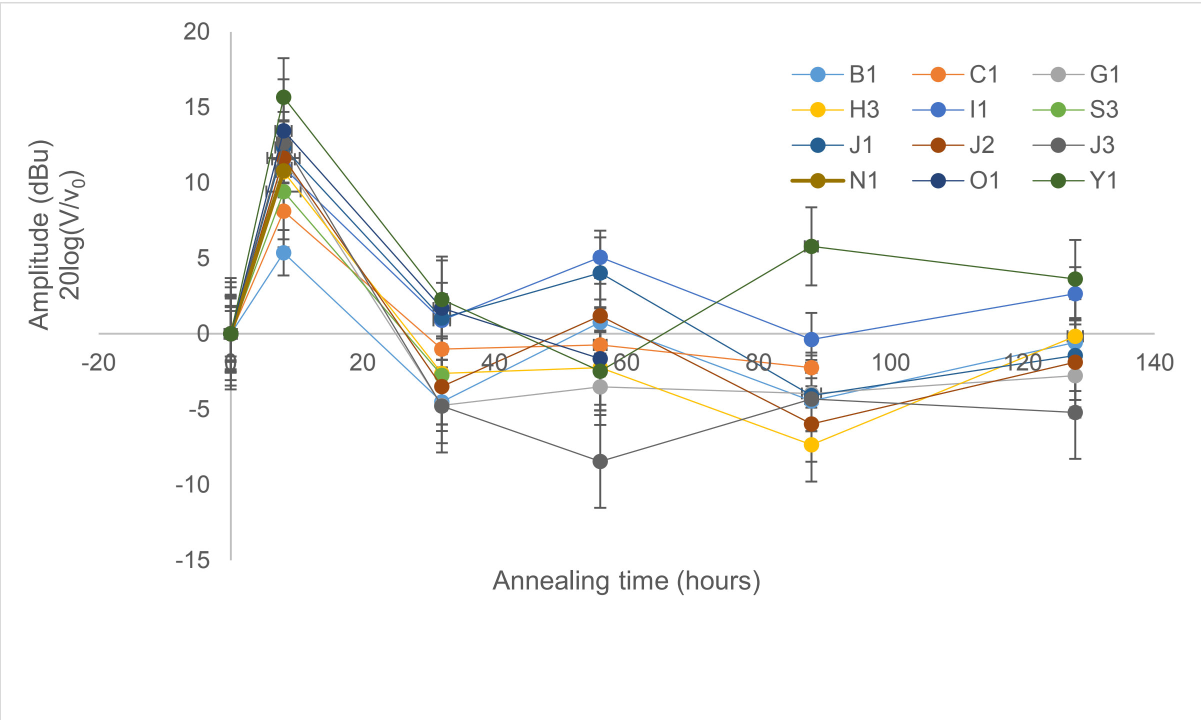

Figure 33: Amplitudes (dB) of shear pump wave 2 with respect to annealing time (hours) (frequency domain) for twelve samples

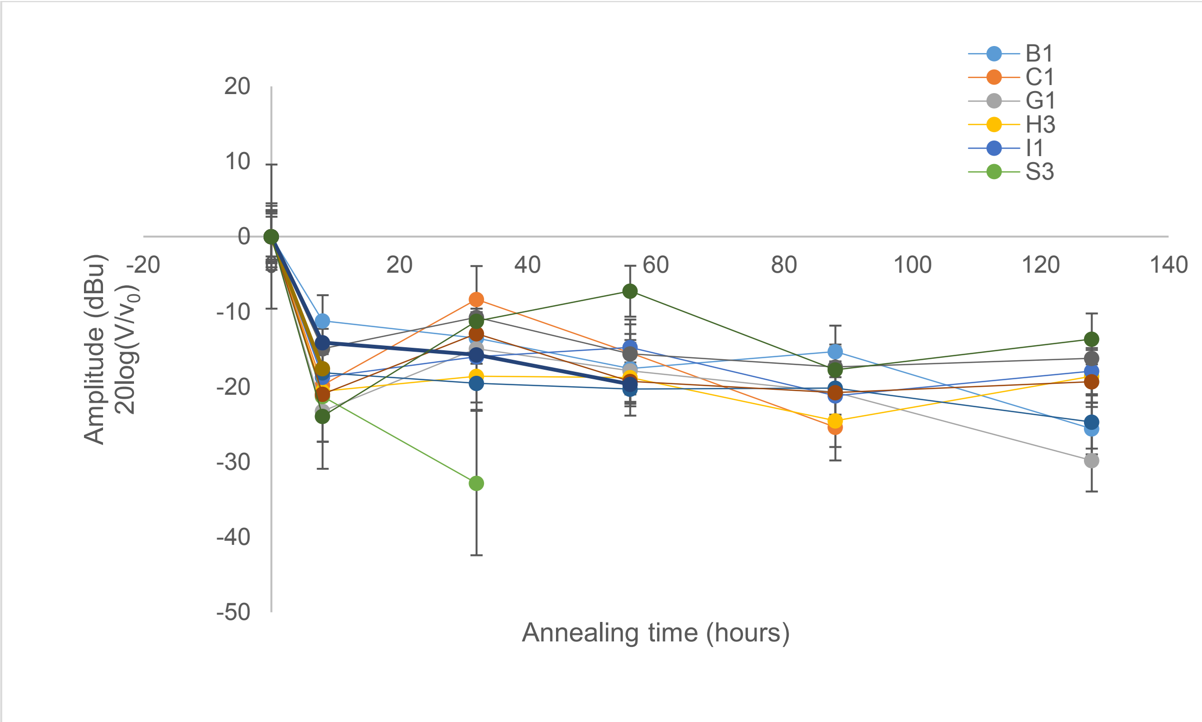

Figure 34: Amplitudes (dB) of generated wave with annealing time (hours) (frequency domain) for twelve samples

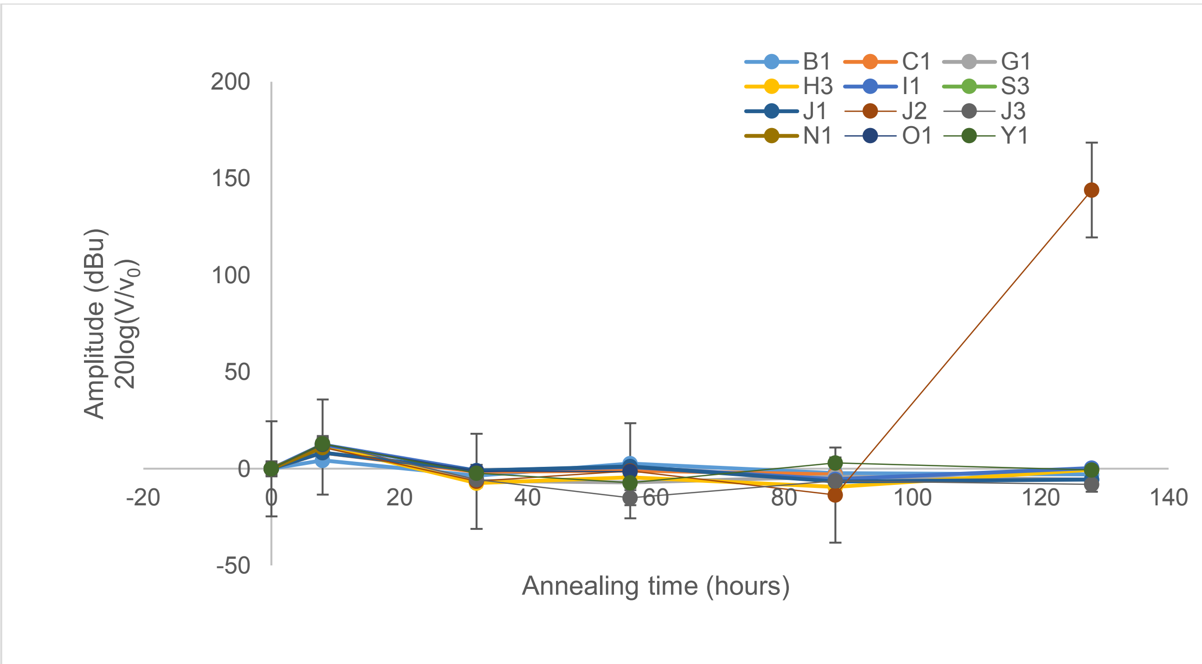

Figure 35: Amplitudes (dB) of generated wave with respect to annealing time (hours) (time domain) for twelve samples