An Investigation into the Use of Ultrasound to Evaluate the Thermal Ageing of High Density Polyethylene (HDPE)
Abstract

As polymeric materials age, various mechanisms can take place that alter their bulk physical properties. The proportion of the crystalline phase in High Density Polyethylene (HDPE) has been shown to change with thermal ageing using Differential Scanning Calorimetry (DSC). To investigate the change in crystallinity during ageing, an ultrasonic testing technique has been developed to monitor the corresponding change in Young’s modulus, which is related to the proportion of the crystalline phase. Ultrasound is of interest as a novel analytical technique because it is non-destructive, in contrast to tensile testing, which is the conventional technique for calculating Young’s modulus.

Results are reported on the use of ultrasound to measure the longitudinal and transverse speed of sound through HDPE, with varying degrees of thermal ageing for up to 5 weeks at 110 °C. These initial measurements were carried out at room temperature, after the ageing process had occurred. This testing technique was then extended to in situ analysis of the ageing process.

5 Keywords

Thermal ageing, ultrasound, polyethylene, degradation, NDT.
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1 Introduction

The primary objective of this project was to verify whether ultrasound can be used as a novel analytical technique to monitor the ageing-induced changes in mechanical properties in high density polyethylene (HDPE). The principal advantage of ultrasonic analysis is that it is a non-destructive technique which can probe the mechanical properties of materials. The conventional technique which has the equivalent capability is tensile testing. This technique involves pulling a sample apart and in the process, destroying it. To establish whether ultrasound is a valid technique for this application, it has been correlated with other conventional techniques which have been reported in the literature to monitor the ageing process under investigation. The ultimate objective of this work is to develop the technique to enable real time measurement of the ageing-induced change in crystallinity of HDPE using ultrasound.

1.1 Analytical Techniques

1.1.1 Ultrasound

Ultrasound waves are classified as mechanical waves which propagate at frequencies above the limit of human hearing (around 16 to 20 kHz). The frequency used for materials analysis in this project was in the megahertz range (2.25 to 5 MHz).

The waves are generated by piezoelectric materials which have the ability to generate electrical currents when subjected to mechanical stress and vice versa. Ultrasonic waves travel by the transmission of vibrations through particles in a medium. Subsequent particles start their vibration one after the other with a slight time delay and as a result, the vibrational motion travels with a finite velocity which is characteristic of the medium.

There are several different types of ultrasound wave that can propagate in solid materials: longitudinal waves, shear waves, Rayleigh waves (or surface acoustic waves) and Lamb waves (or plate waves).¹ Changes in transit time, attenuation, scattering, and frequency content can be correlated with changes in physical...
properties such as hardness, elastic modulus, density, homogeneity, or grain structure.\textsuperscript{2} Attenuation is determined by the energy losses in compressions and decompressions in ultrasonic waves, which include absorption and scattering contributions. The ultrasonic velocity is determined by the density and the elasticity of the medium.\textsuperscript{3}

The parameter of interest in this project was the ultrasonic velocity and the waves that were of interest were longitudinal and shear waves. In longitudinal waves, the particles of the medium vibrate in the direction of the propagation, whereas in shear waves, the particles of the medium vibrate in a direction perpendicular to that of the propagation, as shown in Figure 1.\textsuperscript{4}

![Diagram to illustrate the propagation of longitudinal and shear waves.\textsuperscript{5}](image)

Figure 2 shows the experimental setup for an ultrasonic probe coupled to a test sample in pulse-echo mode. In this mode, the probe is acting as both the transmitter and the receiver of ultrasound and \( t \) is the time between two consecutive ultrasound signals, i.e. the time it takes for an ultrasonic wave to travel through the test sample twice. The ultrasound wave travels from the probe into the test sample and continues until it reaches the interface between the sample and air. At this point, most of the ultrasound wave is reflected back because of the acoustic impedance mismatch between the test sample and air. When the ultrasonic wave returns to the probe, a signal is generated on an ultrasound scan.
Figure 2: Schematic of experimental setup in pulse-echo mode.

The ultrasonic velocity is determined by a simple distance-time calculation, as shown in Equation 1.

\[ V = \frac{2 \times D}{t} \]

Equation 1

In the above equation, \(D\) is the thickness of the test sample and \(t\) is the time interval between two consecutive wave reflections.

Using the longitudinal and shear velocities (denoted as \(V_L\) and \(V_S\), respectively), the Poisson’s ratio of the material, \(\mu\), can then be calculated, using Equation 2.

\[ \mu = \frac{1 - 2 \left( \frac{V_S}{V_L} \right)^2}{2 - 2 \left( \frac{V_S}{V_L} \right)^2} \]

Equation 2

Assuming that the density of the material, \(\rho\), is known, the Young’s modulus of the material, \(E\), can then be calculated using Equation 3.

\[ E = \frac{V_L^2 \times \rho \times (1 + \mu) \times (1 - 2\mu)}{1 - \mu} \]

Equation 3

The primary advantages of ultrasonic analysis are that it is a non-destructive technique (because the amplitudes of the deformations in the waves are so small),
opaque samples can be analysed (unlike analytical techniques which rely on the transmission of light), and it is relatively easy to alter the propagation of the ultrasound waves because they are synthesised electronically.  

A research group in the Department of Engineering for Innovation at the University of Salento in Lecce (Italy) have compiled a large body of work on materials analysis using ultrasound.  

The applications include monitoring water sorption by hydrogels and the curing of an epoxy resin. The application of ultrasound to monitor the ageing of polymers is, however, relatively novel and has yet to be reported in the literature.  

1.1.2 Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical technique often used for studying the phase transitions in polymers. This was the main technique used to correlate with the ultrasonic data obtained. In DSC experiments, a material is heated or cooled along with a reference material of known heat capacity, at the same heating or cooling rate. The heat flow to both the sample and the reference is the same until a thermal event occurs in the sample, such as melting. During the thermal event, in order to keep the temperature of the sample and the reference the same, more heat needs to be transferred to the sample (or removed from the sample depending on the process under study). The DSC records this heat flow as a function of temperature or time. The peaks on the DSC graph identify thermal transitions in the sample due to changes in enthalpy $\Delta H$ as temperature increases. The area between a DSC curve and its extrapolated baseline indicates the total heat of reaction.

The crystallinity of a polymer can be calculated using the melting enthalpy $\Delta H_m$ and Equation 4.

\[
\% \text{ crystallinity} = \frac{\Delta H}{\Delta H_c} \times 100
\]

Equation 4\(^\text{13}\)

In Equation 4, $\Delta H_c$ is the enthalpy of fusion for a 100% crystalline polyethylene standard and is reported in the literature as 293.6 J g\(^{-1}\).\(^\text{13}\)
1.1.3 Dynamic Mechanical Analysis (DMA)

The theory of DMA is summarised by K. P. Menard. The technique involves applying an oscillating force to a sample and analysing the material’s response to that force. Specifically, this involves measuring the amplitude of the deformation at the peak of the sine wave, and the lag between the stress and strain sine waves. The properties of the sample which are determined are the storage modulus (ability of the material to store energy), the loss modulus (ability of the material to lose energy) and tan delta (the ratio of these two values), which is termed damping. Tan delta is found by dividing the loss modulus by the storage modulus and is a measure of the viscoelasticity of a polymeric material. For completely viscous materials, tan delta is equal to 0.5 (i.e. Newtonian fluid) and for purely elastic materials, tan delta is equal to 0 (i.e. a spring).

1.2 Background to HDPE

Because of its resistance to solvents, high tensile strength and heat tolerance, HDPE is used in a wide variety of applications, including containers, geomembranes, furniture, pipes, insulation for heavy-duty power cables, and vacuum devices. Indeed, HDPE is one of the largest volume commodity chemicals produced in the world.

J. J. Cheng provides a background to the chemistry and structural features of HDPE in his Ph.D. paper, investigating the effects of microstructure on the creep characteristics of the material. Polyethylene \( (\text{[-CH}_2\text{-CH}_2\text{-]}_n) \) is a semi-crystalline polymer, made up of crystalline and amorphous regions. Crystalline regions contain highly ordered and densely packed molecular chains and occur at low chain branching concentrations. Where there is a significant amount of side branching from the primary chains, the close and layered packing of the molecules is prevented and the resulting arrangement is of lower density and is termed amorphous. The crystalline lamellae provide structural integrity, whilst the amorphous parts provide the elastic properties of the material. HDPE has a greater proportion of crystalline regions than low density polyethylene (LDPE), which results in a greater density and strength. The density of HDPE is between 0.941 and 0.965 g cm\(^{-3}\).
Polyethylene is usually crystallized from the melt and the resulting product has a spherulite morphology, where spherulites made up of lamellae are embedded in a matrix of amorphous material. The structural features of these spherulites are illustrated in Figure 3.

![Figure 3: Illustration of spherulite, lamella, and amorphous phase structures.](image)

The parameters which have the strongest influence on the mechanical behaviour of HDPE are the degree of chain branching, the molecular weight distribution, the percentage crystallinity and the morphological structure. The crystallinity of polyethylene is positively correlated with the density and stiffness of the material. Short chain branching (SCB) can have an effect on crystallinity by interfering with the formation of lamellae. The SCB distribution of polyethylene is controlled by the type of catalyst used during the polymerization process. HDPE is generally linear with low SCB content. Figure 4 highlights the structural differences between different forms of polyethylene.
1.3 Literature Overview of Ageing Mechanisms in HDPE

1.3.1 Initiation

Grassie and Scott\textsuperscript{19} outline the reactions involved in the thermal ageing and degradation of polyethylene. Initially, bond scissions occur at weak link structures, with an activation energy ($E_a$) of $\sim 150$ kJ mol\(^{-1}\), which lead to the formation of free radicals.\textsuperscript{20} There are four known weak link structures in polyethylene, namely peroxides, carbonyl groups, chain branches and unsaturated structures.\textsuperscript{19} The weak link structures decrease the dissociation energy of C–C bonds.\textsuperscript{21} As the weak link structures are consumed, the limiting step of degradation shifts towards the degradation initiated by random scission, with an $E_a$ of $\sim 240$ kJ mol\(^{-1}\).\textsuperscript{20} Figure 5 shows the scission reactions which initiate the ageing process.

\begin{align*}
\text{R} - \text{H} & \rightarrow \text{R}^* + \text{H}^* \\
\text{R} - \text{R} & \rightarrow 2 \text{R}^*
\end{align*}

\textbf{Figure 5: Initiation reactions in the thermal ageing of polyethylene.}\textsuperscript{21}

The energy required for the bond scission initiation reactions in the ageing of polyethylene can be provided from heat, radiation, light, or the presence of an initiator, which can come from within the polymer itself.\textsuperscript{22} In the case of thermal ageing, the source is heat.
1.3.2 Propagation

The free radicals formed in the initiation reactions can then break down by $\beta$-scission or undergo intra / intermolecular hydrogen abstraction. The hydrogen abstraction reaction converts primary / secondary radicals to secondary / tertiary radicals with a corresponding increase in stability. This increase in stability is thought to be related to the inductive effect; carbon is more negatively inductive than hydrogen and hence stabilizes radicals to a greater extent. The mechanism for a generic $\beta$-scission reaction is shown in Figure 6.

![Figure 6: $\beta$-scission mechanism.](image)

$\beta$-scission can follow the intermolecular hydrogen abstraction. Secondary radicals can go on to produce vinyl groups and tertiary radicals can go on to produce vinylidene and vinylene groups.

It is thought that $\beta$-scission following intermolecular hydrogen abstraction is the most important propagation reaction in the degradation of polyethylene.\(^{21}\) It results in a significant decrease in the average molecular mass.

1.3.3 Effect of Oxygen

The presence of oxygen increases the rate of polymer degradation through an autocatalytic radical chain reaction. According to W. L. Hawkins,\(^ {22}\) the mechanism for the thermo-oxidative ageing of polymers was developed by Bolland.\(^ {23}\) Oxygen is not involved in the initiation step so the reaction is initiated by the mechanism outlined in Figure 5. The next stage of the reaction is chain propagation and is shown in Figure 7.
R• + O₂ → ROO•
ROO• + RH → ROOH + R•

**Figure 7: Reaction scheme for the formation of hydroperoxides.**

The reaction between the alkyl radical and molecular oxygen (forming the peroxy radical) is a radical pairing process and hence has a low activation energy and occurs with a high frequency.¹⁹ This species then goes on to abstract a hydrogen from the polymer chain, forming a hydroperoxide, and a second radical. This step involves breaking a C – H bond and hence has a higher activation energy. This is the rate-determining step in the auto-oxidation of most polymers.¹⁹

The hydroperoxide which is formed is unstable and decomposes at a fast rate by a homolytic reaction to form oxy– and hydroxyl– radicals, as shown in Figure 8.

ROOH → RO• + HO•
2 ROOH → RO• + ROO• + H₂O

**Figure 8: Unimolecular and bimolecular decomposition of hydroperoxides.**

Transition metal ions are important catalysts for hydroperoxide decomposition and so the way in which the polyethylene is produced (i.e. which transition metals are used and their concentrations) will have an effect on the thermo-oxidative stability of the material. The reactions with metal ions are shown below in Figure 9.

\[
M^{n+} + ROOH → M^{(n+1)+} + RO• + HO^- \\
M^{(n+1)+} + ROOH → M^{n+} + ROO• + H^+ \\
2ROOH → RO• + ROO• + H₂O
\]

**Figure 9: Transition metal catalysis of hydroperoxide decomposition.**²¹

The oxy– and hydroxyl– radicals formed in the decomposition of hydroperoxides are more reactive than the peroxy radicals and lead to the auto-acceleration of the degradation process. They can undergo hydrogen abstraction reactions, initiating new oxidative chains, shown in Figure 10.
\[ \text{RO}^\bullet + \text{RH} \rightarrow \text{ROH} + \text{R}^\bullet \]
\[ \text{HO}^\bullet + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^\bullet \]

Figure 10: Hydrogen abstraction by oxy and hydroxyl radicals.

The decomposition of the hydroperoxide species and ensuing reactions lead to an increase in the oxidation rate.\textsuperscript{22} For every hydroperoxide molecule that decomposes, two new reactive radicals are formed which go on to produce two alkyl radicals which can go through the cycle of reactions again. The chain of reactions involved in the thermo-oxidation of HDPE is conveniently illustrated in Figure 11, starting with the radical species on the left-hand side of the diagram.

![Figure 11: Cycle of reactions in the thermo-oxidative ageing of HDPE.\textsuperscript{24}]

D. Wright\textsuperscript{25} suggests that the thermo-oxidative degradation of polymers proceeds in two stages: an initial induction period followed by a rapid increase in the rate of reaction. Indeed, this is observed in several studies in the literature.\textsuperscript{26,27,28,29,30,33} The end of the induction period is signified by dramatic increases in reaction products and oxygen consumption, and decreases in molecular weight and ductility.

The induction time and hence the durability of the material depend on the physical and chemical structure of the polymer, the efficacy of the stabilising additives (if present), the presence of metal catalysts, the presence of stress and the power of the oxidising medium.\textsuperscript{25} It is also important to note that the in-service durability of the material is dependent on the degradation accumulated during processing. Additionally, Singh and Sharma\textsuperscript{31} report that amorphous regions in the polymer are
more labile to thermal oxidation compared to crystalline regions because of their higher permeability to molecular oxygen.

### 1.3.4 Termination

According to I. Kriston,\(^{21}\) recombination and disproportionation are the two predominant termination reactions of thermal degradation. Termination reactions convert reactive radical species into inert products. The termination reactions have low activation energies and their rate constants depend on the rate of diffusion of the macroradicals in the media.

Similarly to the thermal degradation in the absence of oxygen, termination reactions in thermo-oxidative degradation may involve either coupling of radicals to dissipate their energy (recombination) or disproportionation into inert species.\(^{22}\) Some examples of termination products from thermo-oxidative ageing which have been reported in the literature are ketones, aldehydes, acids and γ-lactones.

The termination reactions of particular importance are chain branching and crosslinking reactions. A generic chain branching mechanism is shown in Figure 12.

![Figure 12: Chain branching mechanism.](image)

In this example, a primary radical is reacting with a secondary radical to form a branched polymer product. Chain branching and crosslinking reactions have directly opposite effects to scission reactions: they lead to increases in molecular weight and structural disorder.

Crosslinking and chain branching reactions are thought to occur simultaneously with chain scission reactions in the ageing of polyethylene,\(^{32}\) as discussed in a paper which uses solid-state NMR to investigate the effects of thermo-oxidative ageing.\(^{33}\)
The factors that affect the rate and the direction of the reactions are: the number of weak link sites in the polymer chain, the type and amount of catalyst residues and the ageing conditions. Crosslinking reactions predominate in the processing of polymers with high concentrations of unsaturated groups (Phillips type polyethylene), while for Ziegler-type and metallocene polyethylenes (containing low unsaturated group contents), the direction of the reactions is determined by the number of vinyl groups and the processing conditions.

2 Experimental

2.1 Instrumentation

The thicknesses of the test samples were measured using a Mitutoyo Digimatic Micrometer MDC-25PJ. The specifications of the micrometer were: resolution = 0.001 mm; measuring range = 0 to 25 mm; quantizing error = ±1 count. The masses of the samples were measured to four decimal places using a Sartorious LA 230P balance. The ovens used for the thermal ageing were Carbolite PF120 models. The temperature of the oven was monitored by three temperature probes, and the temperature values reported were averages of the three values provided.

2.2 Coupling Agents

Sound energy at the ultrasonic frequencies typically used for non-destructive testing is not effectively transmitted through air; air represents a severe acoustic impedance mismatch with respect to both transducer wearplates and typical test materials. Even an extremely thin air gap between the transducer and the test piece prevents efficient sound energy transmission and makes conventional testing impossible. As such, a couplant film (between the transducer and the test sample) is needed to transfer the high frequency ultrasonic energy from the probe into the test material. The coupling agent used in both the ex situ and in situ measurements was Sainsbury’s basics honey.
2.2.1 Special Consideration for *in situ* Measurements

Four potential coupling agents were investigated in this project: water, epoxy, Sylgard 184 and honey. In order to see whether there were any adverse effects on the ultrasound signal induced by temperature, a calibration material was needed which was mechanically stable over the temperature range of interest (≤ 75 °C). Stainless steel was chosen for this purpose. A longitudinal probe (5 MHz) and a shear probe (2.25 MHz) were coupled to a stainless steel test sample with the coupling agent of interest and a measurement at room temperature was made. The system was then put into the 75 °C thermal ageing oven and the velocity was monitored over time.

2.3 Ultrasound Scans

Figure 13 and Figure 14 show typical examples of ultrasound scans which were used for analysis.

![Figure 13: A-scan showing a longitudinal wave propagating through a 5 mm thick block of stainless steel.](image)

The scan shown in Figure 13 is called an A-scan and shows a longitudinal wave propagating through a 5 mm thick block of stainless steel. The velocity of the wave was found by measuring the time interval between corresponding peaks on the first two consecutive ultrasound signals, using moveable cursors. This value, combined with the thickness measurement of the sample, was then used to calculate the velocity, using Equation 1.
The scan shown in Figure 14 is called a B-scan and was used to analyse how the A-scan changes over time. B-scans are made up of vertical strips of A-scans and the bands on the B-scan correspond to signals on the A-scan; white areas correspond to large positive amplitudes in the ultrasound signal and black areas to large negative amplitudes. It is clear to see that the bands on the B-scan are in alignment with the signals on the rotated A-scan on the left-hand side.

### 2.4 *ex situ* Measurements

In *ex situ* measurements, the ultrasound measurements were taken on the test samples on the lab bench at room temperature, when the ageing procedure had finished. A-scans were used predominantly in *ex situ* measurements because it was quicker and it wasn’t necessary to see how the ultrasound signal was changing with time. The frequency of the waves used for all *ex situ* measurements was 5 MHz.

#### 2.4.1 HDPE Rod Samples

Six samples of varying thicknesses were cut from an extruded rod of commercial grade HDPE, pictured in Figure 15. The samples were ground down to create
smooth, parallel faces for ultrasound measurements. Cuttings were taken from the outer surface of the samples for DSC analysis and their thicknesses were measured using a micrometer. The samples were then put into a thermal ageing oven at 110 °C for various times: 0.00, 24.00, 49.50, 96.00, 191.25 and 421.25 hours. When the samples were removed from the oven, they were left to cool at room temperature overnight. Cuttings were then taken from the outer surface of the samples for post-ageing DSC analysis, their thicknesses were measured using a micrometer, and longitudinal velocity measurements were made on the samples using ultrasound.

2.4.2 HDPE Sheet Samples

The experimental procedure below was carried out for two different thicknesses of HDPE sheet: 1 mm and 1.5 mm.

63 samples of approximately uniform dimensions were cut from three sheets of commercial HDPE, pictured in Figure 16. These samples were then divided into 21 groups of three. Each group contained one sample from each sheet, and all the samples within a group underwent the same duration of oven ageing. The thickness and mass of the samples were measured and they were transferred into a thermal ageing oven at 110 °C for various times, ranging from 0 to 36 days. When the samples were removed from the oven, they were left to cool to room temperature overnight. Thickness, mass and velocity measurements were performed on each sample removed. Figure 17 shows the HDPE sheet samples inside a thermal ageing oven and Figure 18 – Figure 19 show how ultrasonic velocity measurements were taken.
2.5 *in situ* Measurements

Two *in situ* experiments were carried out, one on a sample cut from the extruded rod, and the other on a sample cut from a 1.5 mm HDPE sheet. The same *in situ* testing procedure was followed for both samples. For both samples, a 5 MHz longitudinal probe and a 2.25 MHz shear probe were used. The frequency of the ultrasound waves does not affect the velocity calculation.

The thickness of the sample was measured and cuttings were taken from the sample for DSC analysis. Ultrasonic probes were coupled to the test samples using honey. Tape was also used to keep the probes in position. Velocity measurements were
taken on the sample and then the system (comprising the HDPE sample with attached probes) was loaded into a thermal ageing oven at 75 °C, shown in Figure 20 and Figure 21.

![Longitudinal and shear probes coupled to an HDPE sample.](image1)

![In situ systems inside a thermal ageing oven.](image2)

Ultrasonic measurements were taken on the samples throughout the accelerated thermal ageing process. When the required ageing time elapsed, the samples were removed from the oven and cooled overnight, before re-measuring the thickness and mass and performing additional velocity measurements. A proportion of each sample was removed by taking a small cutting for DSC analysis.

### 2.6 Procedure for Analysing DSC Data

Polymer samples were characterized using a Netzch STA 449 C instrument. Samples of between 1 and 10 mg were loaded into the DSC and held isothermally at 30 °C, before heating at a rate of 10 °C min\(^{-1}\) under an argon atmosphere. The melting enthalpy (\(\Delta H_m\)) was obtained and the percentage of crystallinity was determined using Equation 4. A typical DSC trace that the analysis was carried out on is shown in Figure 22.
2.7 Procedure for Taking DMA Measurements

DMA was performed using a TA Instruments Q800 dynamic mechanical analyser using the single cantilever bending arrangement. An isothermal temperature multi-frequency strain experiment was run at $26 \pm 2\, ^\circ C$ using $20\, \mu m$ amplitude and a frequency range of 1 to $20\, Hz$. This was performed on all of the samples that were cut from the rod of commercial grade HDPE. DMA has specific requirements for sample dimensions. As such, the aged HDPE samples had to be processed in preparation for analysis. This involved sanding the faces down and cutting the sides of the samples off to change them from a cylindrical shape to a rectangular shape. The dimensions of the sample were then measured using a micrometer and inputted into the instrument’s software.

Figure 22: Typical DSC trace showing the melting endotherm of an HDPE sample.

In Figure 22, the blue graph is the DSC trace and the green graph is the derivative of this trace. The derivative graph was used to obtain the melting enthalpy. The values highlighted on the derivative trace (at 80.2 and 167.3 °C) correspond to local minima on the DSC trace, where the derivative of the DSC trace was equal to zero. These temperatures were used as the limits for the area calculation on the DSC trace.
Dynamic Mechanical Thermal Analysis (DMTA) was also performed using a TA Instruments Q800 dynamic mechanical analyser using the single cantilever bending arrangement. A temperature step multi-frequency strain experiment was run using the following parameters: amplitude = 20 μm; frequency sweep = 1 to 20 Hz; initial temperature = 30 °C; temperature range = 30 to 110 °C; equilibration time = 15 minutes. The instrumental procedure involved firstly taking measurements over the frequency range at the initial temperature. The temperature was then increased by 5 °C, the system was allowed to equilibrate and the procedure was repeated. This continued until the final temperature of 110 °C was reached.

The purpose of the DMTA experiment was to assess how the mechanical properties of the HDPE under investigation are affected by temperature.

3 Results and Discussion

3.1 *ex situ* Measurements

3.1.1 HDPE Rod Samples

Results from thermal ageing experiments on the commercial grade HDPE rod samples are shown in Figure 23 - Figure 30.

![Graph](image)

*Figure 23: How the thickness of HDPE rod samples changed with oven ageing.*
Before performing ultrasound measurements through the aged samples, the thickness was measured (before and after ageing). It was found that the thickness of the samples changed during the thermal ageing. This can be seen in Figure 23 where the percentage change is given. There was an inherent error in this method because the thickness of the material fluctuated with lab temperature. Therefore, the only way to obtain an accurate value of thickness change would have been to take both of the measurements at identical temperatures.

The change in thickness of the samples may relate to their processing history. Commercial HDPE is often forcibly made into desirable shapes and crystallised from the melt rapidly, such that the product is far away from its thermodynamic equilibrium. The observed changes in thickness may therefore signify a return to equilibrium, as the rod had been extruded and the thermal ageing may have allowed a degree of relaxation.

A slight increase in mass was also noted on samples that had undergone thermal ageing. This may have been caused by thermo-oxidation reactions, which lead to the formation of oxidation products.

![DSC traces for HDPE rod samples](figure24.png)

**Figure 24:** Comparison of DSC traces for HDPE rod samples aged for 0, 2, and 14 days.
Figure 25: How the longitudinal velocities of HDPE rod samples changed with oven ageing.

Figure 26: Correlation between longitudinal velocity and degree of crystallinity.

Figure 27: Frequency sweeps showing how storage modulus changed with thermal ageing (log scales).
Figure 28: Frequency sweeps showing how loss modulus changed with thermal ageing (log scales).

Figure 29: Frequency sweeps showing how tan delta changed with thermal ageing (log scales).

Figure 30: Comparison of tan delta values for all of the samples at 10 Hz.

The DSC data in Figure 24 clearly show that the area under the melting endotherms for the HDPE samples increased with the duration in thermal ageing. This is likely to correspond to an increase in crystallinity with thermal ageing. The reason for this
increase in crystallinity can be explained by X. Shi et. al.\textsuperscript{33} in a study which employed solid-state NMR to look at the effects of thermo-oxidative ageing on the chain mobility and phase composition of HDPE.

Figure 31: Suggested changes in phase structure before and after ageing.\textsuperscript{33}

Figure 31 is taken from the paper by X. Shi et. al.\textsuperscript{33} and shows the changes in phase composition as a result of ageing. The smaller chain fragments which are formed from ageing-induced chain scission reactions have more mobility and can migrate through the polymer matrix to crystallize. The result is an expansion of the crystalline phase, at the expense of the amorphous phase and the interphase. Figure 31 shows that the polymer chains in the amorphous phase (III) are more broken up as a result of ageing.

Grassie and Scott\textsuperscript{19} also explain that the crystallinity frequently increases in semi-crystalline polymers due to the re-alignment of the broken chains in the crystalline domains. The effect of this so-called 'chemicrystallisation' is to reduce the impact resistance (toughness) of the polymer.

The increase in the degree of crystallinity is known to lead to an increase in Young's modulus and this has been detected using ultrasound. Indeed, Figure 25 clearly shows an increase in the longitudinal velocity with ageing and Figure 26 shows the
correlation between the ultrasonic data and the DSC data. The change in longitudinal velocity is significant; at 421 hours, the longitudinal velocity has increased by 10.2%.

The data point on the sample with 96 hours of thermal ageing had a higher than expected degree of crystallinity and longitudinal velocity. The reason for this may be that the sample was significantly thinner than the other samples. As such, it had a larger surface area to volume ratio and a larger interface with the air environment. This may have resulted in thermo-oxidation occurring at a faster rate and hence led to an increase in Young’s modulus at a faster rate, when compared to thicker samples.

Figure 27 - Figure 30 show the data from DMA experiments on the samples cut from the rod of commercial HDPE. There are two distinct regions which are evident in Figure 27 and Figure 28. Both Figures contain two bands of graphs, one containing the samples that had been aged for 0, 1 and 2 days and the other containing the remaining samples which had been aged to a greater extent. This corresponds fairly well to the observable trends in Figure 26: the three samples which had been aged for the longest amount of time had distinctly high and very similar crystalline contents and longitudinal velocities, the other three samples had lower (although less similar) respective properties. The exact ordering of the samples in Figure 27 and Figure 28 is not important. The calculations of the storage and loss moduli are affected by the dimensions of the samples and since the sample dimensions were not uniform, these graphs are not optimised to perform a detailed comparison of the samples; they merely serve as indicators.

Tan delta, on the other hand, is not affected by the dimensions of the samples and can therefore be used for comparative purposes. Figure 30 shows that as the thermal ageing time increased, tan delta increased. This corresponds to an increase in the viscous component of the material. A potential explanation for this is that the smaller chain fragments which are formed from scission reactions have more freedom of movement and lead to a plasticization effect. The trend in Figure 30 correlates well with the trends in Figure 26. It can be inferred from this that chain scission is a dominant ageing mechanism, and is the fundamental cause for the observed changes in mechanical properties in HDPE.

The data point at 96 hours had a lower value for tan delta than expected. There are a few potential explanations for this. The first is that the samples were ground down
before DMA analysis to obtain uniform widths and thicknesses. It is possible, therefore, that the sample which had been aged for 96 hours was ground down to a greater extent than the other samples. Thus, more of the heavily aged material at the surface of the sample was removed. The second factor is that the sample dimensions which were input into the DMA software (and were used in moduli calculations) were an estimate, with an associated error. Some estimates may have been more representative than others and this could have affected the accuracy of the calculations. A final contribution is that the samples were sawed, both initially (in removing them from the rod) and for the DMA preparation. This process was not standardized and some samples may have been affected more than others.

The important point, however, is that the three analytical techniques provided data sets which follow the same general trend. This experiment therefore conclusively proves that ultrasound is sensitive enough as an analytical technique to monitor the ageing-induced changes in the mechanical properties of HDPE.

It was not possible to take shear velocity measurements on the HDPE samples removed from the rod, as it was found that they were too thick. HDPE is a highly attenuative material and shear waves are attenuated to a greater extent than longitudinal waves, since they travel via a less direct path. As such, the shear wave was found to have completely decayed before it returned to the ultrasonic probe twice, and it was not possible to measure the time difference. This meant that it was not possible to calculate Young’s modulus by using ultrasound on the samples cut from the commercial HDPE rod. Instead, the longitudinal velocity, which could be measured, was used as an indicator of Young’s modulus.

It was, however, possible to calculate Young’s modulus of thinner HDPE samples which were cut from sheets of commercial HDPE, and the results for the experiments which involved these sheets are presented below.

### 3.1.2 HDPE Sheet Samples

Due to the large number of samples available from the HDPE sheets, it was possible to acquire an estimation of error in the measurements. However, this also presented a problem. The biggest experimental error which had an adverse effect on all of the ex situ ultrasonic measurements was fluctuation in lab temperature, which was not
accounted for. Because there was a larger amount of samples, it took longer to take micrometer and ultrasonic measurements on the full set; therefore the complete range of measurements was taken over a greater temperature range.

Another advantage of using the sheet samples was that their thicknesses were sufficiently small to allow shear velocity measurements. This, again, presented another problem: the smaller the thickness of the sample, the larger the error in the analytical measurement.

3.1.2.1 1 mm Sheets

Figure 32 – Figure 36 show how the properties of HDPE 1 mm sheet samples changed with thermal ageing. The causes of the observed changes are the same as those for the 1.5 mm samples and are explained in Section 3.1.2.2.

![Figure 32: How the mass of HDPE 1 mm sheet samples changed with thermal ageing.](image)

![Figure 33: How the thickness of HDPE 1 mm sheet samples changed with thermal ageing.](image)
Figure 34: How the longitudinal velocity of HDPE 1 mm sheet samples changed with thermal ageing.

Figure 35: How the shear velocity of HDPE 1 mm sheet samples changed with thermal ageing.

Figure 36: How the Young’s modulus of HDPE 1 mm sheet samples changed with thermal ageing.
### 3.1.2.2 1.5 mm Sheets

Figure 37 – Figure 41 show how the properties of HDPE 1.5 mm sheet samples changed with thermal ageing.

**Figure 37:** How the mass of HDPE 1.5 mm sheet samples changed with thermal ageing.

**Figure 38:** How the thickness of HDPE 1.5 mm sheet samples changed with thermal ageing.
Figure 39: How the longitudinal velocity of HDPE 1.5 mm sheet samples changed with thermal ageing.

Figure 40: How the shear velocity of HDPE 1.5 mm sheet samples changed with thermal ageing.

Figure 41: How the Young's modulus of HDPE 1.5 mm sheet samples changed with thermal ageing.

The ageing profile for the HDPE sheet samples was found to be very similar to that of the HDPE rod samples. One of the noticeable differences is that in the sheet
samples, the thickness was found to increase after thermal ageing. This is presumably because the material has been manufactured and processed in a different way to the extruded rod of HDPE. Another key difference is that the mass of the sheet samples decreased with oven ageing, whereas in the rod samples, it was found to increase. The decrease in mass observed in the HDPE sheet samples may be due to the loss of volatile compounds. These volatile compounds could be plasticiser molecules, which are often added to commercial plastics to give enhanced physical properties, such as flexibility and durability. Alternatively, they could be ageing products, such as short chain alkanes and alkenes. L. N. Dinh et. al. identified a range of outgassing species associated with HDPE in their study at elevated temperatures and in vacuum conditions.\textsuperscript{16}

The density of the sheet samples was not accurately calculated, so an estimate for density (965 kg m\(^{-3}\)) was used throughout in the determination of Young’s modulus. It has been assumed that the density did not change significantly throughout the ageing process, but this is not necessarily true. In order to verify whether the density did change during the ageing process, some future analysis would need to be carried out, possibly using pycnometry. Pycnometry is a technique which employs gas displacement to accurately measure the volume of a test sample. The density can then be calculated, if the mass of the test sample is known.

The degree of ageing was found to be slightly greater for the 1 mm samples than it was for the 1.5 mm samples; the total increases in Young’s modulus were approximately 7% and 5%, respectively. The reason for this may be due to the higher surface area to volume ratio of the 1 mm samples, in comparison to the 1.5 mm samples. As such, there was more of an interface with the air and the rate of thermo-oxidation was greater.

Another point to note is that the change in physical properties is not uni-directional. There are more local fluctuations in the velocity measurements for the sheet samples. There are two potential causes for this behaviour. The first is that chain scission reactions lead to the formation of smaller polymer fragments. These scission products may act as plasticisers and cause a decrease in Young’s modulus, as discussed in Section 3.1.1. The other potential cause is fluctuations in the lab temperature that were not accounted for. In order to help clarify this, future velocity measurements would need to be repeated in isothermal conditions. If the trends
persisted, then it could be confirmed that the fluctuations were due to mechanical changes in the material, rather than experimental errors.

### 3.2 *in situ* Measurements

Prior to commencing *in situ* studies into the effects of ageing on HDPE at 75 °C, an initial investigation into the long-term suitability of coupling agents between the ultrasonic transducer and the HDPE test samples was carried out. The requirements for an ideal coupling agent would be stability with regard to temperature and low chemical interaction with the sample. The coupling agents investigated included: water, Sylgard 184, two part epoxy and honey.

#### 3.2.1 Investigation into the Coupling Agents Between HDPE and the Ultrasonic Transducer

As described in Section 2.2.1, a coupling agent is used to transmit the ultrasonic wave between the probe and the test sample. It was also desirable that the coupling agent would act as an adhesive, so that the probe would be fixed to a single position on the sample, mitigating a potential change in velocity by variations in the thickness of the sample.

Water is an effective coupling agent for longitudinal waves at room temperature. However, it is not appropriate at 75 °C because it evaporates, which causes an air gap to be created between the ultrasonic probe and the test sample and consequently, causes the ultrasound signal to diminish. Additionally, water does not work as a coupling agent for shear waves because it lacks shear elasticity, which is a requirement for shear wave coupling agents. Sylgard 184 and epoxy were also evaluated. However, they could not be used as it was found that after curing between the probe and HDPE sample, they became detached from the surface of the HDPE. This was thought to be due to the low surface energy of HDPE.

Honey was eventually chosen as the coupling agent because it was the only remaining candidate which worked effectively at elevated temperatures, when tested on a reference block of stainless steel. Figure 42 and Figure 43 show how the
ultrasonic velocities change with time at 75 °C, when using honey as a coupling agent.

Figure 42: How longitudinal velocity through stainless steel changes with time at 75 °C.

Figure 43: How shear velocity through stainless steel changes with time at 75 °C.

The starting time value on the x axis in Figure 43 is 112.25 hours. The reason for this is the shear signal could not be observed up until this point. The coupling agent requirements for a shear wave are more particular than those for a longitudinal wave; shear waves can only be transmitted through solids or viscous liquids and the signal will diminish when the coupling agent is a runny liquid. At room temperature, honey is relatively viscous and can therefore transmit shear waves. However, when it is heated up, its viscosity decreases and its ability to propagate shear waves also decreases. During prolonged heating, water begins to evaporate from the honey and as a result, its viscosity gradually begins to increase. After a certain amount of time, its viscosity reaches a level where it becomes possible to propagate shear waves.
again. In this in situ experiment, this point was 112.25 hours, after which the measured shear velocity was reasonably constant.

There is generally very little variation in the ultrasound signals for both longitudinal and shear measurements with time at 75 °C. The maximum change in the velocities corresponds to the instrument detection limit and this explains the quantized appearance of the data in Figure 42 and Figure 43. The reason for the small variations in the signal is not fully understood. However, the cause may be something trivial such as the probe moving position on the surface of the stainless steel sample, or small fluctuations in oven temperature. Even if the variation was caused by an adverse effect from the coupling agent, the change is insignificant when compared to the ageing-induced change expected to be observed in HDPE. It can therefore be said that honey is an appropriate coupling agent for the purpose of this project, and ageing data can be confidently obtained whilst using honey.

Honey is not, however, a perfect coupling agent for this application. On heating the system (comprising the stainless steel test sample with honey coupled probes) from 25 to 75 °C, there was a decrease in the longitudinal velocity from 5.727 to 5.678 mm μs⁻¹. This is thought to be caused by an adverse effect from the coupling agent, rather than a change in the mechanical properties of the stainless steel. The main point of interest in the in situ analysis of HDPE is how the mechanical properties of the material change during prolonged heating at 75 °C, and the accuracy of the velocity measurements is of secondary importance. Consequently, the main requirement of the coupling agent in this experiment was that it provided stable velocity measurements at 75 °C and to this effect, honey was still a good candidate.

### 3.2.2 HDPE Rod

A section of the commercial grade HDPE rod (thickness = 19.25 mm) was measured by ultrasound using longitudinal waves. Measurements were taken in situ at 75 °C and are shown in Figure 45.

The longitudinal velocity at 75 °C was found to be significantly lower than that measured at room temperature (~ 1.83 and ~ 2.14 mm μs⁻¹, respectively). The reason for this is that as HDPE heats up, the polymer chains have more thermal
energy and freedom of movement. This leads to a decrease in Young’s modulus and a corresponding decrease in longitudinal velocity.

The effect of temperature on the mechanical properties of HDPE can be seen in Figure 44. This figure shows the data from a dynamic mechanical thermal analysis (DMTA) experiment. The graphs in green, blue and brown correspond to the storage modulus, loss modulus and tan delta, respectively. The different graphs within each set correspond to different frequencies that measurements were taken at.

Figure 44: DMTA data which shows how the mechanical properties of a commercial grade HDPE rod sample changed with temperature.

Figure 44 clearly shows that there is a decrease in the storage modulus with increasing temperature. As the temperature increases, larger scale movements in the amorphous phase occur and the material takes on a more liquid-like behaviour, with a corresponding decrease in the storage modulus. There is also an increase in tan delta, providing evidence for the increase in motion of the polymer chains with thermal energy. The small hump in the loss modulus graphs occurs at a similar temperature to the hump in the DSC trace in Figure 22, at around 50 to 60 °C. This may be the result of an inhomogeneity in the material or a relaxation phenomenon. It could also be an indication of a second-order melt transition. Because the synthetic route and processing history of the tested material were not known, this feature has not been conclusively identified.
Another contributor to the relative decrease in longitudinal velocity at 75 °C could be an effect from the coupling agent. A decrease in longitudinal velocity was observed in the coupling agent experiment (stainless steel sample with honey coupling agent) when the oven temperature was increased from room temperature to 75 °C, as can be seen in Figure 42. However, the decrease in velocity was significantly greater in the HDPE sample than it was in the stainless steel sample (~ 15% compared to ~ 1%, respectively). This confirms that there is a significant change in the mechanical properties of the material, induced by the change in temperature.

The changes described above are short-term reversible changes and are not associated with ageing. The trend which is shown in Figure 45 is, however, induced by ageing. The reasons behind the changes in longitudinal velocity here are the same as the reasons outlined in Section 3.1. The general upwards trend is caused by an ageing-induced increase in crystallinity and a corresponding increase in Young’s modulus. The key differences between the data in Figure 45 and Figure 25 are: the change in velocity is much smaller in the \textit{in situ} measurements (< 0.5% compared to > 10%) and there is an initial decrease in the longitudinal velocity in Figure 45 in the \textit{in situ} measurements.

There are two main reasons why the change in velocity is much smaller in the in situ measurements. Firstly, the sample in the \textit{in situ} measurements had a thickness of ~ 20 mm, compared to thicknesses of < 5 mm for the samples in the \textit{ex situ} measurements. This meant that the surface area to volume ratio was significantly smaller and the interface with the air was therefore smaller for the \textit{in situ} experiment. Since thermo-oxidative ageing occurs at a much higher rate than thermal ageing in
the absence of oxygen, a decrease in the surface area to volume ratio leads to a
decrease in the rate of ageing and the mechanical properties change at a slower
rate. The other factor is that the oven temperature was 75 °C in the in situ
measurements, compared with 110 °C for the ex situ measurements. The reason
why the in situ measurements were not carried out at higher temperatures was
because the functionality of the ultrasonic probes could be impaired at higher
temperatures (75 °C was the upper-most operating temperature).

It can be seen that there is an initial decrease in the longitudinal velocity within the
first 70 hours of thermal ageing at 75 °C (Figure 45). One reason may be the
plasticization effect from chain scission fragments (described in Section 3.1), which
caused a decrease in Young's modulus and a corresponding decrease in velocity.
But the more likely reason is that of experimental error. One of the experimental
errors was not being able to determine the thickness of the sample in situ; the initial
width of the sample at room temperature was used for all velocity calculations.

It is unlikely that the thickness of the sample remained constant throughout the
experiment, due to the effect of thermal expansion and possible strain relaxation. So
perhaps in this region of the graph, the sample was expanding in the direction being
measured, which caused the thickness to increase and therefore the distance that
the ultrasound wave had to travel to increase. This was not accounted for in
calculations, and so the result was an apparent decrease in velocity. In order to verify
this and enhance the experimental setup, some dilatometry testing is recommended
to calculate the thermal expansion coefficient of the material being analysed, and
obtain accurate information on the thickness of the material at a given temperature.
3.2.3 HDPE 1.5 mm Sheet

Figure 46 – Figure 48 show how the properties of an HDPE 1.5 mm sheet sample changed with thermal ageing.

Figure 46: How the longitudinal velocity of an HDPE 1.5 mm sheet sample changed with thermal ageing at 75 °C.

Figure 47: How the shear velocity of an HDPE 1.5 mm sheet sample changed with thermal ageing at 75 °C.
The apparent trends in Figure 46 – Figure 48 are similar to those shown in Figure 45 and can be rationalised using the same arguments, outlined in Section 3.1. The significant difference with the *in situ* analysis on the 1.5 mm sheet sample is that it was possible to take shear velocity measurements and hence, to calculate an estimate for Young’s modulus at varying degrees of thermal ageing time. This was possible because the HDPE sheet samples were thinner and had more parallel faces and as such, the shear wave was attenuated to a lesser extent. An interesting feature of Figure 48 is that the change in Young’s modulus is not uni-directional. This reflects the complex ageing profile of HDPE and reveals the competing nature of the ageing mechanisms, with regard to their effects on the mechanical properties of the material.

## 4 Conclusion and Future Work

It has been proven that ultrasound is sensitive enough as a technique to monitor the ageing-induced changes in the mechanical properties of HDPE. This has been shown by carrying out *ex situ* analysis on a range of HDPE samples which have been aged from 0 to 17 days at 110 °C. The data collected using ultrasound correlates well with DSC and DMA data. Ultrasonic evaluation has been developed further for *in situ* analysis of the ageing process. The data collected from *in situ* analysis is in line with expectations from the *ex situ* analysis. However, this technique is still in its development stage and there are several experimental errors that have not been accounted for in taking measurements.
The primary objective of the project was to determine if ultrasound could be used to monitor ageing-induced changes, rather than to calculate accurate values of mechanical properties. To this end, the work has fulfilled the objectives. One important consideration for future work on the ultrasonic analysis of HDPE (and indeed, of any polymer) is that polymers are highly attenuative materials. The techniques developed could, therefore, be optimized for small samples but are inherently flawed for samples of a greater thickness.

As mentioned in Section 1, proposed future work would be to develop the ultrasonic method to a point where it is possible to measure, in real time, the ageing-induced change in crystallinity of HDPE. To reach that stage, the accuracy of the velocity measurements would have to be significantly enhanced. For *ex situ* analysis, this would involve taking measurements in isothermal conditions, for example in a temperature-controlled lab. The situation is somewhat more complex for *in situ* analysis. This would first involve finding a better coupling agent which does not affect velocity measurements during heating. The other priority would be to determine how the dimensions of the test sample change with heating, using dilatometry. And finally, pycnometry should be carried out to calculate the density of the test sample and make the Young's modulus calculation more accurate.

## 5 References


