Electromechanical Response of Bulk PZT 95/5 and Associated Polymers across Temperature and Strain Rate

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Submitted in part fulfilment of the requirements for the Degree of Doctor of Philosophy of Imperial College London
Declaration of Originality

I hereby certify that, to the best of my knowledge, all material in this thesis is my own work except where otherwise acknowledged or referenced. This thesis has not been submitted for any degree or other purposes.
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Abstract

“It is the perfection of God’s works that they are all done with the greatest simplicity. He is the God of order and not of confusion.” - Isaac Newton

Piezoelectricity is the ability of certain, non-conductive, materials to generate an electrical charge when pressure is applied to them. The voltage produced is directly proportional to the applied stress. The amount of charge generated can depend on, for example, the applied strain rate or the temperature.

Due to this ability, piezoceramics, such as PZT ceramics, find use in many different applications, primarily as sensors or actuators. Sensors work by detecting pressure, mechanically deforming and thus producing a voltage. Actuators, on the other hand, mechanically deform upon application of an electric field.

To develop a better understanding of the piezoelectric ceramic lead zirconate titanate (PZT) 95/5, a range of studies including varying temperatures, porosities, and strain rates have been conducted. The effects on the voltage output and failure of poled PZT samples of different porosities have been investigated using different compressive strain rates ($10^{-4}$ - $10^4$ s$^{-1}$), reached with quasi-static loading equipment, drop-weight towers, and Split Hopkinson Pressure Bars (SHPBs). The main cylindrical specimens were of 4.4 mm diameter, thickness 0.8 - 4.4 mm, and density 7.3 - 8.3 g cm$^{-3}$. The temperature range of $-20 \degree C$ to $+80 \degree C$ was achieved using purpose-built environmental chambers. The resulting stress-strain relationships are compared; all the samples ultimately displaying a brittle response at failure [1].

To support this work, ideal geometric specimen sizes were identified for the different types of loading experiment, by carrying out a range of strain-rate compression experiments on well-studied materials such as aluminium and copper.

In addition, different experimental platforms were successfully developed in order to reach non-ambient temperatures in the Split Hopkinson Pressure Bar experiments.

Finally, as piezoceramics, when used in real world applications, are often coated in protective layers of polymer, several different types of industrial polymer have been characterised across the full range of strain rates and temperatures.

I ask Almighty Allaah to accept this work, and make it sincerely for Him Alone, and to help the people to benefit from it, for He is the Hearer, the Answerer. Indeed He has power over all things.
And the last of their call will be, "Praise be to Allaah, Lord of the worlds!" - Al-Qur’an [10:10]
Acknowledgements

Indeed, all praise is for Allaah, Lord of the worlds; we praise Him, repent to Him, and seek His forgiveness and help. Peace and prayers be upon Muhammad, his family, his Companions, and all those who follow in their footsteps until the Last Day.

The Institute of Shock Physics acknowledges the support of the Atomic Weapons Establishment (AWE), the Royal British Legion Centre for Blast Injury Studies, Thales Group, and Imperial College London.

Thanks go to Thales for providing two of the epoxy resins used to help prepare the temperature systems, and for permitting me to use the data gleaned for my written work. Many thanks to Ken Kos and James Evans, of AWE, for supplying the ceramic materials for the PZT tests, and to Dr. William Proud, of Imperial College London, for giving me this opportunity. Thanks also to Dr. Jens Balzer and Dr. James Wilgeroth, formally of Imperial College London, for setting me on my way, as well as for the initial work carried out on the Thales polymers.

These experiments would not have been possible without the support, training, and technical advice of a number of people. In particular, I would like to thank David Williams and Paul Brown from the Physics Workshop, as well as Melvyn Patmore from the Optics Workshop and Dr. Miriam Miranda Fernandez from the Department of Materials, for all their help in sample preparation. Many thanks also to Amine Halimi, of the Electrical and Electronics Department, for constant (and sometimes last-minute!) circuit support.

Laboratory access and equipment use was only achieved due to the patience and assistance of both Andy Pullen and Suresh Viswanathan Chettiar, from the Civil and Mechanical Engineering Departments respectively. Many thanks also to Patricia Carry, from the Department of Chemical Engineering, for access to labs, as well as for carrying out DMA analysis on our behalf.

In addition, special gratitude is reserved for Dr. Siti Rosminah Shamsuddin from the Chemical Engineering Department, for technical support and useful discussions, Mohamed Ali for all his ICT support, and for Uswah Khairuddin from the Mechanical Engineering Department, for all her patient help with programming. Many thanks also to my students, Nafisah Mohd Rafiq and Mehrnaz Dehghan-Nayeri, for their assistance in data collection and for agreeing to work highly unsociable hours, as well as lending me their company and humour.
I would also like to thank my good friends in and around Imperial College London, as well as the Islamic Society and its Prayer Room, for helping keep my life entertaining, steady, and sane. In particular, I’d like to give credit to Sadia, Ros, Hafiza, Saira, Dinah, and Shajna, for the walks, talks, and eats.

Particular mention must go to Arsenal Football Club, for giving my heart a fantastic workout these past years, and Southern Railway, for testing my patience. Thankfully, I was able to emerge from this particular contest victorious.

Shukran katheeran to my grandparents, aunts, uncles, and cousins, for the plentiful encouragement and the entertainment supplied generously. However, the utmost gratitude is reserved most especially for my immediate family, without whose love, patience, and support I would not have reached this, nor any, stage in my life. Shaboo and Taqu, Souki Machli and Sunny Bunny, but especially Mum and Dad, may Allaah have mercy on all of you. I ask God Almighty to protect you and to reward you infinitely, both in this life and the next, and I apologise for all the grey hairs.

“My Lord! Bestow on them Your Mercy as they did bring me up when I was small.” - Al-Qur’an [17:24]
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And We certainly gave David from Us bounty. 
[We said]: “O mountains, repeat [Our] praises 
with him, and the birds [as well].” And We made 
pliable for him iron, [Commanding him]: “Make 
full coats of mail and calculate [precisely] the 
links, and work [all of you] righteousness. Indeed 
I, of what you do, am Seeing.”

Sheba 10-11

Chapter 1

Introduction

This research seeks to develop a better understanding of the electromechanical behaviour of the piezoelectric ceramic lead zirconate titanate (PZT) 95/5 with varying temperatures, porosities, and strain rates. Various other materials, including metals and polymers, were studied to help develop the equipment required for experimentation, as well to identify the best specimen geometry to use.

1.1 Motivation

Piezoceramics have a wide range of uses, with applications making use of either the converse or the direct piezoelectric effect. The direct piezoelectric effect is the generation of electrical charge upon application of pressure, whilst the converse piezoelectric effect is the generation of stress on application of an external electric field. As an example, atomic force microscopy takes advantage of the fact that applying an electric field across a piezoceramic can alter its shape, useful for high precision, three-dimensional positioning [6]. Piezoceramics are also heavily used in aircraft and spacecraft systems, in vibration cancellation and optical positioning [7].

In these examples, as well as many others, the piezoceramic components are exposed to a range of storage and operating temperatures. However, there is surprisingly very limited data on the combined temperature-strain rate behaviours of bulk piezoceramics.

For a material to exhibit the piezoelectric effect, its crystal structure must be non-centrosymmetric. Applying a mechanical stress to a piezocrystal induces strain, causing its ions to move relative to one another, and thus creating dipoles. If these dipoles do not cancel each other out, this application of pressure creates net polarisation, resulting in electric charge developing across the material. The amount of charge generated can depend on both the applied strain rate and temperature.

The PZT studied here is 95% lead zirconate and 5% lead titanate, with no added dopants, and is a piezoceramic that is both pyroelectric (affected by temperature), and ferroelectric (having spontaneous polarisation). Many ceramics have some degree of poros-
ity, and bulk PZT can be made more porous by the controlled addition of a poreformer [8]. In some cases, such as thermal insulation, a high degree of porosity is vital [9].

Previous experiments on piezoelectric ceramics have shown that, with increasing porosity, many of their mechanical properties, such as elastic moduli, strength, and toughness, decrease [10]. Fracture energy appears to have a more gradual decrease with porosity than fracture toughness [9].

Pores can act both as micro-crack initiation sites and as channels for propagating these micro-cracks. Many pores link together to form the path of least resistance for the crack. The presence of the pores thus strongly affects the compressive strength of a ceramic material [11]. It has been found that more porous materials exhibit lower fracture toughness at low strain rates [12]. For PZT 95/5 doped with 2% niobium (Pb_{0.99}Nb_{0.02}(Zr_{0.95},Ti_{0.05})_{0.98}O_{3}), it has been seen that pore collapse begins somewhere between 400 - 800 MPa under strain rates between $10^{-4}$ - $10^{-2}$ s$^{-1}$ [13]. It also appears that both the mechanical and electrical properties of PZT 95/5 are sensitive to the level of porosity, but insensitive to pore morphology [14].

A general observation for ceramics between room temperature and the onset of grain boundary softening is that the Young’s modulus and the shear modulus decrease $\sim$1% per hundred kelvin increase [9]. The softening temperature is considerably below the melting temperature of typical crystalline ceramics [15].

Finally, it has been observed that the effective transverse piezoelectric coefficient increases, with a smaller temperature dependence for piezofilms compared to bulk piezoceramics [16].

Whilst much is already known about the general nature and behaviour of many ceramics, significant temperature and porosity studies have yet to be carried out specifically on undoped PZT 95/5 at medium to low strain rates. It is hoped that the research described here will provide a useful data source for future comparison, and go some way to filling a current gap in our understanding of the electromechanical behaviour of these piezoceramics.
1.2 Thesis Structure

Chapter 2 describes the manufacture and usage of piezoelectric ceramics, as well as their
generation of electric charge due to the application of stress. In addition, a description
of the compressive failure of brittle materials is included, with an overview of known
environmental and material effects. A brief introduction on the polymers used to coat
the piezoceramics in practical applications is also included, with a particular focus on the
time-temperature superposition principle.

In Chapter 3, the different mechanical experiments used to characterise the dynamic
stress-strain behaviour of materials are detailed. Developments to allow temperature tests
to be performed, as well as to measure the voltage output from piezoelectric materials,
are explained.

In Chapter 4, the results of preliminary experiments conducted to determine the ideal
specimen geometry to use in compression experiments are presented, elucidating the ef-
fects of both inertia and friction on the observed stress-strain behaviour of several well-
characterised materials.

Chapter 5 introduces the results of aspect ratio, temperature, and strain rate effects
on the mechanical behaviour of several polymers, with a detailed discussion on the time-
temperature superposition principle.

Chapter 6 summarises the results of investigations into the electromechanical behav-
ior of the piezoelectric ceramic PZT 95/5 across a range of strain rates, with partic-
ular focus on the effects of temperature and porosity.

1.3 Publications

- **Khan AS** and Proud WG (2017) Temperature and strain rate effects on the piezo-
electric charge production of PZT 95/5 *AIP Conf. Proceedings* **1793** 100037

- **Khan AS**, Wilgeroth JM, Balzer JE, and Proud WG (2017) Comparison of epoxy-
-based encapsulating materials over temperature and strain rate *AIP Conf. Proceed-
ings* **1793** 110017

- **Khan AS**, Balzer JE, Wilgeroth JM, and Proud WG (2014) Temperature effects
on the mechanical behaviour of PZT 95/5 *J. Phys.: Conf. Ser.* **500** 112038

- **Khan AS**, Balzer JE, Wilgeroth JM, and Proud WG (2014) Aspect ratio compres-
sion effects on metals and polymers *J. Phys.: Conf. Ser.* **500** 182019
Chapter 2

Piezoceramics

Piezoelectricity is the ability of certain non-conductive materials to generate an electrical charge when pressure is applied to them [17]. The voltage produced is directly proportional to the applied stress and can depend on, for example, the applied strain rate or the temperature.

The direct piezoelectric effect was first demonstrated in 1880 by the Curie brothers Pierre and Jacques, drawing on previous work carried out during the 1700s on pyroelectricity [18]. Pyroelectricity is the ability of certain materials to generate a temporary voltage in response to a temperature change [19]. Following a detailed study on the pyroelectric effect by Carl Linnaeus and Franz Aepinus, both René Just Haüy and Antoine César Becquerel predicted a relationship between mechanical stress and electric charge, although neither was able to conclusively demonstrate this [18].

Combining developments in pyroelectric studies with their understanding of the crystal structures which gave rise to the pyroelectric effect, the Curie brothers were able to predict the behaviour of different crystal structures under applied loading [20], and went on to demonstrate the piezoelectric effect in crystals of a number of different materials, including tourmaline, quartz (SiO$_2$), and Rochelle salt (sodium potassium tartrate tetrahydrate), the latter two materials exhibiting the greatest amount of piezoelectricity [18]. However, this discovery was of no practical use at that time, since the piezoelectric effect of these natural materials is small and thus the voltages created too small to be exploited. That was until the outbreak of World War I, during which very high input impedance amplifiers were built, enabling engineers to amplify the electrical signals generated by the piezocrystals [21].

Other naturally occurring piezoelectric crystals include sucrose, silk, enamel, and collagen, found in bone (dry bone exhibits some piezoelectric properties due to the presence of apatite crystals, and the piezoelectric effect is generally thought to act as a biological force sensor [22]). However, it is also possible to manufacture polycrystalline piezoelectric materials with enhanced piezoelectric properties, known as piezoceramics, which are forced to become piezoelectric on application of a large electric field during manufacture [17].
These synthetic substances include barium titanate (BaTiO$_3$), the first piezoelectric ceramic to be discovered [23], and lead zirconate titanate (PZT), the material of interest in this thesis.

## 2.1 Origins of Piezoelectricity

The piezoelectric effect can only happen in non-conducting materials. Piezoelectric crystals acquire a charge when mechanically stressed, either from compression, twisting, or distortion [24]. The word piezoelectric is derived from the Greek word *piezein*, which translates as “to press tight”, or “squeeze” [25]. The piezoelectric effect is linked to the presence of electric dipole moments in solids, which can be induced, as in the synthetic ceramics BaTiO$_3$ and PZT, or directly carried by molecular groups, as in cane sugar [17].

### 2.1.1 Mechanism

When a mechanical stress is applied to a piezoelectric material, the lattice structure of the crystal twists and changes shape, such that the ions in the structure separate and move relative to one another [26]. This displacement of ions, and therefore of charge, results in a dipole moment. In materials with a perovskite structure (see Sec. 2.3), such as PZT, the dipole is created by movement of the central ion in the structure (usually a large metal ion). For a net polarisation to develop, the dipole formed must not be cancelled out by other dipoles in the unit cell, and can therefore only occur in crystals that have a non-symmetrical unit cell [18]. Materials which are centrosymmetric (see figure 2.1), when placed under stress, experience symmetrical movement of ions, meaning there is no net polarisation. Therefore, the piezoelectric atomic structure must be non-centrosymmetric, i.e. there must be no centre of symmetry (see figure 2.2). If, under no applied stress, the ions in the crystal structure are in positions which do not allow any net dipole moment to be formed, the piezoelectric materials are known as non-spontaneously polarised. Ferroelectric materials are spontaneously polarised (see Sec. 2.1.2) [25].

![Figure 2.1: A centrosymmetric crystal structure.](image1)

![Figure 2.2: A non-centrosymmetric crystal structure.](image2)
When a non-centrosymmetric piezoelectric crystal is compressed or stretched, the ions in each unit cell are displaced, causing electric polarisation of the unit cell. Because of the material’s regular crystalline structure, the dipole moment appears in every unit cell in the crystal and the effects accumulate, resulting in the appearance of an electric potential across certain faces of the crystal. This pressure-generated electric charge is exactly proportional to the force acting on the crystal, and is measured in pico-coulombs (pC) [27].

Groups of unit cells whose dipole moments have the same orientation are called Weiss domains [28]. In a monocrystal, the polar axes\(^1\) of all the dipoles lie in one direction (see figure 2.3). If the crystal is cut at any point, the polar axes of the two separate pieces still lie in the same direction as the original crystal, and the crystal is said to be symmetric. However, in a polycrystal, each domain within a material is randomly distributed, such that its moment is not aligned with those around it (see figure 2.4). This crystal is asymmetric, as there is no point at which the crystal could be cut leaving two pieces with the same polar axis as the original [27].

Unpoled piezoceramics are polycrystalline; their dipole moments are randomly aligned. Therefore, although the lattice structure deforms and becomes asymmetric under applied stress, creating dipole moments and thus an electric charge on the material’s crystal surfaces, no overall macroscopic piezoelectric behaviour is detected. However, it is possible to produce a piezoelectric effect if the material is poled, although it is not possible to pole all piezoelectric materials. This process involves applying a strong external electric field (10 - 100 kV cm\(^{-1}\) [29]) to the polycrystal, which causes the material to expand along the axis of the field, but contract perpendicular to this direction.

\(^1\)The polar axis is an imaginary line that runs through the centre of both charges in a molecule.
The entire material will not necessarily be completely poled the first time an electric field is put across it (see figure 2.5). For this reason, the material is often put through a hysteresis loop several times, or the electric field is held for a long time [30], to force the dipoles in the crystal to line up and face the same direction. The majority of the dipoles remain in this orientation even after the removal of the applied electric field [31]. However, this remnant polarisation can be reduced on exceeding the mechanical, thermal, and electrical limits of the material (see Sec. 2.1.3.1).

Some PZT ceramics must also be heated during poling to become piezoelectric, as the heat enables the atoms to move more freely [30]. It has also been observed that the width of the domain increases with increasing temperature, as the phase transition is approached [29]. However, some authors have demonstrated that PZT can be poled successfully at room temperature, if a field slightly larger than the coercive field is applied [30]. This is because the ferroelectric/anti-ferroelectric phase boundary is quite close to the room temperature/pressure state [32].

This poling process can only occur at temperatures below the Curie point, the temperature above which spontaneous polarisation is lost [21]. Before poling, the piezocrystals
Figure 2.7: The direct piezoelectric effect.

have isotropic symmetric cubic unit cells, but exhibit tetragonal symmetry (anisotropic structure) after poling (see figure 2.6). This is because the central ion in the crystal lattice moves out of the plane of the structural ions, causing an imbalance in the charge distribution and thus creating a dipole [30]. Above the Curie temperature, the crystal structure changes; the central ion remains generally in the plane of the structural ions and the material is no longer able to demonstrate the piezoelectric effect [27].

Once the material has been poled, it is able to demonstrate a detectable piezoelectric effect (see figure 2.7). Upon compression of the material, a voltage with the same polarity as the poling voltage can be observed using attached electrodes. Conversely, if the material is stretched, the voltage observed will be of opposite polarity [31].

2.1.2 Ferroelectricity

Ferroelectric materials are also piezoelectric, in that their polarisation changes when mechanical stress is applied to them [33]. All ferroelectrics are both pyroelectric and piezoelectric, but not all piezoelectric materials are ferroelectric or pyroelectric (see figure 2.8) [34]. Heating of a pyroelectric material usually reduces the amount of polarisation detected [19]. Unlike piezoelectric materials, where there is a linear increase in the charge detected under stress, ferroelectric materials initially produce no charge at all, but ‘switch on’ suddenly as a critical pressure is exceeded.

In a piezoelectric which is not ferroelectric, there is no spontaneous polarisation. Assuming the piezocrystal is homogeneous, an applied stress will generate a polarisation in every unit cell. This polarisation is therefore the same throughout the crystal, and will cause a charge to be developed on the surfaces of the piezoelectric. If this procedure takes place while the piezoelectric is in a closed circuit, a current will be recorded, produced by the movement of charge from one face of the crystal to another [21].

Ferroelectric materials are spontaneously polarised [35]. Applied compressive stress
can increase or decrease the polarisation, as well as having no effect at all. This is because the polarisation of a ferroelectric crystal depends on the orientation of the many domains in the ferroelectric crystal, and they are not always oriented in the same direction [33]. Poling of a ferroelectric, much in the same way as any piezoelectric, can align the multiple dipole moments. After application of the external electric field, the domains in the ferroelectric material have a dipole moment pointing in the same direction, so there is a net spontaneous polarisation. On mechanically stressing the material, this polarisation can increase or decrease, but the polarisation will remain in the same direction [35].

Ferroelectrics, just like piezoelectrics, must be non-centrosymmetric [33]. This is because, if the crystal structure had a centre of symmetry, any dipole moment generated in one direction would be forced, by symmetry, to be zero. Ferroelectrics must also have a spontaneous local dipole moment, which can be switched in an applied electric field (i.e. they must possess spontaneous switchable polarisation), and must therefore have a central atom displaced to a non-equilibrium position. There is therefore an inherent dipole moment in the structure, resulting in polarisation. However, how the properties of ferroelectric materials vary on a micro-scale is yet to be properly understood [25].

2.1.3 Polarisation

The change in polarisation when applying a mechanical stress is significantly linked to the piezoelectric effect [33], and can come about either because of re-alignment of the molecular dipole moments under external stress (noticeably in ferroelectric materials), or because this external stress causes a change in the lattice structure, which itself induces dipole moments\(^2\) within. Piezoelectricity can then arise because of varying polarisation strength or direction, as well as manifesting itself as a combination of both, depending on the orientation of polarisation within the crystal, crystal symmetry, and the applied mechanical stress.

\(^2\)The dipole moment is defined as the magnitude of the charge multiplied by the separation distance of the charges, \(\mu=qr\).
The dipole density, or polarisation, $P$, of a crystal can be calculated by summing up the individual dipole moments of each unit cell, and is defined as the dipole moment, $\mu$, per unit volume, $V$, with units [Cm m$^{-3}$]:

$$P = \frac{\Sigma \mu}{V} \quad (2.1)$$

As every dipole is a vector, the dipole density $P$ is also a vector (a quantity with direction). Application of mechanical stress generates polarisation in every unit cell of a homogeneous crystal, resulting in a charge, $Q$, on the surface of a piezoelectric material. This polarisation can therefore also be described as the charge per unit area, $A$, developed on the surface of the crystal:

$$P = \frac{Q}{A} \quad (2.2)$$

This polarisation is directly proportional to the stress, $\sigma$, applied to the material:

$$P = d\sigma \quad (2.3)$$

where $d$ is the piezoelectric coefficient, the volume change when a piezoelectric material is subject to an electric field. While this is a direct effect, the applied stress can be multi-axial, in which case $d$ can be an array of coefficients.

Note, however, that piezoelectricity is not caused by a change in charge density on the surface, but by dipole density in the bulk. While this is a direct effect, the applied stress can be multi-axial, in which case $d$ can be an array of coefficients.

In summary, application of a mechanical stress to a piezocrystal alters its crystal structure, and the ions move with respect to each other, forming a dipole. To develop charge, the crystal structure must be non-centrosymmetric such that the dipole is not cancelled out; net polarisation results in the occurrence of the piezoelectric effect.

### 2.1.3.1 Depolarisation

It is possible for remnant polarisation after poling to be reduced, due to the alignment of dipoles decaying [31]. Depolarisation of the poled materials, and therefore loss of their piezoelectric properties, can occur in three significant ways [37]:

**Thermal Depoling** Heating a piezoelectric material up to its Curie temperature will cause the dipole moments to once again become misaligned. At the Curie temperature, a ferroelectric becomes completely unaligned, and thus completely loses its piezoelectric properties.

**Electrical Depoling** Applying a strong electric field in the opposite direction to the already poled material will depolarise the piezoelectric material. It is possible to use an alternating field, in which case the piezoelectric will only depolarise during the periods where the field opposes the polarisation.
Mechanical Depoling If the applied mechanical stress on the material exceeds a critical level, the atom positions are altered, thus leading to depolarisation of the piezoelectric material [38].

2.1.4 The Converse Piezoelectric Effect

One of the unique characteristics of the piezoelectric effect is that it is reversible. This means that materials which exhibit the direct piezoelectric effect (the generation of electricity on application of stress) also exhibit the converse piezoelectric effect, i.e. the generation of stress on application of an external electric field. The piezoelectric material mechanically deforms, and can either shrink or stretch [24].

When an electric potential is applied to a piezoelectric crystal, a dipole moment is created to oppose this external field, caused by the motion of the ions in each unit cell. This causes a mechanical distortion in the lattice structure, causing the crystal to contract or expand (see figure 2.9). As this occurs throughout the crystal, there is a detectable shape change; however, as there are a large number of unit cells in a crystal, the actual overall shape change is small (the maximum strain usually observed is \( \sim 0.1\% \)) [39].

This converse piezoelectric effect is described by the following equation:

\[
\varepsilon = dE
\]  

(2.4)

where \( \varepsilon \) is the strain, \( E \) is the electric field, and \( d \) is the same piezoelectric coefficient as used in the equations for polarisation (see Sec. 2.1.3).

When an electric potential is applied to a poled piezoelectric material, the dimensions of the individual Weiss domains change, proportional to the voltage. A voltage with the opposite polarity as the poling voltage will cause the piezocrystal to expand, whilst a voltage with the same polarity will cause the material to compress. If an alternating electric current is applied, the piezocrystal vibrates mechanically, with the same frequency
as the oscillating signal (see figure 2.9). The rapid shape changes produce high frequency sound waves, and can therefore be used to provide an ultrasonic sound source, like that used in medical ultrasound imaging [40]. The piezoelectric crystal can vibrate in different modes depending on the applied frequency, and can be made into a variety of shapes to achieve these different vibration modes. This produces a convenient transducer effect between electrical and mechanical oscillations. Piezoelectric materials can also therefore be used, for example, in different scanning microscopes [24].

The converse piezoelectric effect was mathematically calculated by Gabriel Lippmann, a year after the discovery of piezoelectricity, but it was the Curie brothers who were able to experimentally confirm its presence in piezoelectric crystals [24].

2.2 Uses

The piezoelectric effect was first exploited during World War I when quartz, which is also extremely stable, came to be used in sonar [18]. Quartz is now primarily used in watch crystals, and for precise frequency reference crystals in radio transmitters, and was replaced as the most commonly used piezoelectric during World War II by the synthetic ceramic barium titanate, which has advanced to become one of the most important piezoelectric materials in the world [34]. Most of the piezoelectric materials in use in the modern day are ferroelectric synthetic ceramics (see Sec. 2.1.2), as a result of their unusually high dielectric constants (ε for PZT can be up to 6000, depending upon doping and orientation), as well as their ability to produce larger voltages when stressed [17]. Initially, these materials were used in high-dielectric capacitors, but then came to be used in piezoelectric transducers, positive temperature coefficient (PTC) devices, and electro-optic light valves [21]. More recently, ferroelectric ceramics have been employed as high displacement piezoelectric actuators (see Sec. 2.2.1) [35] and in ultrasonic transducers, for example, in medical ultrasound imaging. Whilst ultrasound has a wide range of medical and industrial applications (ultrasonic time-domain reflectometers are used in structural engineering to find flaws inside cast metal and stone objects), it can also be exploited commercially, for example in television remote controls, as well as in echolocation devices to aid drivers in parking their cars [40].

After the Second World War, there was an increase in the number of piezoelectric materials discovered and utilised, across a variety of fields [18]. Naturally occurring Rochelle salt produces a comparatively large voltage upon compression, and was used in early crystal microphones [21]. Ceramic phonograph cartridges reduced the cost and maintenance of record players, as well as making them easier to build [35]. Piezoceramics were developed for use in radios and televisions, and have wide usage in acoustic applications [23]. A common use of piezoelectrics is within ignition sources, which work by the generation of sparks on the compression of a ceramic disc [41]. Piezoelectric ceramic materials have
also found use in the control of scanning tunnelling microscopes, due to their ability to produce motions on the order of nanometres (see Sec. 2.1.4) [42].

Currently, the most commonly used ferroelectric material is lead zirconate titanate (PZT) [33]. However, there has been a recent drive by many governments across the world to reduce the industrial use of lead and lead-containing materials [43]. Although the lead in PZT is chemically bound within its crystalline structure, and there is no evidence that this lead can leak out into, and affect, the environment, there has been a marked development in the studies of lead-free and polymer-based piezoelectric materials, particularly in the Far East [44].

### 2.2.1 Sensors and Actuators

Piezoceramics, such as PZT ceramics, are used in many different applications, primarily as sensors or actuators [45]. Sensors work by detecting pressure, mechanically deforming and thus producing a voltage. Actuators, on the other hand, mechanically deform upon application of an electric field [46].

Different types of piezoelectric sensor can be made, to detect three different modes of loading: longitudinal, transversal, and shear. Piezo-materials are therefore useful in strain gauges [47], particularly for detecting stress waves, for example in the Split Hopkinson Pressure Bar (see Sec. 3.4). Piezoelectric materials are also used in highly sensitive chemical and biological sensors as microbalances, as well as for power monitoring in high power applications, for example in medical treatments and in industrial processing [48]. Piezoelectric transducers are often used in the automotive industry to detect engine knock (detonation) at certain frequencies, as well as in fuel injection systems to determine engine load (by measuring manifold absolute pressure (MAP)) [49].

The most commonly used sensors detect pressure variations in sound; for example, piezoelectric crystals in microphones are bent by sound waves, producing a changing voltage [21]. Piezoelectric sensors can also be used in ultrasonic transducers for high frequency sound, as in medical imaging [35]. In this case, the sensor is also used as an actuator, whereby the sensor is affected by voltage and mechanically deforms. The name transducer is often used when the device can act as both a sensor and an actuator [50]. (Note Most piezodevices have this characteristic of reversibility, as piezocrystals can demonstrate both the direct and the converse piezoelectric effect, but both effects are not always employed in every device [51]). Ultrasonic transducers can send ultrasound waves into a body, receive the reflected wave, and then convert this pressure into an electrical signal. As mentioned in Sec. 2.2, quartz was used in World War I to both generate and detect sonar waves [22]. Piezoelectric transducers are also used in electronic drum pads [21].

Devices used primarily as actuators include loudspeakers, in which an applied voltage
causes a piezoelectric film to vibrate mechanically [29]. As a very large electric field is required to mechanically deform a piezoelectric crystal just a little, it is possible to alter these widths on the order of micrometres. Therefore, piezocrystals are widely used to position objects with extreme accuracy, particularly in two types of actuators: direct and amplified piezoelectric [46]. These actuators are used in laser mirror alignment, as they can move large masses over microscopic distances, thus accurately maintaining optical conditions inside the laser cavity and therefore optimising the beam output. The actuators can also be used for fine-tuning the laser’s frequency [52]. This level of accuracy is exploited in atomic force and scanning tunnelling microscopes to keep their sensing needles close to the probes, as well as for micro-scanning in infrared cameras. Actuators are also used on a larger scale for careful and precise movement of a patient within an active CT or MRI scanner [7].

Quartz clocks use a crystal oscillator made from a quartz crystal. Both the direct and converse piezoelectric effect are used to generate regular electrical pulses to mark time. The quartz crystal, like all elastic materials, has a precise natural frequency at which it oscillates, which is used to stabilise the frequency of the applied periodic voltage to the crystal [24]. This property is used in all radio transmitters and receivers, as well as in computers. However, these all use a frequency multiplier to achieve gigahertz ranges [7]. PZT piezoceramics have also found use in pulsed power applications [53].

Piezoelectric materials for sensor and actuator elements must exhibit very high mechanical strength and rigidity, as well as having stable mechanical and electrical properties over a wide temperature range and a long service life [42]. High sensitivity, good linearity, negligible hysteresis (i.e. identical rising and falling calibration curves), and high electrical insulation resistance are further advantageous characteristics [54]. Many synthetic ceramics are used in these devices, as they demonstrate these required properties.

2.3 Ceramic Materials

A ceramic material is an inorganic, non-metallic, material, usually with a crystalline, or partly crystalline, structure, and usually consisting of grains. Ceramics are generally made from compounds of metals and non-metals, and can be described as a lattice with a basis because the atoms are non-identical. Some elements, such as carbon and silicon, can also be considered as ceramics [3]. The crystal structure of ceramics is more complex than metals. Ceramic materials, which can include oxides, nitrides, and carbides, are typically prepared using a sintering process. The heating and subsequent cooling of the solid causes it to gain mechanical strength, as well as giving it a smooth, coloured surface. The word ceramic is derived from the Greek word keramikos, which translates as “of pottery” [3].

Glass is often not considered a ceramic [3], due to its amorphous, non-crystalline, nature. However, the manufacture of glass makes use of several of the steps used in
producing ceramics, and it has many similar mechanical properties to ceramic materials. Generally, glasses are formed in melts, and shaped by casting when fully molten, or earlier, by blowing to a mould. Glasses are transparent as they have no grain boundaries to scatter the light. Subsequent annealing can cause this glass to become partly crystalline, at which point the material becomes a glass-ceramic, and can find use in cooktops [55].

Historically, pottery has been hugely important across the world, with the earliest known pottery objects (discovered in modern-day Czech Republic) dating back to around 29,000 - 25,000 BC. Pottery vessels from 16,000 BC have been found in southern China, as well as in Sub-Saharan Africa, dating from 11,000 - 10,000 BC, and in South America, from 10,000 BC [56]. Until the mid-twentieth century, the most commonly used ceramics in the modern world were not only pottery, but also bricks, tiles, and cement. All these ceramics are made wholly or partly of clay, exploiting minerals such as kaolinite [57].

A variety of different ceramic materials are now used in domestic, industrial, and building products, and use materials such as aluminium oxide (Al₂O₃), or alumina [58]. Modern, or advanced, ceramic materials include carbides of both silicon and tungsten, and have enhanced properties, such as abrasion resistance, making them of great use in industrial applications, for example as wear plates of crushing equipment in mining operations [59]. Advanced ceramics have also found use in medical, electrical, and electronic applications. Ceramic materials have a great range of useful properties, such as their strength, but their properties also vary widely. For example, porcelain (a silicate ceramic containing silicon oxide [57]) is useful in making electrical insulators, whilst other ceramic compounds are superconducting.

Many of the modern synthetic piezoceramics, such as BaTiO₃ (the first piezoelectric ceramic discovered), Zn₂O₃, and PZT, have a crystal perovskite structure, the same as the natural compound calcium titanium oxide (CaTiO₃), first discovered in 1839 by Gustav Rose in the Russian Ural mountains. The structure takes its name from the Russian mineralogist L.A. Perovksi (1792 - 1856) [60]. The general chemical formula for perovskite compounds is ABX₃, where ‘A’ and ‘B’ are two different-sized cations (the ‘A’ atoms are larger than the ‘B’ atoms, with a valence of ‘A’ cations from +1 to +3, and of ‘B’ cations between +3 and +6 [29]), and ‘X’ is an anion that bonds to both. Most common perovskite compounds are oxides and, as such, this ‘X’ is the oxygen atom, which appears in the face centre of the cubic unit cell (see figure 2.10).

Typically, in such a unit cell, the ‘A’ atom sits at the cube corners, whilst the ‘B’ atom sits at the body centre positions. Even slight alterations in the relative ion sizes and positions affect the cell’s properties such that, for example, if a comparatively smaller ‘B’ cation is positioned slightly off-centre within its octahedron, it will attain a stable bonding pattern. This results in an electric dipole, responsible for the ferroelectric nature demonstrated by many piezoceramics. If there are two different cations in the ‘B’ positions, the perovskite structure becomes complex, and there are now also the possibilities of ordered
and disordered variants [61].

Many high temperature superconducting ceramic materials also have perovskite-like structures. They often have three or more metals, including copper, and some vacant oxygen positions. One example is yttrium barium copper oxide, which can be insulating or superconducting depending on the material’s oxygen content. Other ceramic superconductors include bismuth strontium calcium copper oxide and magnesium diboride (MgB$_2$) [62].

Due to their wide-ranging properties (see Sec. 2.4), synthetic ceramics have found use in several differing applications. For example, titanium carbide is used in space shuttle re-entry shields, whilst uranium oxide is the fuel in nuclear reactors [63]. Zinc oxide is a semiconductor and therefore used in varistors, whilst silicon nitride is used as an abrasive powder. A possible replacement in the future for platinum in catalytic converters in diesel vehicles is a cobalt-based perovskite material. Barium titanate, just like lead zirconate titanate, displays a ferroelectric behaviour, and is used in electromechanical transducers, ceramic capacitors, and data storage elements [58].

2.3.0.1 PZT

Lead zirconate titanate, or PZT, was developed at the United States National Bureau of Standards in 1954 [33]. It has now overtaken barium titanate as the most commonly used piezoelectric ceramic, due to its higher sensitivity and higher operating temperature [33]. PZT is both ferroelectric and pyroelectric, meaning that its mechanical, electrical, and thermal responses are inter-related, as well as being history-dependent. PZT is a creamy-white solid, insoluble in all solvents, and is formed under extremely high temperatures, with the particulates filtered out using a mechanical filter.

The chemical formula of PZT is Pb(Zr$_x$Ti$_{1-x}$)O$_3$, where $0 \leq x \leq 1$. PZT has a perovskite structure, with the Zr and Ti ions randomly placed in the ‘B’ sites [33]. Changing the value of $x$ can change the composition of PZT, and therefore its properties [64], as shown
Figure 2.11: The phase diagram of PZT. M represents the monoclinic phase. The rhombohedral and tetragonal phases are both ferroelectric, whilst the cubic phase is antiferroelectric [2].

in the phase diagram in figure 2.11. For example, if the PZT used is at 50% Mol PbTiO$_3$, then it is near the rhombohedral/tetragonal phase boundary, allowing it to form different polarisation states. The dipole moments can form in many different orientations, making for easy poling of the material, thereby making it a useful piezoelectric. The PZT of interest to this project is 95% lead zirconate, and 5% lead titanate, such that its chemical formula is Pb(Zr$_{0.95}$Ti$_{0.05}$)O$_3$.

PZT has high piezoelectric and dielectric characteristics, with a piezoelectric constant $d_{33} \approx 150 - 250 \mu$m V$^{-1}$ and dielectric constant (at room temperature) $\approx 500 - 700$. Its Curie temperature can be higher than 300°C. It has been found that PZT has optimum dielectric and piezoelectric properties when the value of $x$ in the chemical formula of PZT is around 0.53 [45], such that the material is at the morphotropic phase boundary (MPB). Depending on orientation and doping, the dielectric constant of PZT can range from 300 to 3850. When the ratio of zirconium to titanium is 95/5, the maximum dielectric constant has been recorded at 10000, and the Curie temperature, $T_C$, at 250°C.

PZT 95/5 (95% lead zirconate, 5% lead titanate, with no added dopants) is a piezoceramic, and also both pyroelectric (affected by temperature) and ferroelectric (has spontaneous polarisation). A number of properties of PZT 95/5 are recorded in table 2.1 [5].
Table 2.1: Properties of PZT 95/5. The quantities denoted by * were measured at 25°C, 1 V, and 1 kHz [5].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant and loss* - Unpoled (-/%)</td>
<td>350/2.00</td>
</tr>
<tr>
<td>Dielectric constant and loss* - Poled (-/%)</td>
<td>295/1.97</td>
</tr>
<tr>
<td>Dielectric constant* - Depoled (-)</td>
<td>225 est.</td>
</tr>
<tr>
<td>Dielectric constant [MV m$^{-1}$]</td>
<td>8.0</td>
</tr>
<tr>
<td>Remanent polarisation $P_r$ [C m$^{-2}$]</td>
<td>0.32-0.38</td>
</tr>
<tr>
<td>Coercive field $E_c$ [MV m$^{-1}$]</td>
<td>1.2</td>
</tr>
<tr>
<td>Piezoelectric coefficients $d_{33}/d_{31}$ [x10$^{-12}$ C N$^{-1}$]</td>
<td>68/-16</td>
</tr>
<tr>
<td>Piezoelectric coefficients $g_{33}/g_{31}$ [x10$^{-3}$ Vm N$^{-1}$]</td>
<td>26.3/-6.0</td>
</tr>
<tr>
<td>Piezoelectric coupling $k_p/k_{31}/k_t$ [-]</td>
<td>0.18/0.11/0.46</td>
</tr>
<tr>
<td>Elastic compliance $s_{11}^E/s_{12}^E/s_{33}^E$ [x10$^{-3}$ m$^2$ N$^{-1}$]</td>
<td>7.68/-1.97/8.37</td>
</tr>
<tr>
<td>Elastic stiffness $c_{11}^E/c_{12}^E/c_{33}^E$ [x10$^9$ N m$^{-2}$]</td>
<td>130/-508/120</td>
</tr>
<tr>
<td>Acoustic velocity/Poisson ratio [m s$^{-1}$]</td>
<td>4200/0.26</td>
</tr>
<tr>
<td>Thickness mode $N_t/Q_m$ [Hz m]</td>
<td>2100/15</td>
</tr>
</tbody>
</table>

The Curie temperature is the temperature at which the spontaneous polarisation disappears [33]. Above this temperature, PZT has a cubic structure. It is thus centrosymmetric, and does not demonstrate a spontaneous dipole moment. The material behaves simply as a dielectric with linear polarisation. As can be seen from the phase diagram of PZT (figure 2.11), changing the temperature of the material changes its crystal structure. Below the Curie temperature, the PZT 95/5 changes to a rhombohedral phase. This leads to movement of the atoms within the structure, resulting in a dipole moment, and the material is now ferroelectric. Generally, it is the movement of the smaller zirconium and titanium ions which lead to the material having the spontaneous polarisation.

Not only is PZT piezoelectric, and therefore useful for both sensor and actuator applications, it is also both pyroelectric, and can be used as a heat sensor, and ferroelectric, such that its spontaneous electric polarisation can be reversed in the presence of an electric field. As a result of its greater piezoelectric properties, PZT has replaced Rochelle salt in lighters and in ultrasonic transducers, and has found use across a number of applications, such as capacitors and ceramic resonators for reference timing in electronic circuitry. Its unique range of properties can be modified and enhanced by changing the ratio of zirconium to titanium, as well as by doping with, for example, niobium and lanthanum [61]. For example, in 1975, Sandia National Laboratories was working on lanthanum-doped PZT (PLZT) anti-flash goggles to protect aircrew from burns and blindness in case of a nuclear explosion. These PLZT lenses could turn opaque in under 150 microseconds [65].

Doping of PZT with either acceptors, creating oxygen (anion) vacancies, or donors, creating metal (cation) vacancies, aids domain wall motion in the material. Typically, acceptor doping creates hard PZT, while donor doping creates soft PZT. In general, the greatest difference between hard and soft PZT is in their piezoelectric constants. Soft PZT
generally has a higher piezoelectric constant than hard PZT, however it has larger losses in
the material due to internal friction, whilst in hard PZT, impurities reduce domain wall
motion, thereby lowering the losses in the material. Soft PZT powders generally have
high coupling, high charge sensitivity, high density, a high Curie temperature, fine grain
structure, as well as a clean, noise-free frequency response. Conversely, hard PZT powders
have a higher mechanical quality factor, which reduces mechanical loss and enables a lower
operating temperature, a low dissipation factor, which ensures cooler, more economical
operation, and high dielectric stability [21].

Soft PZT ceramic powders are used in sensors, particularly when high sensitivity
and/or coupling are required, such as in flow or level sensors, ultrasonic nondestructive
testing and evaluation applications, and for accurate inspections of automotive, structural,
or aerospace products. Hard PZT powders are used when high power characteristics are
important, for example in the generation of ultrasonic or high-voltage energy in ultrasonic
cleaners and sonar devices [7].

PZT can be used for manufacture of uncooled staring array infrared imaging sensors
for thermographic cameras, and be used both in a thin film form, or as a bulk material [29].
PZT films are made using chemical vapour deposition [66].

2.3.1 Production of Ceramics

The production of ceramics usually requires around six steps [3]: Milling → Batching →
Mixing → Forming → Drying → Firing [67].

Milling The large material pieces are reduced to smaller sizes in a number of ways.
If cemented material is broken up, the individual particles retain their shape, but the
particles can themselves be ground smaller, in which case the material is said to be pul-
verised. Generally, milling is carried out using a variety of mechanical methods, including
attrition, compression, and impact. Attrition can be carried out using a wet scrubber
(also known as a planetary or wet attrition mill), where paddles create vortices in wa-
ter. In these, there are particle-on-particle collisions, resulting in the material breaking
up and/or particle shearing. The jaw, roller and cone crushers are types of compression
mills. These apply force on the material, resulting in it fracturing. Impact mills make
use of a milling medium, or the particles themselves, to cause fracturing, through the
ball mill, which has material that tumbles, fracturing the material, or a shaft impactor,
which causes both particle-on-particle attrition and compression. Engineering ceramics
are almost always made from powders as they cannot be cast in the liquid state due to
their high melting temperature [68].

Batching The oxides are weighed according to need, and then prepared for the next
procedure.

Mixing Mixing can be carried out using several different mixers, for example, ribbon
mixers (for cement), Mueller mixers, and pug mills. All these machines can be used for both wet and dry mixing.

**Forming** Ceramics are not amenable to a great range of processing and, as such, the mixed materials have to be made into the desired shape, either by reaction in situ, or by ‘forming’ powders into the desired shape (some methods use a mixture of both). Forming can involve shaping by hand, which includes a rotation process called “throwing”, extrusion, for example of “slugs” to make bricks, dry pressing or cold compaction to make shaped parts, injection moulding, where the ceramic powder is mixed with a polymer binder, tape casting [10], for example for very thin ceramic capacitors, or slip casting, to make, for example, ornaments and wash basins, where the ceramic powder is mixed with a fluid and poured into a porous ceramic mould [69]. Forming produces a soft, pliable “green” body, which can be shaped and, after shaping, will remain in that form, ready for drying [68].

**Drying** The water or binder is removed from the formed material. Spray drying can be used to prepare powder for pressing. Other dryers include tunnel and periodic dryers. Controlled heat is applied to remove the water; rapid heating can cause cracks and surface defects. The dried part is smaller than the green body, and brittle. A small impact will cause crumbling and breakage [68].

**Firing** The dried parts are again heated controllably, such that the ceramic powder particles are compacted and bind chemically. The materials are glazed and fired, resulting in a material with a smooth coloured surface, which has acquired mechanical strength through the sintering process. Generally, manufactured materials are sintered to form a solid body, as opposed to spin-coated. Spin-coating involves pressing crystalline grains which have been oriented in the same way, whereas sintering presses grains randomly together, resulting in a material with different properties [63].

### 2.3.1.1 PZT

The manufacture of PZT powders uses a similar approach to that outlined above. High-purity raw materials are chosen, weighed according to requirements, and then transferred to wet mills. Here they are milled to achieve a uniform particle size distribution. The material is then dried and prepared for calcining. Calcination is carried out in air at a high temperature (around 1000 °C) to remove chemical contaminants from the material, and the PZT forms in the desired phase. Lead oxide is a large proportion of the PZT, but is also hazardous, with a relatively high vapour pressure at calcining temperatures. It is therefore possible to alter the desired composition by allowing too much lead to evaporate during the firing procedure; this must thus be controlled accordingly. After calcining, the PZT powder is again milled, to ensure homogeneity, as well as to prepare it for the addition of an organic binding agent. The resulting binder-containing slurry is then spray dried, to evaporate water from the material. It is important in this process to
regulate the temperature to avoid decomposition of the solids in the slurry. Once the PZT powder has been spray dried, it is now free-flowing, and in the form of binder-containing hollow spheres with a narrow particle size distribution. The uniform PZT spheres allow air to escape throughout the compaction process, resulting in lamination-free green ceramic shapes [70].

It is also possible to create piezoelectric films [29], as well as ceramic ‘whiskers’, such as those in figure 2.12, which are elongated single crystals, with diameters of 0.1 - 10 \( \mu \text{m} \) and lengths of 10 - 1000 \( \mu \text{m} \) [71]. Due to their nearly perfect crystal structure and lack of grain boundaries, ceramic whiskers have high strength and stiffness. They are able to withstand high temperatures, whilst maintaining strength and hardness. As such, these whiskers have been used as reinforcing materials in ceramics, improving material resistance to crack growth. Whiskers can be created using pyrolysis, the thermochemical decomposition of a material at high temperatures without the participation of oxygen [72]. However, the resulting whiskers are highly non-uniform, there is \( \sim 10 - 30\% \) loss in whisker material, and minute whiskers, which are harmful for health (akin to asbestos) are almost always created. An alternative method for producing ceramic whiskers is to use a carefully selected catalyst to control their growth and formation. If all the catalyst particles are of the same size, then all the whiskers will be of the same diameter. The material is introduced into the reactor as a vapour and liquified on the surface of the catalyst. The whiskers then grow off the liquid surface, with a catalyst particle remaining at the outer tip of the whisker. Using this method, it is possible to grow uniform whiskers, as well as whiskers of larger diameters [71].

Piezoelectric films have an extremely high output voltage, about 10 times greater than ceramic materials [29]. They are thin, light, and flexible, and can therefore be stuck onto shaped designs using readily available glues. The piezofilms also have high mechanical

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and dielectric strength, and are impact resistant. They also have a wide frequency range (between 0.001 - 10^9 Hz), low acoustic impedance (useful for sonar and imaging), and are resistant to moisture and many chemicals [73]. However, piezofilm is a weaker electromechanical transmitter than most piezoceramics [66]. Piezofilms are manufactured as thin films or sheets, with thicknesses between 5 µm - 2 mm. The material is stretched at temperatures between 60 - 80°C, resulting in a change in crystalline phase. This is followed by thermal polarisation; electrodes are deposited on the film by evaporation in a vacuum, and an electric field (500 - 800 kV cm\(^{-1}\)) is applied to align the dipoles at a temperature of about 100°C. The material, still under the applied electric field, is then cooled; this “freezes” the polar alignment [74].

2.3.2 Porous Ceramics

Ceramics naturally retain a little porosity during manufacture, but it is also possible to add artificial porosity [75], predominantly by manipulation of the sol\(^4\) used to make the original ceramic material (e.g. by the addition of ions) [76]. One method for silicon-containing ceramics involves replacing some of the silica in the original gel or sol with cations of another metal [77]. This metal-substituted gel (or sol) can be dried and fired, yielding porous ceramic materials. It has been observed that these materials had several improved properties when compared with their non-porous counterparts, such as better thermal stability and intrinsic negative charge on their surfaces [78].

An alternative method involves the freeze-casting of camphene [79], an organic compound with the chemical formula C\(_{10}\)H\(_{16}\). Camphene is added to the warmed ceramic material to create a slurry, which is then ball-milled and cast into a mould at just below room temperature. The “green” solid which is formed now has concentrated ceramic particle walls, with a three-dimensional network of tiny interconnected camphene fibres. This frozen camphene is removed through sublimation, and the remaining material is now sintered for a few hours at temperatures of around 1200°C. The resulting ceramic material does not display defects such as cracks, and an increase of porosity has shown to lead to a decrease in the samples’ permittivity [79].

\(^4\)A sol is a suspension of very small particles dispersed evenly throughout a continuous liquid medium.
2.4 Properties of Ceramics

Ceramics are crystalline, inorganic, non-metals. Generally, they have low densities, high moduli, and high melting points (and thus, excellent creep strength at 1000°C). As many are oxides, they are completely resistant to oxidation.

As described in Sec. 2.2, ceramics have found use across a variety of applications, based on the above mentioned properties. Despite the higher cost of manufacturing ceramics (due to the difficulty of making complex shapes, as well as the nature of the procedure), and the brittle nature of these materials, ceramics are used in a number of products, including fuel cells and automated oxygen sensors [49]. Zirconium dioxide ceramics are used in the manufacture of knives, as their blades stay sharp longer than steel knives, although they are far more brittle and snap if dropped on a hard surface. Sialon (silicon aluminium oxynitride) has high strength, high thermal, shock, chemical and wear resistance, and low density [80]. These ceramics are used in non-ferrous molten metal handling, weld pins, and the chemical industry.

Covalently-bonded silicon carbide, silicon nitride, and sialons (Si₃N₄ and Al₂O₃ alloys) are very well-suited for high-temperature structural use. High creep resistance, low expansion, and high conductivity make them resist thermal shock well, in spite of their typically low toughness. Precise shapes, such as turbine blades, can be formed without the need for machining, by hot-pressing fine powders, vapour deposition, or by nitriding silicon which is already pressed into shape [81].

Ceramic materials are heat resistant, although their characteristics can vary with temperature. Ceramics can withstand temperatures up to 1600°C, and there are a number of ceramic products currently available which can operate regularly above 540°C [67]. These materials are also chemically inert, and can withstand chemical erosion when subjected to acidic or caustic environments. For example, silicon nitride is used for ceramic ball bearings, as it is more chemically resistant than steel and therefore does not rust [80]. These ball bearings are particularly useful in high speed applications, as the heat from friction during rolling can cause problems for metal bearings. In addition to these desirable properties, these ball bearings are electrically insulating, deform less under load and can therefore roll faster, as well as being of higher hardness and therefore less susceptible to wear. It has been reported that ceramic ball bearings have triple the lifetimes of ordinary metal ball bearings. However, they are far more expensive [49].

Several ceramics have poor thermal conductivity, leading to high thermal stresses, and all have very low toughness. In addition, ceramics are generally not very compliant, and have a high stiffness [81].

The bonding in ceramic materials is usually ionic or covalent, or a mixture of the two. As such, these materials tend to fracture before any significant plastic deformation takes place, resulting in poor toughness of these ceramics. In addition, these materials tend to
have some level of porosity. These pores, and indeed other microstructural imperfections, act as stress concentrators, further decreasing the materials’ toughness, and reducing their tensile strength. These combine to give catastrophic failures, culminating in the brittle behaviour of these ceramics.

Ceramics, like metals (but unlike polymers) have a well-defined Young’s modulus: the value does not depend significantly on loading time (or frequency, if the loading is cyclic). Ceramic moduli are generally larger than those of metals, reflecting the greater stiffness of the ionic bond in simple oxides, and of the covalent bond in silicates [82].

Since ceramics are largely composed of light atoms, and their structures are often not close-packed, their densities are low. Ceramics are also the hardest of solids; ionic or covalent bonds present a huge lattice resistance to the motion of a dislocation. Covalent bonds are localised - the electrons which form the bond are concentrated in the region between the bonded atoms. When a dislocation moves through the structure, it must break and reform these bonds as it moves. Ionic bonds are electrostatic - the electrostatic repulsion between like ions opposes shear requiring the movement of like ions over like ions, further increasing lattice resistance [82].

However, large lattice resistance results in brittleness; the fracture toughness of these ceramic materials is low. Even at the tip of a crack, where the stress is intensified, the lattice resistance makes slip very difficult. Metals have high toughness as energy is absorbed at the crack-tip, making the propagation of the crack much more difficult, whilst in ceramics, the energy absorbed is small [82].

Generally, this brittleness of ceramics can create major design problems. These can be overcome by creating ceramics with a fibrous structure, akin to wood. Ceramic-matrix components combine strong, perfect fibres, such as silicon carbide or alumina, and grown by special techniques, in a matrix of ceramic (silicon carbide or alumina again) made by conventional means [81].

In 1980, Toyota experimented with ceramic engines, which ran at temperatures above 3300 °C. No cooling system was required, thereby reducing the engine weight and resulting in improved fuel efficiency. However, manufacture of these ceramic engines proved difficult, and there was a high level of machine failure due to slight imperfections growing into cracks. It has therefore not been possible to mass-produce ceramic engines [49].

Finally, piezoceramics have high electrical resistivity, and large dielectric constants due to their ferroelectric nature, as well as being highly charge sensitive [18]. They are also generally non-conducting (neither electrical nor of heat) and, as such, can be made into insulators to carry and isolate electrical conductors. Modern/advanced ceramics such as silicon carbide have additional properties such as abrasion resistance and can be used, for example, as wear plates of crushing equipment in mining operations [83].
2.4.1 Piezoelectric Material Properties

Physically, piezoelectric ceramics are hard, chemically inert, and not vulnerable to humidity and other atmospheric conditions. Their mechanical properties are comparable to other, well-known, insulation ceramics, and they are manufactured by much the same processes [84].

By slightly varying the chemical composition of the piezoceramic materials, it is possible to emphasise one or more specific properties such that differing requirements can be achieved. For this reason, several grades of piezoceramic are available, each manufactured to suit a particular application [84].

Piezoceramics have modulus values on the order of 10 - 100 GPa, with densities typically between 7000 - 8000 kg m\(^{-3}\). Piezoelectric polymers, on the other hand, are softer materials, with elastic moduli on the order of 1 - 3 GPa, and densities between 1000 - 2000 kg m\(^{-3}\) [41].

In general, piezoelectric materials can produce strains in the order of 0.1%. Hard piezoceramics can produce stresses on the order of 10 MPa, whilst the softer piezoelectric polymers can produce stresses on the order of 0.1 MPa [41].

The product of stress and strain is called the *Volumetric Energy Density*, which is defined as the capacity to do work per unit volume. All piezoelectric materials have energy densities on the order of 10 - 100 kJ m\(^{-3}\). For achieving the highest stresses, the strains in piezoceramics may be limited by 0.1%, but will be on the order of 10 - 100% for piezoelectric polymers [41].

Since piezoelectricity is associated with molecular changes, the response time for piezoelectric materials is very small (on the order of a few microseconds) [83].

Several models have been developed for the non-linear switching of ferroelectric polycrystals under a combination of mechanical stress and electric field [85], and compared with measured behaviour [86]. These assume that the polycrystal consists of a set of bonded crystals, and that each crystal comprises a set of distinct crystal variants [87]. This research draws upon elastic-plastic crystal plasticity theory. Within each crystal, the switching event, which converts one crystal variant into another, causes a progressive change in remnant strain and polarisation, and to a change in the average linear electromechanical properties [88].

Devices made of polycrystalline ferroelectric ceramics often have complicated configurations. High stress and high field areas exist, and can lead to fatigue cracking and failure of the device. Furthermore, stresses generated during operation can cause depolarisation and therefore make the material ineffective for actuation. A robust model that captures ferroelectric switching is thus highly desirable [87].

As such, these models incorporate the dissipation of energy associated with domain wall motion, and the particular type of hysteresis found in ferroelectrics. It is thus im-
important to consider the resistance to domain wall motion arising from anharmonic lattice interactions, and from pinning defects such as dopant ions and ion holes. Also included are experimental observations that domains do not switch completely between distinct states of strain and polarisation; rather a single crystal switches by the progressive movement of domain walls, driven by a combination of electric field and stress [87].

How easily domains are able to move is dependent on the strains imposed by surrounding crystals, as well as on the crystal size itself. In a polycrystalline ceramic, domain reorientation is affected by the size of individual grains, by the presence of impurities and pores which prevent domain wall movement, by stresses imposed by surrounding grains, by the nature of the grain boundaries, and by the presence of second-phase particles. Thus, the microstructure, the purity of the initial starting materials, and the manufacturing and firing procedures all have a strong effect on resulting properties. As a result, products made by similar processes may have variations of as much as 15 - 20% in the dielectric constant measured at some fixed applied voltage [89].

2.5 Fracture of Brittle Materials

Mechanical fracture can be due to overload, or forced, fatigue, or creep fracture, and occurs at the material’s elastic limit. Overload fracture happens due to an increasing load applied abruptly, while fatigue fracture happens due to cyclic loading. Creep fracture is due to long loading times at high temperature [89].

Fracture can occur as shear fracture, cleavage fracture, or both. Shear is macroscopically ductile fracture, and a result of plastic deformation, with slip in the direction of planes of maximum shear stress. Shear fracture only happens in ductile materials. The failure of a ceramic material in many applications is often caused by brittle fracture (see figure 2.13), which is characterised by very low plastic deformation and low energy absorption prior to breaking [89]. This occurs to such a limited extent that cracks are sharp to an atomic level. Resistance to fracture is provided by the crystal lattice, and not by dislocation movement [3].

Cleavage fracture is microscopically brittle fracture, and occurs almost completely without microscopic deformation, perpendicular to the largest tensile stress [89]. If the external tensile force, $F$, exceeds the maximum external force for certain atomic distances, the atoms separate and the bonds between the atoms break. Ceramics typically fail by cleavage fracture along the weakest planes, but non-parallel specimens can also contribute to premature fracture [12].

The specimen cross-section does not fail simultaneously everywhere. Instead, cracks form locally as the atomic bonds break. This is due to either local stress concentrations in the material, caused by the specimen’s geometry, microstructure, or by previous plastic deformations, or due to microstructurally weak points which aid crack formation,
for example, grains with their cleavage plane perpendicular to the maximum principal stress [3][90].

Initially the crack cannot propagate, since the microstructure (grain orientation) and/or stress level change in the vicinity of the initial crack. Therefore, the crack remains stationary and only propagates (stably) if the load is increased. However, once the critical crack length/stress level is reached, the crack propagates quickly and unstably through the specimen, and without the need to increase the applied stress [3]. This limit can be calculated using fracture mechanics.

This cleavage fracture is usually, like shear fracture, trans-crystalline (through the grains and along certain crystallographic planes) but can also be inter-crystalline (along the grain boundaries) [89][90]. Cleavage fracture surfaces are usually imperfect, and can contain numerous steps or cleavage lines, for example because of the transition of the crack to a neighbouring grain with slightly different orientation, or because of cutting through a screw dislocation (a one-dimensional lattice defect). Often, there is a thin layer next to each fracture face where plastic deformation occurs, and this can be detected by electron microscopy. It is also possible to get crack branching (subsidiary cracks) [12]. On the other hand, when grain boundaries are embrittled, for example by precipitates, cleavage fracture can be inter-crystalline. In this case, the grain structure can be clearly seen in a scanning electron microscope image [91].

The ceramic material fails by cleavage fracture if its cleavage strength is reached before its yield strength, but it yields if the yield strength is reached before its cleavage strength (in this case the material behaviour is ductile). Since flow stress increases due to work-hardening, failure by cleavage fracture can occur even after plastic yielding. A
Figure 2.14: Toughness-strength diagram. For ceramics, the compressive strength $R_{cm}$ is approximately the same as the cleavage strength $\sigma_c$. The diagonal lines represent pairs of $K_{IC}$ (fracture toughness) and $\sigma_{limit}$ with constant critical crack length $a_c$ in mm [3].

Macroscopically ductile but microscopically brittle cleavage fracture develops, although this can only happen in a multi-axial state [3].

Cleavage fracture is favoured by a number of conditions, including loading, at high strain rates or at low temperature, because yield strength depends on these two parameters whereas cleavage strength is almost constant. Increasing the yield strength of a material will increase the likelihood of breaching the material’s cleavage strength. This implies that high-strength materials are more likely to fail by cleavage fracture than low-strength materials. Ceramics can be toughened by modifying the microstructure of the solid to reduce stresses near the crack tips [9].

Often, cleavage strength cannot be measured experimentally. Ceramics usually fail because a micro-crack, already present in the material, propagates and causes failure at a stress below its cleavage strength [92]. The pores remaining after compaction in the ceramic manufacturing process can be considered defects, and act as initial cracks. They can then also cause failure by crack propagation. As there is no plastic deformability, the material cannot unload these initial cracks by evening out stress concentrations, or dissipate energy [93] during crack propagation. Therefore, the fracture toughness of ce-
Figure 2.15: Load cases in fracture mechanics [3].

Figure 2.15: Load cases in fracture mechanics [3].

Ceramics is comparably small (see figure 2.14). Because of the crack sensitivity of ceramics, even small defects can determine the strength; the pre-cracks and pores formed during manufacturing are thus crucial for the mechanical behaviour and for determining the material strength [90][94]. The theoretical strength of a perfect ceramic without any defects is technically irrelevant [9].

Usually, ceramics contain cracks of different sizes with different orientations. The strength of the ceramic is determined by the cracks with the lowest failure strength. Under tensile loads, for piezoelectric ceramics [95], cracks can, depending on their orientation, be loaded in all modes, I, II, or III (see figure 2.15), but under compressive loads only in modes II or III, as the stress component perpendicular to the crack surface closes the crack [96]. Because the fracture toughness is much smaller for mode I than for modes II or III, ceramics under tensile loads usually fail in this mode and are thus more sensitive to tensile than to compressive stresses. The compressive strength of ceramics is therefore usually 10 to 15 times larger than its tensile strength [9]. Because the size of the initial cracks is stochastically distributed, statistical methods are required to analyse the strength of ceramics (see Sec. 2.5.0.3).

The fracture toughness is primarily determined by the strength of the chemical bonds within the ceramic, because this determines the energy needed to create fresh surfaces [93]. Beyond that, other effects within ceramics can occur that impede crack propagation, because they require additional energy and thus increase the fracture toughness, strengthening the ceramics. One such example is crack deflection where, for example, particles can be added to the ceramic, deflecting the crack from its straight path, and thus increasing the surface of the crack per advanced distance. This therefore requires additional energy for crack propagation and thus increases the fracture toughness [9][90].

Ceramic materials can be strengthened by reducing the defect size or the size of the initial cracks in the material, which increases the critical stress but does not affect the fracture toughness, or by crack deflection, by adding particles, or reinforcing the ceramics using fibres [94]. In this second method, the energy dissipation during crack propagation
is increased, thereby also increasing the fracture toughness. The formation of micro-cracks during crack propagation can, depending on their distribution, also increase the fracture toughness due to the extra energy dissipated [9].

### 2.5.0.1 Fracture toughness

A number of problems are encountered when testing ceramics [97]. Unlike for metals, which can be tested using a universal testing machine with the appropriate grip, it is important to design the experimental setup around the special requirements of a particular test mode, such that all aspects of the testing system must be chosen to obtain valid results [98].

A basic assumption of linear elastic fracture mechanics is the existence of the critical stress intensity factor $K_C$ which defines the initiation of fracture [98]. Under certain circumstances, this critical value can be regarded as a materials constant, the fracture toughness, $K_{IC}$ [99]. For any material, this number describes the risk of failure due to a defect in the material. In fracture toughness testing, critical fracture is initiated at an artificial defect, such as a notch or a sharp crack [92].

However, there are a number of problems with conducting fracture toughness measurements on ceramic materials, even at room temperature (where ceramics can be considered to be linear elastic), as they can produce a number of different results [98]. Particle-sized cracks commonly pre-exist in dense ceramics. These materials are full of cracks and voids left by the manufacturing process [82].

When a sharp crack is used as the initiating defect for a fracture toughness test, two problems arise; crack length measurement and the dependence of $K_{IC}$ on crack length [96].

Crack lengths can be measured using, for example, direct observation during controlled loading, or the identification of the starting crack length on the fracture surface after the test. These methods produce equivalent results [96].

For specific materials such as coarse-grained alumina and zirconia, a dependence of the $K_{IC}$ values on the lengths of the natural cracks as starting defects has been found [3].

$K_{IC}$ does not depend on the depth of the notches, but on the notch width, although only above a width of $>100 \ \mu m$. The fracture toughness is known to depend on grain size, chemical composition, and crystal structure. Crack-domain interactions in the ferroelectric structure also give rise to increased fracture toughness [100]. Crack growth rates in these materials have been shown to be accelerated by the presence of moisture in the environment, which can significantly increase the probability of failure [101].

However, these aforementioned statements are only valid for certain materials, and only at high loading rates; for low loading rates, there is an additional loading rate influence [3]. Also, electrical fields affect fracture and fatigue of piezoelectric materials. As such, classical fracture criteria in terms of stress intensity and total potential energy release rate are not valid for piezoelectric materials [102].
It has been found that the fracture toughness of engineering ceramics can vary between 1 - 10 MPa m$^{1/2}$, one or two orders of magnitude lower than of metals, with a crack sensitivity with critical crack length on the order of µm, and a yield strength on the order of GPa, also lower than in metals [3]. The failure strain in ceramics is generally ~0.1%, but can be as high as 0.5% in the strongest materials. Equivalent fracture stresses are in the range 250 - 2500 MPa, depending on the material’s Young’s modulus $E$. The surface fracture energy is typically around 40 J m$^{-2}$, whilst the elastic energy at fracture is proportional to the product of failure strain and fracture stress; the stronger the material, the more catastrophic the fracture process [98].

Ceramics have fracture toughness values $K_{IC}$ which are roughly one-fiftieth of those of good, ductile metals. In addition, they almost always contain cracks and flaws. The cracks originate in several ways. Most commonly, the production method leaves small holes; sintered products, for instance, generally contain angular pores on the scale of the powder (or grain) size. Thermal stresses caused by cooling or thermal cycling can generate small cracks. Even if there are no processing or thermal cracks, corrosion (often by water) or abrasion (by dust) is sufficient to create cracks in the surface of any ceramic. And if they do not form any other way, cracks appear during the loading of a brittle solid, nucleated by the elastic anisotropy of the grains, or by easy slip on a single slip system. The design strength of a ceramic is thus determined by its low fracture toughness and by the lengths of the micro-cracks it contains [82].

Fracture toughness can be increased by a factor of 2 - 3 by the addition of, for example, particles, short whiskers, or transformation toughening particles of zirconia. It is also possible to reinforce the ceramic matrix with strong ceramic filaments, increasing the fracture energy by 3 - 4 orders of magnitude, and resulting in a work of fracture of 100 kJ m$^{-2}$. For example, for PZT 95/5 doped with 2% niobium, the strength of the material increased from roughly 558 MPa to 940 MPa under confining pressures of 400 MPa [13]. However, these ceramic materials are highly anisotropic and fail in a complex manner, as they do not tend to obey the basic concepts of fracture mechanics [98].

2.5.0.2 Compressive Failure of Ceramics

Applying external forces to a solid body results in deformation which, if it does not exceed a critical value, disappears on removal of the forces. This is known as elastic deformation [90].

When stress is increased beyond a critical value, typically of order $10^{-3}E$, there are two extreme types of behaviour: the material may fracture in a brittle manner, like most ceramics, or it may deform plastically in a ductile manner, like many metals. Ideal brittle fracture occurs in the absence of significant plastic flow and, after fracture, apart from the new fracture faces, the material returns to its original state. Plastic deformation is permanent and, unlike elastic deformation, remains after removal of the external forces [90].
Ceramics can exhibit both types of behaviour over different temperature ranges. For example, glass shows both extremes at particular temperatures. At low temperatures, ideal brittle fracture occurs, whereas at temperatures near the softening temperature, very extensive plastic flow occurs [90].

The elastic properties of ceramics are central in determining mechanical behaviour, and are directly dependent on crystal structure and bonding. Stiffness, hardness, and strength are all closely interrelated, high stiffness being associated with good mechanical properties. Elastic constants can be related to the atomic bonding forces for simple crystals with ionic bonding. Elastic moduli decrease slightly as temperature is raised and the lattice expands; a typical reduction for ceramics is $\sim 1\%$ per 100 K in the range $0 - 1000^\circ$C. However, the situation becomes more complex at high temperatures when anelastic behaviour is observed [90].

Generally, strains produced by a particular stress are dependent on the direction of application of stress. Most engineering materials can be regarded as isotropic for the purposes of elastic deformation analysis. Although individual crystallites show anisotropic behaviour, and different crystal phases exhibit different elastic properties, these effects are on much too fine a scale to be of concern in engineering components [90].

In a general state of stress, tensile or compressive strain in a particular direction depends on the tensile or compressive stresses in all three orthogonal directions. Shear strains, however, are related simply to individual shear stresses [90].

For materials in the form of a single crystal, we are faced with the complication that the elastic constants are anisotropic - strains produced by a particular stress depend on the direction of application of that stress. If a general stress is applied to a crystal, the resulting strain is comprised of a number of components that are all linearly related to the stress components through the compliance constants. This means that if a cubic element of crystal is loaded in tension normal to one face then, not only will it elongate in the tension direction, but it may also shear such that the edges of the element are no longer orthogonal [90].

For isotropic materials, just two independent elastic constants are required. For crystalline materials however, the number of constants required depends on the complexity of the crystal structure. For example, three constants are required for cubic crystal structures [90].

For metals, the strength measured in compression is the same as that measured in tension. For brittle solids however, the compressive strength is roughly 15 times larger [81]. Most literature on brittle materials therefore places a great emphasis on the effects of tensile forces [90]. There is a need to accurately know the strength of brittle materials in compression, both to distinguish between competing statistical, micro-mechanical theories of strength, and to provide data necessary for engineering designs for the optimum use of these materials as load bearing elements. The scope of application of high density,
high-strength brittle materials as structural elements is increasing rapidly [103].

In compression, cracks at an angle to the compression axis propagate stably, requiring a progressive increase in load to make them propagate further. In addition, they twist and bend out of their original orientation to run parallel to the compression axis [82]. Fracture is not caused by the rapid, unstable propagation of one crack, but the slow extension of many cracks to form a crushed zone [81]. The stress-strain curve rises and reaches a maximum when the density of cracks is so large that they link to give a general crumbling of the material. It is not the size of the largest crack that counts, but that of the average [82]. Therefore, a brittle material’s strength in compression is, on average, a whole order of magnitude larger than its strength under tensile stress [90].

After production and before loading, brittle materials already contain cracks, due to a natural porosity and other manufacturing processes. At low compressive stresses, the material is linear elastic but, even still, new, small cracks can nucleate at grain boundaries. Above 50% of the ultimate crushing stress, the cracks propagate stably, giving a stress-strain curve that continues to rise. Above 90% of the maximum stress, some of the cracks become unstable, and continue to grow at constant load, linking with neighbouring cracks. A failure surface develops at an angle of 30° to the compression axis. The load passes through a maximum and then drops, sometimes suddenly, but more usually quite slowly [82].

The distribution of crack lengths within a ceramic material, as described in Sec. 2.5.0.3, gives rise to a number of different consequences. A large sample will fail at a lower stress than a small one, on average, because it is more likely that it will contain one of the larger flaws. As such, there is a volume dependence of the strength. For the same reason, a brittle rod is stronger in bending than in simple tension; in tension the entire sample carries the tensile stress, while in bending only a thin layer close to one surface (and thus a relatively smaller volume) carries the peak tensile stress. And so, the modulus of rupture is larger than the tensile strength [81].

Compared with bending strength data, there is a lack of reliable compressive strength data. However, a comparison between available compression and bending strength data shows up significant differences. The compressive strength is higher by a factor of about 5 - 30 than the bending strength. A detailed analysis of experimental results shows that cracks start to grow in a stable way at a critical stress, whereas fracture is observed at higher stress [96].

Several fracture mechanical analyses of crack development under compressive loading have been carried out [104]. Ceramic samples containing a controlled number and size of crack-line flaws have been modelled and tested in simple compression. In situ scanning electron microscopy has been used during loading to observe crack initiation, growth, and linkage, and Young’s modulus, the stress for the initiation of crack growth, and that for final failure have been recorded [105]. This chain of events has been modelled, and a
theory of damage mechanics suggested [106].

Crack growth in compression is stable; final failure requires the simultaneous growth and interaction, under increasing load, of many cracks [106]. By contrast, crack growth in tension is unstable; one crack, once started, grows rapidly under decreasing load to failure. The process of compressive failure has been studied in model materials such as PMMA, and analysed using concepts of fracture mechanics. However, few experimental tests of these models on real ceramics have been carried out, due to the difficulties which arise of observation and characterisation of the cracks [105].

A critical stress is required to initiate crack growth, and depends on the initial crack length and orientation, on the coefficient of friction, and on the stress state. This fracture initiation is then followed by a region of stable crack growth at increasing load. The extent of this region is dependent on the size and concentration of cracks, and on loading rate. The interactions of the growing cracks increases the stress intensity driving crack growth, leading to instability and final fracture. All specimens eventually fail by slabbing parallel to the applied compressive load [105][106].

Young’s modulus decreases with increasing crack concentration, with a slight dependence on crack size at a given crack concentration. The fracture initiation stress and the ultimate compressive strength both decrease with crack size and concentration. The difference between fracture initiation and ultimate strength decreases with increasing crack concentration [105].

Fracture occurs by the initiation and propagation of micro-cracks from the tips of the existing cracks. The micro-cracks initiate roughly perpendicular to the original crack, but quickly curve to become parallel to the compressive axis. These are known as wing-cracks. At low levels of damage, the growing micro-cracks avoid each other. The growth of one micro-crack can be arrested by the initiation and propagation of a nearby micro-crack. Macroscopic failure occurs when the density of the micro-cracks reaches a point when the load cannot be supported by the remaining intact area, or when these cracks extend to the sample surface. Micro-cracks coalesce below the surface, causing slabs of material to spall off [105][106].

The behaviour of crack growth, in compression, from pre-existing cracks depends on the confining pressure. Simple axial or radial compression causes a few cracks to propagate and combine to give failure on planes parallel to the maximum compressive stress (slabbing). A small confining pressure prevents this unlimited crack growth - failure occurs by the interaction of cracks to give macroscopic shear failure. Larger confining pressures limit the growth of individual cracks even further, and the sample deforms in a pseudo-ductile way, with large-scale deformation taken up by many short, homogeneously distributed micro-cracks [106].

Tensile fracture of a brittle solid is far more simple and better understood. A single flaw, the longest or most favourably oriented, propagates unstably when the stress inten-
sity at its tip exceeds the critical stress intensity (or fracture toughness) of the solid [106].

2.5.0.3 Weibull statistics

Weibull statistics are used to describe fracture in brittle materials [82][96].

The difference in defect sizes within ceramic materials causes a difference in their mechanical properties because, unlike metals and polymers, ceramics cannot compensate for inner defects via plastic deformation. Therefore, it is not enough to simply state a failure load, but instead a failure or survival probability must be calculated. This is done by statistical fracture mechanics [99].

The \textit{probability of failure}, \( P_f(\sigma) \), is the probability of the component failing when the stress \( \sigma \) is applied. For example, in a cluster of macroscopically identical specimens, if the probability of failure is given as \( P_f(300 \text{ MPa}) = 0.4 \), 40% of the specimens will fracture at or below the applied load of 300 MPa.

Usually, in tension, ceramics fail as soon as a crack starts to propagate. Therefore, their strength is determined by the stress value at which the first, and thus critical, crack starts to grow. The probability of failure is then given by the probability that the critical crack has a certain failure stress. If the applied loads are tensile, one of the cracks that is at least partially loaded in mode I will govern the strength [107].

To describe the probability of failure, a statistical approach is needed that takes into account the statistical distribution of the density and size of the cracks [94].

Consider a component with homogeneous stress distribution and known number of defects. The size distribution of the defects can be used to determine the failure probability. It is equal to the probability that at least one crack has the critical crack length. As the critical crack determines failure, only the largest defects are relevant. The probability of finding a large defect becomes smaller with increasing defect size; therefore, different defect size distributions will look similar in the relevant region. The details of the defect size distribution are therefore not important [3][82].

Because the number of defects differs between different components, the defect density distribution must also be taken into account by using it to accumulate the probability of failure for all possible numbers of defects [89].

From these statistical considerations, it can be shown that the failure stress \( \sigma \) of the critical defect is distributed according to the Weibull distribution. From this, and taking into account the volume of the component, the probability of failure can be calculated as:

\[
P_f(V) = 1 - \exp \left[ \frac{V}{V_0} \left( \frac{\sigma}{\sigma_0} \right)^m \right]
\]

(2.5)

where \( V_0 \) is the reference volume and \( m \) the Weibull modulus, which quantifies the scatter of the strength values, and is thus a measure of how strongly the edge in a plot of the probability of failure is rounded off. A larger Weibull modulus reduces the scatter of the
failure stress [3]. For \( m \to \infty \), there is no more scatter, and the value of \( \sigma_0 \) becomes insignificant. (Note The reference stress \( \sigma_0 \) depends on the material and the specimen volume, \( V_0 \)).

The probability of survival, \( P_s \), can also be used, and is defined as:

\[
P_s = 1 - P_f
\]

(2.6)

### 2.5.1 Porosity Effects

Most ceramics have complex microstructures, comprising several phases, each of which is usually anisotropic [90]. Most ceramics prepared by powder compaction and heat treatment also have some degree of porosity [89]. In some cases, such as when ceramics are used as thermal insulators, a high degree of porosity is vital [9]. Standard PZT can be made more porous by the addition of a poreformer, which makes the material more spongy and therefore less dense [8]. The porosity of the PZT, like other ceramics, can be controlled, as discussed in Sec. 2.3.2.

In principle, it should be possible to calculate the effective elastic constants for the material from the elastic constants of the constituent phases, or the elastic constants may be measured by direct experiments. Either way, the average elastic constants for the ceramic are known, and these can then be used for calculating its engineering performance [90].

A porous ceramic represents the limiting case of a two-phase material, where one phase has zero stiffness [90]. Porosity can be characterised by the volume fraction of pores present, and their size, shape, and distribution compared to other phases [89].

Young’s modulus decreases with increasing porosity, but the rate of decrease becomes less as the porosity increases. This is due to a reduced effect per pore as the pores become more closely spaced at higher porosities [90]. Fracture energy appears to have a more gradual decrease with porosity than the fracture toughness [9].

Indeed, many mechanical properties, such as elastic moduli, strength and toughness, decrease with increasing porosity [10]. In addition, both electrical and thermal conductivity also decrease with increasing porosity [89]. The elastic constants depend not only on the porosity, and thus the density, of the ceramic, but also on the shape of the pores themselves. A number of studies are available in literature [96].

It is not, however, possible to use one simple model to represent the general behaviour of all porous ceramics, since the shape of their pores can differ depending on how the ceramics were processed [9], but these differing relationships can be used to provide a useful, if rough, description.

For example, Nielsen [9] derived the following equation for the Young’s modulus, \( E \), of a solid with pore volume fraction \( P \):

\[
E = \frac{E_0}{1 - P}
\]
\[ E = E_0 \frac{(1 - P)^2}{1 + (\rho^{-1} - 1)P} \]  

(2.7)

where \( \rho \) is the Nielsen shape factor and \( E_0 \) is the Young’s modulus for a fully dense material.

\( \rho \leq 0.4 \) can be used for materials with the porosity characteristic of joined particles.

\( 0.3 \leq \rho \leq 0.7 \) is for porosity that resembles ribbons or dendrites.

\( 0.6 \leq \rho \leq 1.0 \) is for pores enveloped by a solid phase [9].

Rice [9] related toughness of the material, \( K_C \), to its porosity, \( P \):

\[ K_C(P) = K_0 \exp(-bP) \]  

(2.8)

where \( K_0 \) is the fully dense toughness [9].

Ostrowski and Rödel [9] had a different relationship between the toughness and the porosity, involving the crack tip toughness:

\[ K_C(P) = K'_0 \left(1 - \frac{P}{P_0}\right)^n \]  

(2.9)

where \( K'_0 \) is the crack tip toughness extrapolated to 100% density.

The compressive strength of porous materials is generally not controlled by single or isolated pores, since compressive failure is typically one of cumulative damage or cracking. This is in contrast to tensile failure, in which catastrophic failure from the single weakest flaw is the case. Isolated pores or clusters are believed to have less effect in compression. The high stresses and progressive failure in compression may provide opportunity for pore shape and stress concentrations to come into play via progressive cracking as load increases. This may increase the porosity-dependence of compressive strength [108].

The failure of porous cylinders under axial compression occurs by vertical slabbing, wherein micro-cracks grow or combine to form contiguous vertical failure planes. Assuming that micropores in the ceramic are negligible, it can be confidently assumed that, under compression, failure planes form vertically parallel to the loading direction, and the samples fail by brittle crushing [108].

It is observed that on vertical failure planes, failure zones are formed at locations on the pore boundaries where the tensile stresses are maximum. Since tensile failure occurs in ceramics at a much smaller load than compressive failure, porous brittle structures loaded in compression fail at regions where tensile stresses are maximum. It is believed that porous brittle materials fracture predominantly due to tensile stresses at pore boundaries [108].

Failure occurs for a prescribed multi-axial external load at that defect which has the most favourable orientation to the stress field [96]. Pores can act as micro-crack initiation sites (the micro-cracks nucleate from the pores at the highest strain rates) but also as
channels for propagating the micro-cracks. As such, the presence of the pores appears to affect the compressive strength of a ceramic material [11]. In previous experiments, it appears that at lower strain rates, the porosity of particles in fractured specimens was greater than in the unfractured specimens. Thus, it appears that the presence of the pores had lowered the fractured specimens’ toughness [12]. It has been seen for PZT 95/5, doped with 2% niobium, that pore collapse begins somewhere between 400 - 800 MPa under strain rates between $10^{-4} - 10^{-2}$ s$^{-1}$ [13]. It also appears that both the mechanical and electrical properties of PZT 95/5 are sensitive to the level of porosity, but not to the pore morphology [14].

2.5.2 Temperature Effects

Study of the dynamic fracture of ceramics at extreme temperatures is still in its early days. Indeed, literature on impact studies of ceramics, which are designed for use in heat engines(!), is predominantly limited to testing at room temperature. This is primarily due to the lack of suitable testing procedures for both sub-zero and elevated temperatures [109]. Early studies have shown that the electromechanical behaviour of PZT 95/5 has significant temperature dependence [1][110].

Ceramic materials at low temperatures can be considered to be linear elastic [98]. However, it has been observed that as the temperature increases, the behaviour of piezoelectric ceramics under tensile stress becomes nonlinear. Moreover, the stronger the nonlinearity, the higher the fracture strength [111].

If a stress is applied to a ceramic specimen at an elevated, homologous temperature, with $T/T_m$ of at least 0.3 (where $T_m$ is the absolute melting temperature), the strain of the component increases with time at constant load [3].

As the temperature is decreased toward absolute zero, the slope of curve of elastic constant as a function of temperature approaches zero. As the temperature increases toward the Debye temperature (the highest temperature that can be achieved due to a single normal vibration), the slope approaches a constant for many ceramics. It is possible to use this constant to estimate the values of a number of mechanical properties of the ceramic, including the elastic moduli at high temperatures [3]. It has been seen that the elastic constants of many single piezocrystals generally decrease slowly as the temperature is further increased [112].

For polycrystalline ceramics, this variation with temperature also holds, but an additional effect is superimposed [9]. At some temperature characteristic of the grain boundary phase, the measured elastic moduli decrease rapidly from the linear decrease characteristic of material free from grain boundaries. The additional rapid decrease is attributed to grain boundary softening and sliding, and is not really an elastic effect.

A general observation for common ceramics between room temperature and the onset
of grain boundary softening is that the Young’s modulus and the shear modulus decrease about 1% per hundred kelvins of temperature increase [9]. The softening temperature is considerably below the melting temperature of typical crystalline ceramics [15].

Statically loaded ceramic specimens may show delayed failure in the absence of inelastic deformation processes (static fatigue) at all temperatures [98]. The external environment can influence performance, and at high temperatures the rate of oxidation of non-oxides can control the propagation of surface defects. In most high-quality ceramics, internal defects are generally less susceptible to sub-critical crack growth processes than surface or near-surface defects, which can be strongly influenced by the environment.

For alumina materials at room temperature in air, a slight increase in the fracture toughness values, $K_{IC}$, with loading rate has been observed. This is because sub-critical crack growth in a corrosive environment (for example, air) takes place prior to rapid fracture at loading rates. This growth is usually not accounted for when calculating $K_{IC}$ [9].

At high temperatures for two-phase materials, there is a strong dependence on temperature and loading rate, due to the change in viscous or plastic state of the second phase. This dependence vanishes if very high loading rates are applied [15].

Finally, it has been observed that the effective transverse piezoelectric coefficient increases, but with a smaller temperature dependence for piezofilms than for bulk piezoceramics [16].

### 2.5.3 Pressure Induced Phase Transitions

Diffraction is used in order to see to which phases a material transitions. Typically, new phases are obtained for PZT between 3 - 5 Mbar [113]. PZT can transition between ferro and anti-ferro phases under pressure [50][114][115]. There appears to exist a domain-switching zone [116], which increases fracture toughness, and the efficiency of phase transition also appears to increase with applied stress [117].

Stress-induced phase transformations can produce additional compressive residual stresses during crack propagation, thereby increasing the crack-growth resistance, $K_{IR}$. This is because of particles in the matrix that can increase their volume by a phase transformation, causing toughening. Initially, the particles are in a thermodynamically unfavourable state, but cannot transform to the thermodynamically stable phase because of a nucleation barrier [3].

If a large enough tensile stress is applied, for example, at the crack tip, it can take less energy to transform the particles to the phase with the greater volume than to deform them elastically. This can also be understood by considering the stress-strain relationship of a volume element passed by the crack tip (see figure 2.16). The phase transformation starts when the elastic energy is sufficiently large [3]. Because the particle was metastable
prior to the transformation, the transformation occurs even when the stress reduces as the volume increases. During the transformation, tensile stresses in circumferential and compressive stresses in radial directions around the particles are superimposed to the external load. After unloading, part of the volume increase remains and compressive residual stresses are generated that reduce the stress on the crack and thus may partly or totally close it. Because of the tensile stresses in circumferential directions around the particles, micro-cracks can form and cause further dissipation of energy [3].

Zirconium dioxide (ZrO$_2$) is a particularly clear example of transformation toughening. Pure ZrO$_2$ solidifies at a temperature of 2680°C in a cubic lattice that is stable down to a temperature of 2370°C. Here, ZrO$_2$ transforms to a tetragonal phase. On further cooling, the monoclinic phase becomes stable at 1170°C. This usually occurs by a martensitic, diffusionless phase transformation in which the volume grows by 3% to 5% and the material is sheared by 1% to 7%. This process is very difficult to prevent during the manufacture of pure zirconium dioxide, and causes residual stresses that are so large they damage the material excessively by crack formation. Thus, pure zirconium dioxide cannot be used for load-bearing applications [3].
2.6 Associated Polymers

The decision to study polymers was undertaken with the ultimate goal of investigating the effects (if any) of encasing PZT with a polymer. In future work it is hoped that, after different polymers (and PZT) have been mechanically characterised, a polymer of choice will be placed either side of PZT, and the effects on the materials’ properties, as well as the interactions between the surfaces of the piezoceramic and the polymer, will be studied under mechanical compression. An additional benefit to initially studying polymers is that, since the PZT samples are limited, the methodology can be refined with the more readily available polymers.

The mechanical and thermal response of epoxy-based thermosets under compression has been well-characterised over the past several decades [118]. Due to their varying properties, they are widely used in a variety of applications, ranging from insulating electrical components, to encapsulants used in the aerospace industry.

2.6.1 Previous Studies on the Mechanical Behaviour of Polymers

Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form. They do not soften at a specific temperature but appear to undergo a gradual change. The glass transition temperature has been found to decrease upon water absorption, due to the presence of strong hydrogen bonds. The strength and toughness of epoxy resins below this temperature depend on the mechanism of the movement of short segments in the solid state but, above this temperature, the mechanical properties are influenced by cross-linking density and the molecular weights between the cross-links [119].

An overview of the behaviour of epoxy thermosets under compression was provided in two papers in 1998 [118][120]. The authors studied the effects of strain rate, composition, and temperature on the yielding behaviour of epoxy, and compared the results to known models, finding that the behaviour of structurally related polymer systems generally followed previously generated models. It was observed that the yield stress increased with increasing cross-linking, due to the restriction of molecular motion by these cross-links. However, it was noted that the yield stress of the material was predominantly influenced by the rate of applied strain. Both the yield strain and the yield stress decreased as the temperature was increased, until the glass transition temperature was reached, after which there was no more yielding.

Others have further studied the effects on temperature and applied strain rate on epoxy, making use of quasi-static testing apparatus and Split Hopkinson Pressure Bar (SHPB) systems [121]. Whilst also observing the same trends of increases in yield stress
with strain rate, as well as a decrease in yield stress as temperature was increased, a large rise was observed in the yield stress during the transition from quasi-static loading rates to those obtained during SHPB tests.

It has been observed that the strength of epoxy resins decreases with the strain to fracture, as well as with temperature. The final fracture of the destructed specimens occurs along the plane perpendicular to the direction of the maximum tensile stress under an angle of 45° to the longitudinal and transverse direction. The yielding of the epoxy resins is controlled by the acting shear stress [122].

Several authors have described the compressive behaviour of some polymeric materials in five distinct stages (linearly elastic, non-linearly elastic, yield-like behaviour, strain softening, and nearly perfect plastic flow). Many others have observed strain softening at yield, followed by strain stiffening at higher compressive strains for different strain rates [123].

Different sample geometries have also been experimented on. Cubic, prismatic, and cylindrical compression samples all experience a decrease in the stress at yield, but only cubic samples strain-harden before failure. Strain-softening in all geometric samples takes place after yield, followed by nearly perfect plastic flow for cylindrical and prismatic samples; this region is relatively short in the cubic samples as they strain-harden. It has been observed that the compressive yield strength of an epoxy material under high strain rates is much higher than under lower strain rates. The elastic modulus appears to increase with increasing strain rate [124].

Modelling of deformation of thermosetting resins has been carried out by several authors [125]. These authors carried out a range of compression experiments to investigate the effect of strain rate on epoxy resins, in the process developing a constitutive model capable of accurately simulating the observed experimental response, particularly between strain rates of $10^3 - 4.5 \times 10^3$ s$^{-1}$. This model included both post-yield strain-softening and adiabatic heating, thus enabling such accuracy.

Similar compressive studies have been carried out on syntactic foams [126]. It was observed that the main failure mechanism appeared to be via shear planes acting at \(\sim 45^\circ\) to the direction of the applied loading force, and that the compressive modulus of the syntactic foam was lower than a pure resin sample by a factor of 2. Other investigations [127] have shown responses highly dependent on strain rate, peak stresses dependent on foam density, and that failure occurs between micro-balloons at lower strain rates, but through micro-balloons at higher strain rates.

The yield strength and the elastic modulus of syntactic foams have been seen to be linearly dependent on the bulk density of the foams, as well as the volume fraction of micro-balloons. The percentage of micro-balloons and the composition of the resin matrix greatly influence the ease with which a syntactic foam can be manufactured [128]. It has been observed that temperature, in terms of micro-mechanical behaviour, predominantly
affects the behaviour of the matrix [129].

Syntactic foams are known for their high compressive strength, low moisture absorption, and good damping properties [130]. They can be designed with specific physical and mechanical properties depending on the intended use. As such, different matrix resins can be chosen, and the micro-balloons made from polymers, ceramics, or metals. Different densities of syntactic foams can be obtained by changing the volume fractions of the matrix resin and micro-balloons in the structure, or altering the inner and outer radii of the micro-balloons. Successful modelling of the mechanical behaviour of syntactic foams has recently been achieved [131].

2.6.1.1 Time-Temperature Equivalence

It is well known that the mechanical response of polymers is highly dependent on the applied loading frequency. It is therefore not sufficient to use properties measured under static loads in the analysis of dynamic tests. In addition, the frequency dependence is not constant, but is greatest over the range(s) of frequencies corresponding to any particular polymer’s transition(s) at the test temperature. Furthermore, the effects of frequency and temperature are interlinked through the time-temperature superposition principle: changes in one can be related to changes in the other. This means that the variation in the mechanical properties observed at a single frequency or loading rate at various transition temperatures will also be observed at a single temperature at various frequencies [132][133].

This is due to the same underlying microstructural processes. The universal function for temperature dependence of viscosity, and mechanical and electrical relaxations, in amorphous polymers and other super-cooled, glass-forming liquids, arises because the rates of all these processes depend predominantly on temperature, through their dependence on free volume [132][133][134].

Typically, the strain rate sensitivity of polymers is larger at higher rates. However, caution is required upon interpreting the gathered data, since similar behaviour is observed in other materials, the relevant strain rates are often those at which inertial effects also become important, and, finally, the change in rate sensitivity usually occurs when the test equipment is changed from screw or hydraulically driven devices to Hopkinson bars. However, this highlights the importance of integrating rate and temperature dependence of polymeric materials [132][133].

A unique feature of polymers is that they allow data interpretation through time-temperature superposition. By performing experiments over a range of temperatures at a single strain rate, and over a range of strain rates at a single temperature, and noting that increasing log(strain rate) is equivalent to decreasing temperature, the data at fixed temperatures can be mapped onto those at fixed strain rates, and vice versa. These mapped results can then be compared to other methods for measuring the thermo-mechanical
response of polymers, for example, dynamic mechanical thermal analysis [132][133].

The time-temperature superposition principle states that increases in the strain rate or frequency of the applied loading have the same effect on polymers as decreases in temperature [132]. It has primarily been investigated using the well-known Williams-Landel-Ferry (WLF) equation [135]:

\[
\log(a_T) = \log\left(\frac{\dot{\varepsilon}}{\varepsilon_{T_s}}\right) = -C_1 \frac{T - T_s}{C_2 + (T - T_s)}
\]

(2.10)

where \(a_T\) is a shift factor, \(\dot{\varepsilon}\) and \(\varepsilon_{T_s}\) are two frequencies of interest with corresponding temperatures \(T\) and \(T_s\), and \(C_1\) and \(C_2\) are experimentally derived constants [136].

The WLF method uses a reduced variable approach to separate time and temperature, allowing material properties to be expressed in terms of a single function of each variable, and was based on the progressive disentangling of long chain polymer molecules under stress [134].

The frequency shift factor, \(a_T\), is fundamental to the WLF technique, and allows correlation of the effects of increasing temperature with decreasing frequency, and decreasing temperature with increasing frequency [137].

To use this WLF method, a number of isothermal measurements are made at different temperatures over a range of frequencies. A reference temperature is chosen, and the material property data at that temperature is not altered on the frequency axis. A shift factor is calculated for each remaining set of isothermal data, and data taken at temperatures above the reference temperature is shifted to the left, towards lower frequencies, whilst data taken at lower temperatures is shifted to the right, towards higher frequencies. This shifting of data to higher or lower frequencies is controlled by the constants in the WLF equation, which determine the magnitude of the shift factor [137].

The WLF model effectively states that relative molecular mobility is only dependent on the difference between \(T_g\) and \(T\), where \(T_g\) is the ultimate glass transition temperature [118], and has been extremely successful for predicting small-strain deformations in a variety of amorphous polymers, with little or no alteration to the coefficients in the model. It is, however, claimed to be valid only for temperature excursions of \(\pm 50^\circ C\) [136].

It has thus been determined that the observed increase in rate sensitivity of amorphous or semi-crystalline polymers is due to underlying polymer transitions, which would normally be observed below room temperature, but have been shifted to room temperature as the strain rate has increased [132][133].

Because the range of strain rates which can be accessed experimentally is much smaller when compared to the equivalent range of temperatures, it is difficult to observe the effects of more than one transition in a single polymer through strain rate alone. As such, a related approach has been used very successfully to develop models for high rate behaviour [132][133][138].
Whilst time-temperature superposition has been successfully used to interpret high rate data, a further benefit would be to be able to replicate the behaviour of polymers at high rates in low rate experiments. In order to do this, the intrinsic rate dependence of polymers must be isolated from the effects of dynamic loading [132][133].

If the specimen is too large, the stress induced by the specimen inertia can become significant compared to the intrinsic material strength - these inertial effects can be quantified using well-established equations and then minimised in the high rate experiments. A second difference between static and dynamic loading is specimen heating [135]. A proportion of the plastic work done on the specimen is converted to heat; at low strain rates, this heat has time to conduct out of the material, so the experiment is isothermal, however, at high strain rates, the heat remains in the sample and the experiment is adiabatic [139]. The limit at which this happens depends on the thermal diffusivity of the material and the dimensions of the sample [132][133].

Several experiments have been carried out on a number of different polymeric materials, where the high strain rate response has been successfully demonstrated in low strain rate experiments, though further research is still required. One such successful method entailed increasingly heating the sample to simulate plastic work being converted to heat, and that heat remaining in the sample [139]. Another method involved loading a specimen in stages, thus allowing the material to cool before reloading. This test is best carried out using a loading device that allows the experiment to be stopped and restarted as required [132][133][136].
Chapter 3

Experimental Testing

Whilst there are several ways to investigate the numerous properties of ceramics, this thesis focuses on the electromechanical properties of PZT. Of particular interest to this research is how both temperature and porosity affect the failure of PZT 95/5 ceramics, as well as the voltage developed upon compression, over a range of strain rates. As such, the experiments to be carried out will extend from quasi-static testing to dynamic loading techniques.

Different compressive strain rates will be achieved using quasi-static testing equipment, drop-weight towers, and Split Hopkinson Pressure Bars. Purpose-built environmental chambers will be used to achieve and maintain low temperatures, of $-20^\circ$C, and elevated temperatures, of $+80^\circ$C.

Preliminary experiments were carried out to ensure that the sample reached thermal equilibrium prior to compression. 10 x 10 mm cylindrical samples of the materials of interest were placed in an enviro-chamber, with wire thermocouples placed in the centre of the samples, as well as towards their surface. The time taken for the samples to reach the desired temperature (both high and low) was then observed. Repeats of these tests showed that a period of 10 - 15 minutes was sufficient for all materials. To be certain that the samples had indeed reached thermal equilibrium before subsequent compression, all the samples were left in their respective temperature environments for the longer period of 20 minutes. This approach provides a suitable degree of confidence in the sample being at temperature prior to compression.
3.1 Fundamental Concepts

In order to study the strength of materials, it is necessary to understand some basic concepts and properties of these materials. When investigating the ability of a material to withstand applied stress without failure, the material behaviour under a range of stresses and strains is considered. A number of methods are used to predict and observe the response of a material under loading, taking into account properties such as yield strength, stability, and material stiffness. Strength refers to the load carrying capacity, stability to the ability of a material to maintain its initial configuration, and stiffness to the deformation or elongation of the material [81].

There are three main types of loading: transverse, axial, and torsional [81].

**Axial Loading** The forces are applied parallel to the longitudinal axis of the sample, causing it either to extend or shorten.

**Transverse Loading** The forces are applied perpendicular to the longitudinal axis of the sample, causing it to bend and deflect from its original position. Internal tensile and compressive strains change with the change in curvature of the sample. Shear forces are also induced, causing shear deformation of the material and increasing the deflection of the sample in the transverse direction.

**Torsional Loading** Torsion is the twisting of the sample due to an applied torque, but only axial loading will be considered in this thesis.

Applying load to a material induces internal forces, the intensity of which is called stress. These stresses cause deformation of the material, known as strain [140]. The applied stress can be tensile, compressive, or shear.

Uniaxial stress is expressed as force acting on an area \( \sigma = \frac{F}{A} \), where the area can be the undeformed or deformed area, for engineering and true stress respectively. Compression is caused by an applied load reducing the length of the material along its axis, whereas tensile stress is caused by forces pulling in opposite directions, thereby stretching the material along its axis [3]. For most materials, their compressive strength is comparable to their tensile strength; however, for ceramics and other brittle materials, the compressive strength is generally an order of magnitude higher than their tensile strength [90]. Shear stress is caused by a pair of opposing forces acting parallel, causing faces of the material to slide relative to each other [3].

Strain is defined as the deformation of the material per unit length, whereas deflection is used to describe how much a material bends under a load. Elasticity is the ability of a material to return to its previous shape once the applied load is removed. If the applied stress is directly proportional to the resulting strain, this perfectly linear elastic behaviour is described by Hooke’s law, and the constant of proportionality is known as the Young’s Modulus, \( E \). This modulus of elasticity can be used to determine the stress-strain relationship in the linear-elastic portion of the stress-strain curve, which is below
the yield point [3].

The elastic modulus measures the resistance of a material to elastic deformation. Low modulus materials are floppy and deflect a lot when they are loaded, and have a lower natural frequency than materials with a higher modulus. Sometimes these features are desirable, where structures such as springs and cushions are designed to deflect, but in most mechanical applications, deflection is undesirable [81].

All solids are linear elastic at small strains. The area under the stress-strain line is the elastic energy stored per unit volume. Since the material is elastic, all this energy stored during loading will be recovered upon unloading [81].

In a loading test, as the load increases, the specimen at first is strained elastically, or reversibly. Above a limiting stress, the elastic limit, some of the strain is permanent. This is known as plastic deformation. Yielding is the change from elastic to measurable plastic deformation, whilst the yield strength is the nominal stress at yielding. In many materials, this is difficult to spot on the stress-strain curve. In such cases, it is better to use a proof stress, which is the stress which produces a permanent strain equal to a specified percentage of the specimen length. A common proof stress is one corresponding to 0.1 percent permanent strain [81].

All solids have an elastic limit beyond which they behave irreversibly. A totally brittle solid will fracture. Other engineering materials deform plastically, changing their shapes permanently [81].

The yield strength of a material is the stress at the onset of plastic flow, and the point on the engineering stress-strain curve (as opposed to the true stress-strain curve) beyond which the material experiences deformations that will not be completely reversed upon removal of the applied load. The ultimate strength refers to the point on the same curve which corresponds to the stress that produces fracture [3].

Most ceramics have enormous yield stresses. In a tensile test at room temperature, ceramics almost all fracture long before they yield; this is because their fracture toughness is very low (see Sec. 2.5.0.1) [81].

Pure metals are very soft, and have a high ductility. By work-hardening (the increase in stress needed to produce further strain in the plastic region) and alloying, the strength of metals can be increased, though their yield strengths will still be lower than most ceramics. Polymers generally have even lower yield strengths than metals, but can be strengthened by being made into composites [81].

Compressive and tensile strengths are the points at which the material fails under compressive or tensile loading respectively. Impact strength is the ability of the material to withstand a suddenly applied load, and is expressed in terms of energy. It can be measured using the Izod or Charpy impact test, both which measure the impact energy required to fracture a sample. In order to increase a material’s impact strength, the stresses should be distributed evenly throughout the material and its volume should be as
large as possible, with a high modulus of elasticity and a high material yield strength [3].

A material’s strength can be increased, for example, by work(strain)-hardening and grain boundary strengthening (grain boundaries impede dislocation movement) [91]. However, artificially increasing the material’s strength can have a negative impact on other mechanical properties of the material. For example, yield strength can be maximised through grain boundary strengthening by reducing the grain sizes, but extremely small grain sizes will make the material more brittle. Repeated loading can lead to fatigue, as brittle cracks are initiated at stress concentrations, for example near holes and corners, and grow until the material fails [3].

Dislocations are line defects in the crystal lattice of a material, which make slip easier by gliding. Slip typically occurs along very specific slip systems, dependent on the crystal type, and can be inter-crystalline or trans-crystalline. The movement of these dislocations can affect fracture as well as work-hardening [3].

3.2 Quasi-Static Testing

Quasi-static testing is used to determine the response of materials under very low strain rate conditions. In these experiments, the forces act on both sides of the specimen. A typical machine used in these tests is the Instron testing machine, which can be used both in compression and tension to uniformly load a sample. It is a servo-hydraulic machine, the middle section of which can move vertically up and down. The force is measured by a load cell, and the distance by a capacitive or inductive setup [12].

Under compression, the machine is designed to load uniformly and compress a specimen, impact free, until the material is compressed to a pre-defined limit (for example, a particular compression height or compression load). If the material is being tested uniaxially under tension, it is usual to use a dog-bone shaped specimen sample - the specimen will be loaded uniformly and stretched, free from impact, until fracture occurs. However, it is generally possible to test a number of different specimen sizes and shapes [141].

In materials science, the compression test is used predominantly to test metals and polymers. This is because the tensile and compressive strengths of these materials are the same. For brittle solids, however, the compressive strength is roughly 15 times larger [81] (see Sec. 2.5.0.2 for more detail). There is therefore a huge lack in the available literature on the compressive strength of brittle materials [90].

For these experiments, the universal testing machine Instron 5584 250 kN, limited to 100 kN and instrumented with a 150 kN load cell, in the Mechanical Engineering Department at Imperial College London was used (see figure 3.1). The tests were stopped when 50% of the original specimen height was reached, a force of 90 kN was obtained, or the material fractured. Each test was repeated in order to attempt to account for variability.
The Instron machine is a servo-hydraulic machine and is computer-controlled, automatically outputting force-time and displacement-time data. This data can then be converted to find both the engineering and true stress-strain relationships of the material. The recorded data can also be used to help characterise the material and calculate a number of other material properties, such as the ultimate tensile stress and the upper and lower limits of yield stress.

Compliance testing was carried out in order to calibrate the Instron testing machine, and then correct the obtained data. These experiments were performed across the full range of strain rates without the presence of specimens between the compression anvils, and compressed to the upper limits of the loads which the materials under investigation were expected to experience.

The temperature of the samples was controlled by use of a thermostatically-controlled environmental chamber (see figure 3.2), which encompassed both the steel column adapters and the sample mounted in-between the compression platens between the steel rods. Cold gas from a liquid nitrogen steel container is pumped through the enviro-chamber to achieve sub-zero temperatures, and the enviro-chamber has an in-built forced convection heating system, allowing higher temperatures to be attained.
3.2.1 Data Analysis

The force-time and displacement-time data output from the Instron can be manipulated to give both the engineering and true stress-strain relationships experienced by the compressed material, using the following equations:

\[ \sigma_e = \frac{F}{A_0} \quad (3.1) \]

\[ \varepsilon_e = \frac{\Delta h}{h_0} \quad (3.2) \]

\[ \sigma_{true} = \sigma_e (1 + \varepsilon_e) \quad (3.3) \]

\[ \varepsilon_{true} = \ln(1 + \varepsilon_e) \quad (3.4) \]

where \( \sigma_e \) is the engineering stress, \( F \) is the compressive load (or force), \( A_0 \) is the initial sample area, \( \varepsilon_e \) is the engineering strain, \( \Delta h \) is the change in sample height, \( h_0 \) is the initial sample height, and \( \sigma_{true} \) and \( \varepsilon_{true} \) are the true stress and true strain respectively.

These equations can also be used to analyse the data output from drop-weight exper-
3.3 Drop-Weight Towers

In drop weight experiments, as in quasi-static tests, the machines are computer-controlled, and automatically output the force-time and displacement-time data. High-speed cameras can be used to provide an additional way of calculating the specimen length during compression, as well as observing deformation modes.

A drop-weight (tower) machine (see figure 3.3) can be used to apply strain rates of the order of $10^2$ s$^{-1}$ to a specimen. A typical drop-weight machine consists of a mass holder for steel (the mass of which can be exchanged as desired), with a fitted accelerometer to lift it to the required impact velocity. The mass slides down between two external guiding rods, and its velocity can be measured. There is also an anti-rebound braking device mounted on the machine (usually at the base), used to prevent the mass from hitting the specimen more than once [142].

The specimen itself is mounted between two steel rollers (see figure 3.4), and a load cell to measure the force is attached below the second anvil. All the anvils are guided by aluminium alloy plates to prevent slipping of the specimen during impact. It is possible to use a high speed video camera, such as the Phantom 12.1, to observe the deformation behaviour of the specimens [141].

For these experiments, the spring-loaded Instron (Dynatup) 9250HV machine in the Civil Engineering Department at Imperial College London was used. This machine can drop a mass up to 90 kg from a height on to a specimen, resulting in impact velocities up to 20 m s$^{-1}$. High speed imaging was used in order to study the different failure modes experienced by the materials under compression. In addition, the smaller drop-weight tower in the Bioengineering Department at Imperial College London was used, when recovery of the brittle piezoceramic PZT 95/5 was desired.
Figure 3.3: Instron drop-weight tower.

Figure 3.4: The impact area of a drop-weight testing machine.
3.4 Split Hopkinson Pressure Bars

A Split Hopkinson Pressure Bar (SHPB) is shown in figure 3.5, and is used to characterise the stress-strain behaviour of a variety of materials [142][143] under uniform axial stress. SHPBs can reach strain rates of the order of $10^4$ s$^{-1}$ [144].

Two similar SHPB systems were used: one at the Cavendish Laboratory, Cambridge, and one in the Bioengineering Department at Imperial College London. The system is composed of a single-stage gas gun with a 150 cm, 12.8 mm bore barrel, with three bars (input, output, and momentum capture bars) held in V-stand mounting blocks by plastic cable-tie straps, and a striker bar inserted in the gun barrel. The gas used to fire the striker bar can be either helium (as at the Cavendish Laboratory) or compressed air (as at Imperial College London).

The specimen sample is placed between the input and output bars. The gas gun is fired, and the striker bar hits the input bar. The striker bar velocity is limited to below 15 m s$^{-1}$, as the glue connecting the strain gauges to the bars fails above this speed [141]. The velocity of the striker bar is measured at the end of the guiding tube, using a laser diode array and detectors [145]. In this system, the diode separation is 44 mm. The longer the striker bar, the longer the duration of the compressive pulse.

The bars used for these experiments are made of Inconel Steel 718, used because its impedance (density) is unaffected over a large temperature range [146], and tungsten. Their properties are listed in table 3.1. Whilst it is usual to use bars with similar impedances, often accomplished by using the same material for the striker bar as for the input and output bars, the lengths of the bars can vary.

Calibration of the input and output bars, by conducting compression experiments in the absence of specimens, gives $k$ and $b$ bar constants for both bars [147], which are required to carry out Split Hopkinson Pressure Bar experiments; these values are also listed in table 3.1.

Upon impact of the striker bar onto the input bar, an elastic wave (compressive stress pulse) is generated in the input bar and travels along its length. Semiconductor strain gauges in the middle (lengthwise) of the input bar [148] measure the elastic wave. At the input bar-specimen interface, the input pulse is partially transmitted into the specimen and partially reflected back along the bar. This reflected wave travels back along the
### Table 3.1: Properties of the Inconel 718 and tungsten Split Hopkinson Pressure bars.

<table>
<thead>
<tr>
<th>Property</th>
<th>Inconel 718</th>
<th>Tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( \rho_b ) [kg ( m^{-3} )]</td>
<td>8269</td>
<td>16900</td>
</tr>
<tr>
<td>Wave Speed ( c_0 ) [m ( s^{-1} )]</td>
<td>4980</td>
<td>4406</td>
</tr>
<tr>
<td>Impedance ( Z ) [kg ( m^{-2} ) ( s^{-1} )]</td>
<td>( 41.3 \times 10^6 )</td>
<td>( 75.3 \times 10^6 )</td>
</tr>
<tr>
<td>Elastic Modulus ( E_b ) [GPa]</td>
<td>205</td>
<td>411</td>
</tr>
<tr>
<td>Striker Length ( L ) [mm]</td>
<td>182</td>
<td>151</td>
</tr>
<tr>
<td>Input/Output Bar Length ( L_b ) [mm]</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>( k_{input} )</td>
<td>55885</td>
<td>97803</td>
</tr>
<tr>
<td>( k_{output} )</td>
<td>55512</td>
<td>97942</td>
</tr>
<tr>
<td>( b_{input} )</td>
<td>0.0547</td>
<td>-0.03653</td>
</tr>
<tr>
<td>( b_{output} )</td>
<td>0.0099</td>
<td>-0.0902</td>
</tr>
<tr>
<td>Diameter ( D_b ) [mm]</td>
<td>12.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>

input bar as a tensile wave, due to the difference in acoustic impedance between the specimen and the bar material. This wave can also be detected by the strain gauges on the input bar [149]. The partially transmitted wave travels through the specimen and into the output bar, and is then recorded by the strain gauges on the output bar, also positioned halfway along the bar.

Thus, it is possible to record the complete incident, transmitted, and reflected pulses [150]. The resistance change from the strain gauges is converted to an input (from the input bar) and output (from the output bar) voltage, and is recorded by the attached oscilloscope [151], here a Tektronix DPO 3034, sampled at 25 MS \( s^{-1} \) (chosen due to the rate of compression wave propagation through the Hopkinson Bar system). The obtained voltage-time data can then be used to calculate, for example, the stress-strain relationship of the material [152][153].

If the specimen is in stress equilibrium (~3 reverberations) and deforms at a constant volume, the rate of deformation is directly proportional to the amplitude of the reflected stress wave, whilst the amplitude of the transmitted wave is directly proportional to the stress the specimen supports [154].

#### 3.4.0.1 Temperature experiments on the Split Hopkinson Pressure Bar

A number of different heat exchange systems were developed to achieve the different (both high and low) temperatures required for these SHPB experiments. The systems can achieve temperatures between the range of \(-100^\circ C\) and \(+100^\circ C\). Due to the metallic construction of the SHPB, an initial pre-testing period of one hour was required in order to allow the components of the apparatus (rail-mount, bars, etc.) to reach thermal equilibrium before placing the sample in-between the bars.

For achieving elevated temperatures, two different setups were used. For the relatively lower temperatures of \(+45^\circ C\), a 125 W ceramic band heater (connected to a thermostatic
Figure 3.6: Ceramic band heater for achieving high temperatures using a Split Hopkinson Pressure Bar.

Figure 3.7: Enviro-chamber for achieving low temperatures using a Split Hopkinson Pressure bar.

controller) was placed, non-contacting, on the ends of the input and output bars around the specimen sample (see figure 3.6). However, this system was found to be too inefficient for achieving higher temperatures as, despite the temperature rating of +150°C on the ceramic band heater, it was not found to achieve much higher temperatures than +50°C. Therefore, a different system was needed to achieve significantly higher temperatures.

A system making use of a heating plate and a hot air blower was devised. To achieve temperatures of +80°C and heat the samples evenly, they were first placed on a heating plate at +80°C for 20 minutes, being turned every five minutes to ensure thermal equilibrium throughout the sample. The sample was then transferred quickly to the nearby SHPB system, whose ends were being heated by a hot air blower, positioned at 30 cm above the sample.

Due to difficulties in securing liquid nitrogen regularly, two different systems needed
to be devised for achieving sub-zero temperatures. The first involved cooling of the test specimens in-situ, with the sample held between the input and output bars. A chamber was built such that it fitted around the sample and the ends of the input and output bars, without impeding the movement of the bars. Gas from a Cryolab 20 liquid nitrogen dewar was passed through the enviro-chamber and around the sample, cooling it down (see figure 3.7), and the temperature inside the chamber was regulated using a thermocouple located within the chamber. The entire chamber was designed so that it could be securely mounted on a rail carriage, allowing for complete alignment with the rest of the SHPB system.

Perspex windows were added to the chamber, to enable use of high-speed imaging using, for example, a Phantom 12.1, which could then be used to further study dynamic compression and failure modes. This setup also allows for sample recovery for post-experimental analyses, such as scanning electron microscopy studies.

The second system, to be used when liquid nitrogen was unavailable, employed dry ice but, this time, the specimens had to be cooled before being placed in the cooled SHPB system. A polystyrene box was filled with dry ice. A contraption was set up 1 cm above the dry ice, where preliminary experiments had shown the temperature of the air was at $-20^\circ$C. The samples were held for 20 minutes, as reasoned in Sec. 3, before being placed in the system, which itself was cooled down using pellets of dry ice to ensure that the sample would not heat up upon contact.

### 3.4.1 Data Analysis

The data output from Split Hopkinson Pressure Bars is in the form of voltage-time data. These voltages can be manipulated into giving stress-strain relationships [152][153] as shown:

$$ F = kV(1 + bV) \quad (3.5) $$

$$ \sigma_b = \frac{F}{A_b} \quad (3.6) $$

$$ \varepsilon_b = \frac{\sigma_b}{E_b} \quad (3.7) $$

where $F$, the force transmitted by the bars, is a function of $V$, the recorded voltage, and $k$ and $b$, bar constants calculated during calibration (see Sec. 3.4). $\sigma_b$ and $\varepsilon_b$ are the stress and strain supported by the bars, whilst $A_b$ and $E_b$ are the cross-sectional area and Young’s Modulus of the bars respectively.

The strain obtained from both the input and output bars can be analysed to give an input strain ($\varepsilon_i$), reflected strain ($\varepsilon_r$), and a transmitted strain ($\varepsilon_t$). These strains can
then be manipulated to give the engineering stress and engineering strain rate experienced by the sample (which can further be used to give the true stress-strain behaviour of the material using the same equations given in Sec. 3.2.1):

\[
\sigma_e = \frac{EA_b}{2A_0} (\varepsilon_i + \varepsilon_r + \varepsilon_t) \quad (3.8)
\]

\[
\dot{\varepsilon}_e = \frac{c_0}{h_0} (\varepsilon_i - \varepsilon_r - \varepsilon_t) dt \quad (3.9)
\]

where \( c_0 \) is the sound wave speed in the bars, and \( dt \) the time interval. This engineering strain rate can be integrated to give the engineering strain experienced by the sample.

**Note** An inherent assumption for all this data analysis is that the volume of the specimen remains constant. This is not a valid assumption for ceramics, as they are brittle and therefore fracture at relatively lower strain rates; as the material fractures, its volume increases (as the fracture itself also takes up volume). Thus, only the engineering stress-strain relationship (which only takes into account initial sample dimensions) can be calculated for brittle materials, whereas it is possible to calculate the true stress-strain relationships for, amongst others, polymers, and metals [155].

### 3.5 Diagnostics

A number of methods are used to obtain data from these experiments. For example, stress gauges are used to record longitudinal and transverse stress, as well as spall and dynamic compressive strength, whilst surface strain measurements are detected using a combination of strain gauges and high speed photography. Finally, temperature can be measured using spectroscopy or pyrometry.

Field et al. [156] have compiled a comprehensive description of suitable diagnostics for high strain rate testing, some of which are described here.

Typically, strain gauges take measurements at a single point, combining data with a high level of accuracy (of the order of micro-strain) with good time resolution (of the order of tens of nanoseconds). However, they only give information at one point in the field of view, and they need to be bonded to the specimen, which can affect the stress field. There is therefore a drive to use non-contacting, whole-field optical techniques to measure the displacement, strain, and stress in these shock experiments [157]. Several of these techniques are discussed in this section.

Caustics are used to detect dynamic fracture [158]. A laser is reflected off the surface of the specimen, and detected by a nearby camera. The intensity distribution is affected by the surface slope distribution, but analysis of general stress fields is difficult. In the presence of a crack however, the surface displacement of the specimen is affected, and the caustic pattern forms a dark, almost circular, region centred on the crack tip. It is also
possible to use this method to observe moving cracks without the need for a high-speed camera.

Laser speckle photography involves recording double-exposure photographs of the granular pattern produced when a laser is shone onto a rough surface. The speckle pattern moves as if it were physically attached to the specimen surface; thus it is possible to measure the displacement field occurring. It is necessary to use high-speed cameras with good spatial resolution for this method. Speckle interferometry is a similar method, but makes use of the interference between two speckle patterns, or a speckle pattern and a smooth reference wave [159].

Shearing interferometry involves the interference pattern formed between two identical images, one of which has been ‘sheared’ or laterally shifted with respect to the other. The fringes represent contours of constant surface gradient, and this method is very useful for dynamic fracture experiments. The specimen must be highly reflecting, which means that it is possible to use lower-power lasers than those required for the methods described earlier [158].

It is possible to measure temperature using non-invasive, whole field, infrared techniques; however, this requires knowledge of the specimen’s surface emissivity, which is often not well-known and can also change during deformation. Dynamic infrared thermography involves infrared high-speed framing photography on millisecond timescales, and can be used to, for example, observe hotspots in propagating adiabatic shear bands [158].

Optical pyrometry is another method used to measure the temperature of the specimen. This works by measuring the brightness and colour of the specimen, and relates this radiance, using Planck’s law, to a temperature. Because many materials do not have the same emissivity at two wavelengths, multi-wavelength pyrometers, which use three or more wavelengths to achieve more accurate temperature measurements, are employed [158].

Optical microscopy can be used to examine the material’s microstructure, but it is not possible to identify different phases within the material. It is possible to use spectroscopy to determine the spectrum of the material’s radiative energy by measuring changes in its intensity and frequency. This data can then be used to study the matter under mechanical methods. Energy dispersive x-ray spectroscopy (EDS) can be used to study the composition of the material. If the sample is non-conducting, the sample surface must be covered with metallic coating (typically gold) to prevent charge build-up. Using this method, it is now possible to determine phases and lattice parameters, and to specify the precise composition of the material [158].

Another method for studying a material is to use a scanning electron microscope (SEM) to scan the sample with a beam of electrons [75]. The electrons interact with the atoms in the sample, and the obtained signal gives detailed information, for example, about the specimen’s surface topography, composition, and electrical conductivity [160].

Digital image correlation techniques can be used to obtain information on object mo-
Figure 3.8: Diagram of a Split Hopkinson Pressure Bar, with the specimen setup including both electrodes and insulation.

tion and deformation using two or more images between which displacement has occurred. The object is photographed before the start of the experiment, and then a series of images is recorded during deformation. Small sub-images from the undeformed and deformed images are selected and then mathematically compared, such that a best-fit displacement in pixels can be found that maps one onto the other. This process is repeated over the whole image, and the answers suitably scaled, allowing a whole field displacement map in SI units to be created [161]. Optical surface profile-tracking, useful for high-resolution strain measurement, is one example of such a method [157].

3.5.1 Measurement of Voltage Output

Since the piezoceramic PZT 95/5 gives out charge under the application of strain, an electrical system is required to measure the voltage output. A potential divider connected to insulated electrodes will be implemented.

Two different sets of electrodes will be used. For drop-weight impacts, due to their relatively low strain-rate nature, brass shim of ~0.3 mm thickness can be used for multiple loading experiments. However, increasing the strain rate increases its deformation upon compression with the much harder PZT samples. As such, 2 mm thick Inconel 718 slices will be used as electrodes for the higher rate Split Hopkinson Pressure Bar experiments, see figure 3.8.

All the electrodes will be insulated from the surrounding metallic loading equipment using thin sheets of mylar and kapton tape. Kapton in particular is used due to its highly
robust and temperature independent nature.

The electrodes ($V_{in}$) will be connected to a simple potential divider circuit (see figure 3.9), designed to reduce the voltage output from the PZT samples to those that can be read on an ordinary oscilloscope. Samples in these experiments will be up to 4.4 mm in thickness, and previous studies on PZT ceramics have shown that voltage output from these components can be up to 20 V mm$^{-1}$. Since the Tektronix oscilloscopes used here have a maximum reading of 10 V div$^{-1}$, a potential divider circuit with $\sim$100x attenuation will be used.

The simple potential divider circuit in figure 3.9 will give an output voltage that can be recorded by the Tektronix oscilloscope (which has an impedance of 1 M$\Omega$). This will be used to calculate the current, $I$, being driven by the PZT during loading, which can further be used to calculate a charge output with time. This data will then be compared to the stress and strain behaviour of the PZT samples, to give a more complete understanding of the electromechanical behaviour of PZT 95/5 under compression.
He said: “That in which my Lord has established me is better, but assist me with strength; I will make between you and them a dam. Bring me sheets of iron,” until, when he had levelled [them] between the two mountain walls, he said: “Blow,” until, when he had made it [like] fire, he said: “Bring me, that I may pour over it, molten copper.”

Chapter 4

Specimen Design

To ensure the validity of results for a given experimental technique, sample dimensions and aspect ratios must complement the load and loading rate. For example, in Split Hopkinson Pressure Bar experiments, it is important that stress equilibrium be reached inside the specimen; the sample should be sufficiently thin to obtain ∼3 internal reflections of the stress wave [162]. The sample diameter should be less than or equal to the diameter of the bars, never expanding beyond the bars’ diameter [149]. It has been suggested that the radial and longitudinal inertia and friction effects can be lessened by minimising the areal mismatch between the bar and the specimens, such that the sample diameter is roughly 0.8 times the diameter of the bar [163]. In addition, the sample diameter should be sufficiently small such that stresses due to radial inertia are negligible [149][164][165].

Previous research has studied the effects of altering the shape and size of samples over a range of compression rates, though few have compared and contrasted how these effects vary. In addition, several discrepancies exist in the published data, most probably due to the wide range of techniques used [166][167][168][169]. This preliminary research was carried out on well-documented non-ceramic materials in order to bridge this gap, and to determine the sample geometry to use for the main purpose of understanding the piezoceramic PZT 95/5 and several polymers typically used to coat it in industrial applications.

The range of strain rates examined here, between $10^{-4} - 10^{4} \text{s}^{-1}$, were achieved using quasi-static, drop-weight tower, and Split Hopkinson Pressure Bar techniques. All the experiments were carried out at ambient temperature and humidity. The engineering stress-strain relationships obtained are compared and discussed.
Table 4.1: Aspect ratios for samples of 4 mm diameter and varying thickness.

<table>
<thead>
<tr>
<th>Sample Thickness [mm]</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4.8</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
</tr>
<tr>
<td>7.2</td>
<td>1.8</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
</tr>
</tbody>
</table>

4.1 Materials

A range of well-characterised materials will be examined here, such that the results obtained can be compared with data from manufacturing companies and other papers. For this purpose, polycarbonate 1000, aluminium 5083, copper 101, and titanium (Ti-6Al-4V) will be experimented upon.

Polycarbonate 1000 is an amorphous thermoplastic polymer with high transparency and toughness, and has a large variety of applications. It has an average density of 1.20 g cm$^{-3}$, and a glass transition temperature of $+145^\circ$C.

Aluminium 5083-H321 has an average density of 2.66 g cm$^{-3}$, and a melting point of $+570^\circ$C. The chemical composition in this aluminium alloy is 92.4% aluminium, 4.9% magnesium, 1.0% manganese, 0.4% silicon, and 0.4% iron, with trace amounts of zinc, titanium, copper, and chromium.

Copper 101 has an average density of 8.92 g cm$^{-3}$, and a melting point of $+1083^\circ$C. It has a high ductility and high electrical conductivity, as well as a high impact strength.

The titanium Ti-6Al-4V has purity 99.6% and is annealed. It has an average density of 4.50 g cm$^{-3}$, and a melting point of $+1660^\circ$C. Titanium and its alloys are characterised by their lightness, strength, and corrosion resistance, and are used widely in aerospace applications.

Cylindrical samples of aluminium, copper, titanium, and polycarbonate have been machined to a constant diameter of 4 mm and thicknesses of 1 - 12 mm. The samples will henceforth be designated by their aspect ratios (ratio of length-to-diameter $l/d$), and will range between 0.25 - 3, see table 4.1.
4.2 Low Strain Rate Effects

Compression rates between 0.001 - 1.0 mm s\(^{-1}\) were adopted, resulting in strain rates as low as 10\(^{-4}\) s\(^{-1}\).

4.2.1 Polycarbonate

![Figure 4.1: Quasi-static stress-strain data for polycarbonate of varying lengths (mm) at a compression rate of 0.001 mm s\(^{-1}\).](image)

![Figure 4.2: Quasi-static stress-strain data for polycarbonate of varying aspect ratios at a compression rate of 0.004 mm s\(^{-1}\).](image)

As can be seen from figures 4.1, 4.3, and 4.4, the stress-strain behaviour of polycarbonate when subjected to quasi-static compression at rates between 0.001 - 1.0 mm s\(^{-1}\) is comparable, except for the samples which buckled. Buckling was seen in all polycarbonate samples of height 12 mm (i.e. an aspect ratio of 3) across all compression rates. Upon increasing the compression rate from 0.001 mm s\(^{-1}\), to both 0.1 mm s\(^{-1}\) and 1.0 mm s\(^{-1}\), buckling is then also observed in polycarbonate samples of height 7.2 mm and 8 mm (i.e. aspect ratios of 1.8 and 2 respectively). Upon comparing the obtained data with that collected previously, shown in figure 4.2 [4], it appears that buckling in aspect ratios higher than 1.8 even begins to appear at compression rates of 0.004 mm s\(^{-1}\).

Regardless of compression rate, yielding in polycarbonate occurred at 70±8 MPa for all aspect ratios. This agrees well with average values on data sheets presented by a number of material production companies, ∼80 MPa, giving credence to this methodology.

For the samples of polycarbonate which did not buckle, though the stress-strain behaviour was very similar, there is still a slight difference in the value of strain at which the material yielded, resulting in a small difference in the elastic behaviour of the polycarbonate. As the thickness of the polycarbonate specimen decreases, we see an increase in the value of strain at which the material yields, resulting in lower values of the modulus of the sample. In other words, as the aspect ratio for samples increases, the slope in the
Figure 4.3: Quasi-static stress-strain data for polycarbonate at a compression rate of 0.1 mm s$^{-1}$.

Figure 4.4: Quasi-static stress-strain data for polycarbonate at a compression rate of 1.0 mm s$^{-1}$.

elastic region steepens, indicating a stiffer response at higher aspect ratios. This is most noticeable at the highest compression rate of 1.0 mm s$^{-1}$ (see figure 4.4).

4.2.2 Aluminium

Figure 4.5: Quasi-static stress-strain data for aluminium at a compression rate of 0.01 mm s$^{-1}$.

Figure 4.6: Quasi-static stress-strain data for aluminium at a compression rate of 0.1 mm s$^{-1}$.

As expected, aluminium supported far larger stresses than polycarbonate (see figures 4.5 and 4.6). As for polycarbonate, the stress-strain behaviour of aluminium when subjected to quasi-static compression is comparable, except for the samples which buckled. However, the samples yield across a larger range as compared to the same aspect ratios for polycarbonate. Nonetheless, as data sheets provided by a number of material providers for aluminium 5083 give yield strengths of 320±50 MPa, this still allows this data to fall within an acceptable range.
Buckling was only seen in aluminium samples of height 12 mm (i.e. an aspect ratio of 3) across all compression rates. This trend has also been observed in other alloys of aluminium [4].

### 4.2.3 Copper

![Figure 4.7: Quasi-static stress-strain data for copper at a compression rate of 0.001 mm s$^{-1}$.](image1)

![Figure 4.8: Quasi-static stress-strain data for copper at a compression rate of 0.01 mm s$^{-1}$.](image2)

As in the aluminium, buckling was only seen in copper samples of height 12 mm (i.e. an aspect ratio of 3) across all compression rates (see figures 4.7 and 4.8). In addition, the copper 101 samples supported slightly larger stresses than the aluminium of the same aspect ratios. Aside from those that buckled, the copper specimens yielded at stresses between 350 - 400 MPa, which can be compared with data sheet values of $\sim$390 MPa.

### 4.2.4 Titanium

The titanium in these experiments was seen to yield at values between 1000 - 1150 MPa (see figures 4.9 and 4.10), which is comparable to values from data sheets of 1000±300 MPa. However, samples of 1 mm thickness (aspect ratio 0.25) did not reach a yield point, regardless of compression rate. At the other end of the scale, all the samples of 12 mm thickness buckled, at almost identical stresses and strains.

Whilst specimens of aspect ratio of 3 buckled, samples of aspect ratios between 1.5 - 2 (i.e. of thicknesses 6, 7.2, and 8 mm) actually sheared. As the aspect ratio increased, the stress at which the samples sheared decreased, see figure 4.10.
Figure 4.9: Quasi-static stress-strain data for titanium at a compression rate of 0.001 mm s\(^{-1}\).

Figure 4.10: Quasi-static stress-strain data for titanium at a compression rate of 1.0 mm s\(^{-1}\).

Figure 4.11: Drop-weight sequence showing the compressive behaviour of a polycarbonate cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass \(\sim\)7 kg, impact velocity \(\sim\)3 m s\(^{-1}\)).

4.3 Drop-Weight Testing

The impact mass used in these experiments was \(\sim\)7 kg, and an impact velocity of \(\sim\)3 m s\(^{-1}\) was adopted. A high-speed video camera, the Phantom V12.1, was used to observe the deformation behaviour of the specimens.

From the obtained high-speed images (figures 4.11, 4.12, 4.13, and 4.14), it can be seen that all four materials, polycarbonate, aluminium, copper, and titanium, deform plastically, due to the large applied strains.

The drop-weight sequences from these experiments have been synchronised with their
Figure 4.13: Drop-weight sequence showing the compressive behaviour of a copper cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s⁻¹).

Figure 4.14: Drop-weight sequence showing the compressive behaviour of a titanium cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s⁻¹).

respective stress-time data graphs. It is thus possible to determine the stress being experienced by the samples at different times during loading. For clarity, these have been included in Appendix A.

At aspect ratios larger than 1.8, we see obvious buckling in polycarbonate (see figure 4.15), and the start of buckling in copper. Aluminium begins to buckle at aspect ratios of 2. This buckling effect in aluminium and copper is far more pronounced in the cylinders with aspect ratios equal to 3, as shown in figures 4.16 and 4.17. Titanium does not appear to buckle at all at these loading conditions (see figure 4.18).

It was observed during quasi-static experiments that polycarbonate and copper samples of aspect ratio 1.8 and larger began to buckle as the strain rates were increased, and we see this behaviour continuing at these higher drop-weight produced strain rates, as just described. In aluminium, as the quasi-static strain rates were increased, buckling began to be observed in aluminium samples of aspect ratio 2, and this is again observed

Figure 4.15: Buckling in a polycarbonate cylinder, aspect ratio 1.8 (diameter = 4 mm, height = 7.2 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s⁻¹).
Figure 4.16: Buckling in an aluminium cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figure 4.17: Buckling in a copper cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figure 4.18: Drop-weight sequence showing the compressive behaviour of a titanium cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).
at drop-weight strains. However, titanium samples under drop-weight loading conditions did not buckle at all, whereas they were seen to buckle at all compression rates during quasi-static tests.

Figure 4.19: Stress-time data for polycarbonate, obtained during drop-weight impact experiments (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figure 4.20: Stress-time data for aluminium, obtained during drop-weight impact experiments (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figure 4.21: Stress-time data for copper, obtained during drop-weight impact experiments (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figure 4.22: Stress-time data for titanium, obtained during drop-weight impact experiments (mass \(\sim 7\) kg, impact velocity \(\sim 3\) m s\(^{-1}\)).

Figures 4.19, 4.20, 4.21, and 4.22 show the stress-time behaviour for polycarbonate, aluminium, copper, and titanium respectively. It can be seen that the stress-time behaviour for all the materials across all aspect ratios above and including 0.75 (3 mm thick and larger) are comparable for the first 0.25 milliseconds, after which the data sets deviate, with the aspect ratios of 1.2 (4.8 mm thick) and below reaching higher peak stresses and earlier in time.
In all materials, samples with aspect ratios of 0.5 and 0.25 (2 mm and 1 mm thick respectively) reach lower initial peak stresses and at a later time, before attaining much higher final stresses than all other aspect ratios.

The larger aspect ratios follow similar trends to each other, this being clearer in aluminium (figure 4.20) and copper (figure 4.21) than the other two materials.

The data for the polycarbonate, though following this same overall trend, has much larger differences between the peak stresses experienced between samples of lower aspect ratio compared with those of larger thicknesses. Titanium, though also following the aforementioned general stress-time trend, varies far less as compared with the other materials; its stress-time data is far more consistent across all aspect ratios.

As expected from data obtained during the quasi-static experiments (see Sec. 4.2), titanium is generally able to support a much higher load as compared with the other three materials, with polycarbonate reaching far lower peak stresses than those experienced by the metals. In addition, as expected from the earlier results of comparable yield stresses attained by copper and aluminium during quasi-static compression, we see that the drop-weight stress-time behaviour of copper is commensurate with that of aluminium, seen clearly in figure 4.23. However, it is interesting to note that samples of polycarbonate, aluminium, and copper, with aspect ratios of 0.5 and 0.25, appear to be able to support loads almost equivalent to those experienced by titanium. This is seen more markedly in figure 4.24.
4.4 Split Hopkinson Pressure Bars

The results presented here are from experiments carried out on the Split Hopkinson Pressure Bar system at Imperial College London (see Sec. 3.4). The bars used were Inconel 718; the striker bar length was 228 mm. The longest striker bar available was used, as it produced a longer duration of compressive pulse, even though this compromise resulted in lower impact velocities being attained. The firing pressures used were 0.25, 0.5, 0.75, and 1.0 bar, resulting in impact velocities of 3.7 - 9.3 m s$^{-1}$, and strain rates between 320 - 10200 s$^{-1}$.

4.4.1 Polycarbonate

![Stress-time data for polycarbonate, at impact velocities of ~4 m s$^{-1}$](image1)

![Stress-time data for polycarbonate, at impact velocities of ~6 m s$^{-1}$](image2)

![Stress-time data for polycarbonate, at impact velocities of ~7.8 m s$^{-1}$](image3)

![Stress-time data for polycarbonate, at impact velocities of ~9 m s$^{-1}$](image4)

Figures 4.25, 4.26, 4.27, and 4.28 show the stress-time behaviour of polycarbonate
samples of all aspect ratios across all the impact velocities. As can be seen, the stress-time relationship is very similar for aspect ratios between 0.5 - 1.5, regardless of impact conditions, and for all aspect ratios at the lowest strain rates (see figure 4.25). The initial peak stress was between 60 - 120 MPa, the stress decreasing with increasing aspect ratio. The initial peak stress was reached at 30±5 µs for the smallest aspect ratios, when the increase in stress slowed down. For aspect ratios ≥1.8, the peak stress is reached much later, between 70 - 80 µs, except at impact velocities ~9 m s⁻¹. For samples of aspect ratio 0.25, the initial peak stress is reached much before, ~10 µs, when the stress increases steeply until ~80 µs, before decreasing rapidly.

Figure 4.29: Stress-strain data for polycarbonate, at impact velocities of ~6 m s⁻¹.

Figure 4.30: Stress-strain data for polycarbonate, aspect ratio 0.5 (thickness of 2 mm).

Figure 4.29 gives an example of stress-strain behaviour for polycarbonate samples of all aspect ratios at impact velocities of ~6 m s⁻¹. We can see that the initial stress-strain behaviour is constant. However, as the aspect ratio of the samples is increased, the strain at which the initial peak stress is reached decreases. An identical post-yield softening is observed, although larger aspect ratios experience lower applied strains. This is true for all the samples, except for the polycarbonate with the aspect ratio of 0.25. This figure also shows the increase in stress after initial peak stress is reached for the sample of 0.25 aspect ratio after a strain of 0.1.

Figures 4.30 and 4.31 demonstrate the similar stresses reached for samples of low aspect ratios (here, 0.5 and 0.75) across the full range of strain rates, whilst figure 4.32 shows the dissimilar stress-strain behaviour of samples with very large aspect ratios, here 1.8.
Figure 4.31: Stress-strain data for polycarbonate, aspect ratio 0.75 (thickness of 3 mm).

Figure 4.32: Stress-strain data for polycarbonate, aspect ratio 1.8 (thickness of 7.2 mm).

4.4.2 Aluminium

Figure 4.33: Stress-time data for aluminium, at impact velocities of $\sim 4 \text{ m s}^{-1}$.

Figure 4.34: Stress-time data for aluminium, at impact velocities of $\sim 6 \text{ m s}^{-1}$.

Figures 4.33, 4.34, 4.35, and 4.36 show the stress-time behaviour of aluminium samples of all aspect ratios at impact velocities of $\sim 4 \text{ m s}^{-1}$, $\sim 6 \text{ m s}^{-1}$, $\sim 7.8 \text{ m s}^{-1}$, and $\sim 9 \text{ m s}^{-1}$ respectively. As can be seen, the stress-time behaviour is very similar for all the aspect ratios, except for those of 0.25, for each impact velocity. Whilst the initial stress-time gradients for the lowest impact velocities across the aspect ratios are relatively dispersed (see figure 4.33), they tend towards each other as the impact velocities increase, see figure 4.36. The stress experienced by the samples was between 350 - 450 MPa, decreasing with increasing aspect ratio, and initially peaking between 10 - 20 $\mu$s, regardless of impact time.

Figure 4.37 gives an example of stress-strain behaviour for aluminium samples of all
aspect ratios at impact velocities of $\sim 7.8 \text{ m s}^{-1}$. We can see that the initial stress-strain behaviour is constant. However, as the aspect ratio of the samples is increased, the strain at which the initial peak stress is reached decreases. An identical stress-strain plateau is observed, although larger aspect ratios experience lower applied strains. This is true for all the samples, except for the aluminium with the aspect ratio of 0.25, which compares with the polycarbonate studied at these rates too, see Sec. 4.4.1. This figure too shows the increase in stress after the initial peak stress is reached for the sample of 0.25 aspect ratio after a strain of 0.1.

Figures 4.38 and 4.39 demonstrate the similar stresses reached for samples of low aspect ratios (here, 0.5 and 2) across the full range of strain rates, and highlights the decreasing strains at which these are reached for both increasing aspect ratios and decreasing impact.
4.4.3 Copper

Figures 4.40, 4.41, 4.42, and 4.43 show the stress-time behaviour of copper samples of all aspect ratios at impact velocities between 4 - 9 m s\(^{-1}\). As can be seen, the initial stress-time behaviour is quite varied, but tends towards a similar gradient as the impact velocities increase. The peak stresses experienced are between 400 - 500 MPa, and are fairly level except for samples with aspect ratio 0.25, where the stress increases over time. These peak stresses are reached over shorter periods of time as the impact velocities are increased.

Figure 4.44 gives an example of stress-strain behaviour for copper samples of all aspect ratios at impact velocities of ∼9 m s\(^{-1}\). We can see that, as the aspect ratio decreases, the
Figure 4.42: Stress-time data for copper, at impact velocities of \( \sim 7.8 \text{ m s}^{-1} \).

Figure 4.43: Stress-time data for copper, at impact velocities of \( \sim 9 \text{ m s}^{-1} \).

stress at which peak stress is reached increases, but that the stress reached is very similar across all aspect ratios. An identical stress-strain plateau is observed, although larger aspect ratios experience lower applied strains. This is true for all the samples, but for the copper with the aspect ratio of 0.25, which compares with the polycarbonate and the aluminium studied at these rates too, see Sec. 4.4.2. This figure too shows the increase in stress after the initial peak stress is reached for the sample of 0.25 aspect ratio after a strain of 0.2, which is later as compared with the polycarbonate and the aluminium.

Figures 4.45 and 4.46 show the different stress-strain behaviour experienced at similar impact velocities for copper samples of widely different thicknesses, here 1 mm and 12 mm respectively. The thicker samples, as just discussed, experience comparable, even stresses from similar strains, but the aspect ratios of 0.25 reach an initial peak stress at strain
∼0.2 and then the stress continues to increase but with a much lower strain dependence.

### 4.4.4 Titanium

Figures 4.47, 4.48, 4.49, and 4.50 show the contrasting stress-time behaviour of titanium samples at differing impact velocities. Only at impact velocities ∼9 m s⁻¹ do we see a trend between aspect ratio and the stress-time behaviour, where increasing the aspect ratio decreases the peak stress reached, whilst increasing the time taken to achieve this peak stress. At lower impact velocities, there is no obvious trend, though the largest aspect ratio of 3 continues to have the lowest stress-time gradient values. The peak stresses achieved were significantly lower at velocities of ∼4 m s⁻¹, and increased with increasing impact velocities. This is in stark contrast with the peak stress behaviour of the other materials in this study where, regardless of loading conditions, the samples achieved pres-
sures within $\sim 100$ MPa of each other. It appears that the peak stress is reached sooner as the firing pressures are increased, but this is not completely obvious within the data sets available.

Despite there not being a clear trend when inspecting the stress-time behaviour of titanium, if we instead focus on its stress-strain behaviour, we see a clearer trend between aspect ratio and the stress-strain curves. All impact velocities show a decrease in the initial stress-strain gradient with decreasing aspect ratio, i.e. the peak stress arrives at a later strain as the thickness of the sample decreases, and this is apparent for all firing pressures, as shown in figures 4.51, 4.52, 4.53, and 4.54. The stress-strain plateau only appears as impact velocities are increased to $\sim 7.8$ m s$^{-1}$, and is present over a larger strain as the impact velocity is further increased to $\sim 9$ m s$^{-1}$.

Figures 4.55 and 4.56 show the different stress-strain behaviour experienced at similar impact velocities for titanium samples of widely different thicknesses, here 2 mm and 12
Figure 4.53: Stress-strain data for titanium, at impact velocities of \( \sim 7.8 \text{ m s}^{-1} \).

Figure 4.54: Stress-strain data for titanium, at impact velocities of \( \sim 9 \text{ m s}^{-1} \).

Figure 4.55: Stress-strain data for titanium, aspect ratio 0.5 (thickness of 2 mm).

Figure 4.56: Stress-strain data for titanium, aspect ratio 3 (thickness of 12 mm).

mm respectively. The thickest samples undergo a comparable stress-strain compression, but the lower aspect ratios do not appear to show any kind of obvious relationship; the results from experiments on titanium samples of 2 mm thickness are given here as an example.
4.5 Discussion

Data from compressive experiments can be used to calculate various material characteristics. A significant assumption during these analyses is that stress equilibrium is rapidly established within the specimen. However, compressive studies on material behaviour can show significant differences between the end pressures experienced by a sample sandwiched between two surfaces. Most often, this is dependent on the specimen’s length and the applied loading rate. The mechanisms responsible for these differences have been shown by several authors to be a combination of strain rate, inertial forces, friction effects, and non-uniform deformation due to wave propagation [166][170][171].

To ensure the validity of results for a given experimental technique, sample dimensions and aspect ratios must complement the load and loading rate. An investigation into the degree of stress uniformity in Split Hopkinson Pressure Bar specimens is particularly relevant to brittle materials, as it has implications on the validity and reliability of dynamic stress-strain curves derived from such experiments [162].

Previous research has studied the effects of altering the shape and size of samples over a range of compression rates, though few have compared and contrasted how these effects vary. Very few authors have proposed a standardised test specimen geometry, in part due to the different requirements that are predicated upon the mismatch in stiffness and densities of the bar material and specimen respectively. In addition, several discrepancies exist in the published data, most probably due to the wide range of techniques used [166][167][168][169][172]. This preliminary research was carried out on well-documented non-ceramic materials to bridge this gap, and to determine the most suitable sample geometry to use in order to reduce the aforementioned stress variability, for the primary purpose of understanding the piezoceramic PZT 95/5 and several polymers typically used to coat it in industrial applications.

The range of low to mid-strain rates examined here, between $10^{-4} - 10^4 \text{s}^{-1}$, was achieved using quasi-static, drop-weight tower, and Split Hopkinson Pressure Bar techniques. All these compression experiments were carried out at ambient temperature and humidity, on four different materials (polycarbonate 1000, aluminium 5083, copper 101, and titanium (Ti-6Al-4V)) with a range of aspect ratios between 0.25 - 3. The sample diameters were $\sim4 \text{mm}$, resulting in sample thicknesses between 1 - 12 mm.

From these experiments, we can conclude that conducting differing compression loading tests on metals with a range of sample geometries does not present significant problems or inconsistencies due to the homogeneity and isotropy of metals. However, this is not true for polycarbonate. Polycarbonate is a polymeric material, and therefore inhomogeneous and anisotropic. This accounts for the larger spread in the stress-strain behaviour of polycarbonate, as compared with the metals, across all the compressive strain rates, as demonstrated in this chapter.
More specifically, quasi-static compression demonstrated yield stresses which were comparable to those found in the literature, as well as those given by manufacturers in their data sheets. From these quasi-static experiments, it was clear that buckling was observed in all materials whose specimen thicknesses were three times their diameter. In addition, polycarbonate buckled from aspect ratios of 1.8, whilst titanium samples of aspect ratio 0.25 did not appear to yield at all.

In drop-weight experiments, buckling in samples of copper of aspect ratio 1.8 began to be observed, and aluminium buckled at aspect ratios of 2 and larger, though titanium did not buckle at all.

Buckling was not observed in any Split Hopkinson Pressure Bar experiments, and stress-time and stress-strain behaviour was generally consistent, but for aspect ratios of 0.25, and this was discerned for all materials.

Overall, buckling was observed in the most slender specimens, and at the lowest strain rates, whilst the specimens with the lowest aspect ratios experienced the most variation in the initial peak stresses reached, and in the applied strains. At the highest strain rates, the thinnest samples displayed stresses higher than expected.

It is thus instructive to discuss these findings in the context of inertial and frictional forces, as well as wave propagation.

For the Split Hopkinson Pressure Bar, one dimensional studies of wave propagation from the incident loading ($\varepsilon_i$), reflected ($\varepsilon_r$), and transmitted ($\varepsilon_t$) pulses can be used to derive the following quantities [170]:

The stress on the front (loaded) face of the specimen:

$$\sigma_{s1} = E \frac{A}{A_s} (\varepsilon_i + \varepsilon_r) \quad (4.1)$$

where $E$ and $A$ are the Young’s modulus and area of the pressure bar respectively, and $A_s$ is the area of the specimen.

The stress on the rear face of the specimen:

$$\sigma_{s2} = E \frac{A}{A_s} \varepsilon_t \quad (4.2)$$

Hence, the average stress is:

$$\sigma_s = E \frac{A}{2A_s} (\varepsilon_i + \varepsilon_r + \varepsilon_t) \quad (4.3)$$

The average strain in the specimen is:

$$\varepsilon_s = \frac{c_0}{l_0} \int_0^t (\varepsilon_i - \varepsilon_r - \varepsilon_t) dt \quad (4.4)$$

where $c_0$ is the phase velocity of infinitely long waves, and $l_0$ is the initial length of the specimen.
Thus, the average strain rate is:

\[ \dot{\varepsilon}_s = \frac{c_0}{l_0} (\varepsilon_i - \varepsilon_r - \varepsilon_t) \]  \hspace{1cm} (4.5)

In order for these average values to represent useful material properties, it is assumed that stress equilibrium exists in the specimen, i.e. that the stress in the specimen is uniform during testing [162]. Therefore, the instantaneous values of the three strain-time histories must satisfy the approximation:

\[ \varepsilon_r = \varepsilon_t - \varepsilon_i \]  \hspace{1cm} (4.6)

Thus, the above equations reduce to:

\[ \sigma_s = E \frac{A_s}{A} \varepsilon_t \]  \hspace{1cm} (4.7)

\[ \varepsilon_s = \frac{-2c_0}{l_0} \int_0^t \varepsilon_r dt \]  \hspace{1cm} (4.8)

\[ \dot{\varepsilon}_s = \frac{-2c_0}{l_0} \varepsilon_r \]  \hspace{1cm} (4.9)

When Split Hopkinson Pressure Bar experiments were carried out at comparatively low strain rates \((<1000 \text{ s}^{-1})\), it was concluded that any longitudinal stress differences were within experimental accuracy, and could thus safely be neglected. However, the Split Hopkinson Pressure Bar is now used to reach strain rates \(>10^4 \text{ s}^{-1}\), and there is significant evidence that non-uniformity arises at these higher rates [170]. In addition, the assumption of uniform stress within a specimen may not hold when the specimen is excessively brittle, because it may fail during the initial loading before stress equilibrium is established, particularly when the wave speed in the specimen is comparatively slow [162].

Another major assumption involved with calculations of the dynamic stress-strain behaviour of a specimen is that a specimen can be approximated as a one-dimensional object in which, at any given cross-section, the stress is the same, i.e. the radial distribution of stress is uniform. However, as the specimen is subjected to a compressive wave, owing to Poisson’s effect, the cross-section of the specimen tends to expand, which is resisted by an inertial effect. Axial inertial effects can only be neglected if the specimen is short enough to attain axial equilibrium in a time much shorter than the entire duration of the test [173].

Because the mechanical impedance of a specimen is usually different from that of the compressive bars, stress in the specimen initially increases from zero, reaching a homogenous state only after several traversals of the loading wave back and forth within the specimen. It is important to know how many transits the wave makes in the specimen,
so that an assessment can be made of how accurate the measured data is, and which part of it is unreliable. Data only becomes reliable after there have been enough reverberations of the stress wave to attain stress equilibrium in the specimen (this is typically 3) [162].

As such, the specimen length should be much shorter than that of the stress pulse, to ensure reasonable uniformity of stress within the specimen. The choice of an appropriate slenderness ratio (the ratio of the length to diameter of the sample) has been previously, but not comprehensively, researched [173]. Non-uniformity of stress in a specimen usually occurs at the beginning of the test, when stress in the specimen is relatively small and the specimen is undergoing elastic deformation [162].

It has been observed that the time required to achieve a uniform stress state in a specimen for a perfectly rectangular incident pulse is noticeably larger than that for a pulse with a finite rise time. This indicates that the inclusion of a rising edge in the incident pulse reduces the time taken to reach a uniform stress state [162].

Stress equilibrium within a compressed Split Hopkinson Pressure Bar specimen has been previously investigated, for example by separately calculating the average stresses at the specimen-bar interfaces, both front and rear, over a range of impact velocities and specimen lengths. The shortest specimens were shown to have very similar front and rear stresses and, at the lowest impact velocities, stress equilibrium was established in the samples soon after initial impact [170].

As the length of the specimen was increased, an increasingly larger difference between the front and rear stresses was observed, and this gap persisted throughout the loading history. This difference was also observed as the impact velocity was increased; stress equilibrium was never achieved, although the two stresses did approach each other as time went on. This serves to indicate that, under these conditions, the specimens underwent non-uniform deformation [170].

In addition, a more slender column deflects more under the same axial load, and so stores more strain energy. Consequently, it can also release more energy to drive the crack band. The notion that instability of a specimen weakened by axial cracks is part of a global compression failure mechanism has been clearly established [167]. If a specimen’s length-to-diameter ratio is too high, the sample will buckle during the test, rendering that test invalid. For brittle materials, an aspect ratio between 1.5 and 2 has thus been suggested [172].

Under the same loading conditions, deformation of shorter length specimens corresponded to higher strain rates than longer ones, and they also experienced the largest variation of strain rate throughout the duration of the test [170][171]. Specimens with a diameter approaching the bar diameter do not provide a constant strain rate during the test [171].

It has been seen that softer materials take a much longer time to reach dynamic stress equilibrium than stiffer materials of the same specimen geometry. Additionally, shorter
specimens reach equilibrium much faster in Split Hopkinson Pressure Bar testing. Thus, in softer specimens, it seems advantageous to use a smaller aspect ratio [169].

At the same strain rate, higher and more uniform stresses were observed for smaller diameter specimens, but these also gave rise to more oscillating stress-strain curves. Conversely, an increase in diameter decreased the magnitude and number of these oscillations, but produced more barrelling, giving an overestimation of the deformation stresses [171].

In some simulated experiments, it has been found that an increase in the length of specimen gives a better approximation of the actual mechanical behaviour of the materials. Other simulations on specimens with the same \( l/d \) ratios have found that, although a larger plastic strain is reached for smaller-diameter specimens, larger inaccuracies and oscillations in the stress-strain curves are observed, and smaller stresses than the assumed behaviour are seen for the plastic range. Moreover, the strain rate increases as the specimen diameter decreases, and is more uniform for smaller diameters. Therefore, the strain rate in the region where the specimen is considered to be deforming uniformly is much more consistent in smaller specimens than in larger-diameter specimens [171].

It has been found that, in smaller-size specimens, the friction-affected surface to volume is larger, and can lead to higher calculated stresses at high strain rates. Larger specimens having the same \( l/d \) ratio as that of smaller specimens display lower stresses than the smaller specimens and, for the same strain rate, the larger specimen size leads to less plastic deformability. However, no significant difference in the flow stress behaviour for different specimen geometries was reported. It is also mentioned that the increased flow stress and deformability with reduction of specimen size may be attributable to a disproportionate increase in the specimen surface area related to material volume [171].

Thus, clear differences between the end forces in a compression Split Hopkinson Pressure Bar specimen have been observed, and can lead to significant variation in the stress-strain results depending on whether the analysis assumes that the reflected strain is equivalent to the difference between the transmitted and incident strains or not. Non-uniform deformation will render it difficult to use external measurements to represent valid bulk material properties [170].

One of the most important sources of error in dynamic tests is the inertial response of the specimen. As the rate of deformation increases, so the force required to accelerate the material also increases. This affects the measured stress. Theoretical models can assess the magnitude of this error [165].

It is difficult to obtain values for the inertial contribution from experiments, due to the unreliability of calculating first and second derivatives from the measured strain or velocity data. In addition to performing numerical differentiation on noisy data, there are likely to be other spurious effects due to non-ideal conditions in the test. For example, strain histories derived from pressure bar records are often subject to various effects of dispersion, such as superimposition of the well-known Pochhammer-Chree oscillations. Also,
non-equilibrium in the specimen due to wave propagation is likely to modify externally measurable quantities, particularly at the beginning of deformation [165].

Effects like these can have a dominant effect upon the derived values of strain rate, and corresponding predicted inertia forces are of no physical significance. Thus, it is not usually valid to apply this theory to correct experimental force measurements by simply assessing and cancelling inertial contributions. The most appropriate use is to simply ensure that inertial errors are negligible [165].

It is possible to use apparatus with small dimensions to minimise inertial contributions at very high strain rates. However, the maximum strain rate is then limited by the pressure bar strength and signal dispersion [165].

It has been found that inertial errors can be reduced to negligible levels for compression experiments up to strain rates of $10^5 \text{s}^{-1}$, by limiting specimen dimensions to less than 1 mm. Theoretical and simulation results indicate that there is no specific specimen aspect ratio which causes effective cancellation of the inertia terms, though it is possible to minimise their total contribution by selecting appropriate geometry. However, the presence of inertia may cause other errors by creating non-uniform deformation [165].

Even if a specimen is deforming uniformly, a stress gradient will develop along its length because of inertial forces. Several authors have analysed this effect [174], considering energy balance, and the following expressions for the pressures at the front ($\sigma_{s1}$) and rear ($\sigma_{s2}$) specimen faces have been derived [170]:

$$\sigma_{s1} = \sigma_y - \rho \left( \frac{a^2}{8} + \frac{h^2}{3} \right) \ddot{\varepsilon} + \rho \left( \frac{a^2}{16} - \frac{h^2}{3} \right) \dot{\varepsilon}^2 + \frac{\rho hv}{2}$$

(4.10)

$$\sigma_{s2} = \sigma_y - \rho \left( \frac{a^2}{8} - \frac{h^2}{6} \right) \ddot{\varepsilon} + \rho \left( \frac{a^2}{16} + \frac{h^2}{6} \right) \dot{\varepsilon}^2 - \frac{\rho hv}{2}$$

(4.11)

where $\sigma_y$ is the compressive yield stress of the specimen, $\rho$ its density, $a$ and $h$ are the specimen radius and thickness respectively, and $v$ is the velocity of its rear face.

Taking values of $\ddot{\varepsilon}$ from the initial slopes of each of the lines from graphs of strain rate vs time show that $\ddot{\varepsilon}$ increases with specimen length, as does the stress difference $\Delta \sigma_i$ [170].

As an example, for the longest and shortest specimens of copper (since this is the densest material experimented upon in these tests) at the highest strain rates used, we can see that the term containing $\ddot{\varepsilon}$ is on the order of $10^8$, by far the largest term in the above equations. As such, in these tests, the terms in $\dot{\varepsilon}^2$ and $\dot{v}$ can be neglected. Hence, the difference between the two end pressures can be given by:

$$\sigma_{s2} - \sigma_{s1} \approx \Delta \sigma_i = \frac{h^2}{2} \ddot{\varepsilon}$$

(4.12)

Evaluating this equation for the longest and shortest specimens of copper, we obtain
values for $\Delta \sigma_i$ between 0.2 - 300 kPa. These values are fairly negligible compared to the obtained material strength values, which are found to be on the order of $10^2$ MPa.

Predicted values of $\Delta \sigma_i$ will apply during the rapid rise of strain rate at the beginning of a test, and are a significant fraction of the differences between the front and rear stresses, varying with specimen length in the same manner. However, strain rate decreases over most of the deformation, hence the later contribution from the $\ddot{\varepsilon}$ term will be a small, negative value. Although at this stage the other inertia terms may be more significant, inertia does not fully explain the continuing difference between the end pressures. In this case, non-uniform deformation due to wave propagation effects is also likely to be playing a significant role [170].

A steady stress state in the specimen is built up by multiple reflections of elastic and plastic stress waves. Thus, the higher the wave propagation speed and the shorter the specimen, the quicker uniformity of stress and strain is achieved [170].

If the front and rear stress signals approach each other but do not meet, this gap is likely to be a lasting consequence of the non-uniform strain during the early stages of deformation. In addition, if the specimen becomes slightly tapered towards the rear face, then both the increased stress and strain at the front end will contribute to the total force, and hence to the apparent increase in stress. However, the amount of non-uniformity required to explain the observed effects is small, and may not be detected in recovered specimens [170].

In an ideal compression test, deformation is uniform under a compression velocity $u$, and the local strain rate at any point in the specimen is given by $\ddot{\varepsilon} = u/h$, where $h$ is the instantaneous height of the specimen. Thus, to reach a given value of strain rate, a longer specimen needs to be subjected to a proportionately higher compression velocity than a shorter one. Deformation is controlled by wave propagation and by dislocation motion within the specimen, processes which are associated with absolute velocities. Hence, it is likely that two situations with the same macroscopic strain rate but with differing impact velocities will display differences in deformation behaviour. This suggests a qualitative link between specimen dimensions and high strain rate properties [174].

Inertia (due to accelerating the material in the sample from rest [175]) and wave propagation effects can make a substantial contribution to the observed stress differences between the ends of compression Split Hopkinson Pressure Bar specimens. Under these conditions, using equations equivalent to calculating only the rear end stress will produce a much lower value than the average stress. Although the average stress is the more reliable measure, a significant stress gradient should be taken as an indication that the measurements may not represent valid, uniform material characteristics. Thus, the condition of stress uniformity needs to be examined for each experimental configuration, in order to check the validity of Split Hopkinson Pressure Bar results [170].

Using thinner specimens will help to achieve a more uniform deformation state more
quickly, but will increase the effects of friction, and cause a wider variation of strain rate throughout the test. In addition, increasing the rise time of the loading pulse by an appropriate experimental means will reduce the effects of dispersive distortion, and improve the uniformity of deformation [170].

Friction is an additional external process which is also influenced by impact velocity. Larger specimens deformed at the same strain rate involve longer radial displacements at higher velocities than in the case of small specimens. Lubricant breakdown is more likely under large displacements, and loss of lubricant by jetting is enhanced at high velocities. Hence, large specimens may be subject to velocity-dependent frictional restraint [174].

Interfacial friction is a major cause of erroneous results in a typical Split Hopkinson Pressure Bar experiment. Friction at the bar-specimen interfaces causes the ends to be constrained against free expansion, and creates a state of non-uniform triaxial stress in the specimen, which can result in barrelling of the specimen [176]. During the compression test the specimen shortens and expands. At the pressure bar-specimen interface a frictional constraint exists due to this radial expansion. The frictional effects are highest when the specimen is at rest, then reduce once the static friction is broken and the specimen starts sliding. If the ends are restrained at the beginning of the test, the middle section of the specimen must deform. This results in a barrel shaped specimen, clearly not uniform. By applying a thin film of lubricant at the interfaces, this frictional constraint can be greatly reduced [172].

The interfacial frictional effect in a compression test can be established by [166]:

\[
P = \left(1 + \frac{\mu}{n} \frac{d}{l}\right) \sigma_y
\]  (4.13)

where \(P\) is the applied mean pressure, \(\mu\) is the coefficient of friction, \(n\) is a number (which equals 3 [177]), \(d\) and \(l\) are the diameter and length of the cylindrical specimen respectively, and \(\sigma_y\) is the intrinsic yield stress of the material (when \(\mu = 0\)).

Interfacial friction is highly dependent on the material being tested. Friction can dominate strain rate effects, though is not a significant issue for polymers [124]. Friction in compression tests, between rigid platens and material specimens, restricts both elastic and plastic expansion, adding error into measurements; this friction can lead to specimen barrelling [149], introducing transverse stresses that increase the apparent axial stiffness of the specimen.

Several ways of minimising this friction have been suggested. This includes using bars with highly polished ends, as well as polishing the specimen surfaces (though not too smooth, otherwise the lubricant will be squeezed out and the friction increase [175]), and the use of a thin layer of well-characterised lubricant, for example molybdenum disulphide (MoS\(_2\)). In addition, whilst sandwiching the sample, it is ensured that the sample is free to slide, and specimens should be of an appropriate aspect ratio [173]. Friction effects can
be strongly reduced by the use of compression platens that are both hard and smooth. These friction effects are more pronounced in ductile materials than in brittle materials, although they are still fairly significant [164].

Specimen dimensions have been found to be influential if frictional or inertial effects are significant [178]. With proper lubrication of specimen-bar interfaces, no considerable barrelling has been found up to 15% strain [171]. In addition, friction has been seen to decrease at higher strain rates [142]. At these higher strain rates, the lubricant also has less time to squeeze out from between the specimen and the anvils; as such, low strain rate upsetting is a more severe test of the right lubricant [175].

In addition to specimen geometry and suitable lubrication, there are further sample considerations to take into account during experimental preparation.

Sample flatness and surface parallelism are important conditions in most compression testing standards, so samples have to be machined down with careful precision. Aligning compression equipment normal to the central axis of the sample, with an even contact, avoids creating a point contact on the specimen, producing a stress concentration that can initiate failure, or inducing a bending, causing premature failure. It is more difficult to avoid this effect in brittle materials than in softer, ductile materials.

Thoroughly polishing sample surfaces minimises the influence of surface flaws on the material's mechanical properties. Finally, to reduce bending moments, the material sample is placed in the centre of the anvils with negligible offset [164].

Taking into account all the aforementioned considerations, several authors [142] have suggested the most ideal specimen geometries to use in compression experiments. Lindholm [150] and others [168][172] found that specimen dimensions, in particular samples with aspect ratios \(l/d\) ranging from 0.2 - 2.0 and 0.5 - 2.0, had almost no effect on the stress for high strains, and only a small effect at small strains, indicating that frictional effects were not significant. Higher stresses and strain rates were seen for smaller-diameter specimens. Yet others [169][171] have found that the optimum specimen geometry is a solid cylinder with an \(l/d\) ratio between 0.50 and 0.75, when the diameter ratio between the specimen and the bar is 0.5 (other authors suggest \(\sim 0.8\) [154]), whilst it has also been noted that an aspect ratio of 1.0 should be used for moderately high strain rates, and \(\sim 0.5\) for very high strain rates.

A longer specimen takes more time to attain stress equilibrium compared to a shorter specimen made of the same material. This implies that a shorter specimen is better in terms of stress uniformity throughout the length of the sample. However, the shorter the sample, the greater the effects of interfacial friction. In the case of cylindrical specimens, the critical slenderness ratio, based on the considerations of inertia, axial uniformity of stresses, and interfacial friction, has been researched widely. For a sample of diameter \(d\) and length \(l\), an accepted value of slenderness ratio is \(l/d = 0.5\). A less restrictive slenderness ratio is given by \(l/d \leq 1.0\) [173].
A large aspect ratio specimen can reduce the friction and the subsequent barrelling effect in compression tests; however, this may produce shearing or even buckling [166]. In order to minimise the friction effects, an aspect ratio in the range 1.5 - 2.0 has been suggested. Thus, the conditions for minimum friction and inertia effects cannot be satisfied simultaneously, and a general suggestion of $0.5 < l/d < 1.0$ can be taken as a compromise between these two effects [154].

If much thinner specimens are used, $0.01 < l/d < 0.1$, the uniaxial stress condition of the specimen changes to plane-strain condition. In this case, friction and radial inertia effects become important [154]. Using a thinner specimen will therefore facilitate a quicker process of equilibrium. However, the effects of interfacial friction between the specimen and the bars may become more significant. In the design of a dynamic experiment for soft material property determination it is thus necessary to select a properly reduced specimen thickness. It has been demonstrated that, even though a thin specimen is used, the dynamic stress equilibrium may not be achieved when the incident loading rate is very high [47].

Friction at the specimen-bar interfaces causes the state of stress to deviate from the uniaxial stress condition, and leads to spuriously stiff results. Decreasing the specimen length can greatly increase the accessible strain rate range for a given experiment. However, as the $l/d$ ratio of the specimen becomes smaller, the effects of friction at the interfaces become substantial if the coefficient of friction at the specimen-bar interfaces is not sufficiently low, leading to inaccurate measures of the stress. For quasi-static compression tests, specimen $l/d$ ratios of 1.5 to 3.0 are recommended in various ASTM standards, with proper use of lubricant. In contrast, for conventional compression bar tests, $l/d$ ratios of 0.5 - 1.0 are widely used [142].

Other experimental techniques have found that, even under non-uniform strain rate conditions, longitudinal and radial inertia effects can be significantly minimised at the following slenderness ratio [176][171]:

$$\frac{l}{d} = \sqrt{\frac{3\nu}{4}}$$

(4.14)

where $\nu$ is the Poisson’s ratio of the specimen. For $\nu = 0.33$, the optimal $l/d$ ratio to reduce the effects of inertia is 0.5.
4.6 Conclusion

To ensure the validity of results for a given experimental technique, sample dimensions and aspect ratios must complement the load and loading rate. For example, in Split Hopkinson Pressure Bar experiments, it is important that stress equilibrium be reached inside the specimen; the sample should be sufficiently thin to obtain \( \sim 3 \) internal reflections of the stress wave [162]. The sample diameter should be less than or equal to the diameter of the bars, never expanding beyond the bars’ diameter [149]. It has been suggested that the radial and longitudinal inertia and friction effects can be lessened by minimising the areal mismatch between the bar and the specimens, such that the sample diameter is roughly 0.8 times the diameter of the bar [163]. In addition, the sample diameter should be sufficiently small such that stresses due to radial inertia are negligible [149][164][165].

Previous research has studied the effects of altering the shape and size of samples over different compression rates, though few have compared and contrasted how these effects vary, and several discrepancies exist in the published data, most probably due to the wide range of techniques used. This preliminary research was carried out on well-documented non-ceramic materials to bridge this gap and determine the ideal sample geometry to use for the main purpose of understanding the piezoceramic PZT 95/5 and several polymers typically used to coat it in industrial applications, across a wide range of strain rates.

This research found that buckling was observed in the most slender specimens \((l/d > 1.8)\) at the lowest strain rates, whilst the specimens with the lowest aspect ratios \((l/d < 0.25)\) experienced the most variation in the initial peak stresses reached and the applied strains. This can be understood in terms of both the inertial and frictional forces experienced by the specimens.

Increasing the aspect ratio increases the time taken for a sample to reach stress equilibrium. However, if a sample is too short, it will suffer from inertial and frictional confinement, as well as errors in strain calculations due to end effects. Conversely, if a sample is too long, it will buckle.

For short, stubby samples, friction dominates the deformation, often resulting in a barrel shaped specimen. By lubricating the ends with a thin layer of grease, these frictional effects can be minimised. However, even when great care is taken to eliminate friction, the use of relatively short specimens will introduce an apparent increase in stress very similar to reported strain rate effects [143].

It has been seen that a reduction in the initial \(l/d\) of a short compression specimen will have the same effect as an increase in the coefficient of friction for the same specimen geometry. It has also been demonstrated that barrelling will be initiated at lower values of strain as the ratio of the coefficient of friction to the specimen \(l/d\) is increased [143].

With these observations, it was decided to select aspect ratios between 0.25 and 1.5 for the proposed low-to-high strain rate experiments on the piezoceramic PZT 95/5, with
the aim that the observed stress-strain behaviour would be consistent, repeatable, and coherent.
He arranges [each] matter from the heaven to the earth; then it will ascend to Him in a Day, the extent of which is a thousand years of those which you count.

Chapter 5

Mechanical Response of Polymers

A number of industrial polymers are investigated here, for both strain rate and temperature effects. Scotchcast® 8 and Stycast® 1090 were provided by the Thales Group, whilst Mixes M173 and M207F were provided by AWE Aldermaston.

Each loading test was repeated three times in order to attempt to account for variability introduced by different material casts, an example of which is shown in figure 5.1. For clarity, and to avoid making the graphs difficult to interpret, the data chosen in the graphs in this chapter will be from a representative specimen. Additional data supporting the claims made in this chapter are included in Appendix B.

Scotchcast® 8 is a low-stress, highly moisture-resistant, epoxy resin that cures at room temperature. It has a compressive strength of ~5 MPa and a tensile strength of ~12 MPa [179].

Stycast® 1090 is a low density, syntactic foam epoxy encapsulant (an epoxy filled with micro-balloons). It has good moisture and chemical resistance, and compressive and tensile strengths of ~83 MPa and ~32 MPa respectively [179].

Both materials are commercially available, and generally used to coat and protect sensitive electrical and electronic components.

Mix M173 is a clear epoxy resin, made of a number of different compounds: 32.13% LY564, 48.19% CY208, and 19.68% HY2954. LY564 is a low viscosity epoxy resin, HY2954 is a cycloaliphatic diamine, and CY208 is a white solid araldite resin.

In contrast, Mix M207F is an opaque epoxy, loaded with alumina powder (~70% composition), and with the resin MY750 (~23% composition) and a hardener HX152 (~7% composition).
Figure 5.1: Split Hopkinson Pressure Bar data for Scotchcast 8 (aspect ratio 1; height = diameter = 10 mm) at a temperature of $-20^\circ \text{C}$ and impact velocity $\sim 10 \text{ m s}^{-1}$.

Table 5.1: Polishing method.

<table>
<thead>
<tr>
<th>Grinding Disc</th>
<th>Disc Surface $[\mu m]$</th>
<th>Liquid Medium</th>
<th>Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Carbide</td>
<td>120</td>
<td>Water</td>
<td>2</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>320</td>
<td>Water</td>
<td>2</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>800</td>
<td>Water</td>
<td>2</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>2500</td>
<td>Water</td>
<td>8</td>
</tr>
<tr>
<td>Diamond</td>
<td>6</td>
<td>Diamond $[6 \mu m]$ Suspension</td>
<td>7</td>
</tr>
<tr>
<td>Diamond</td>
<td>3</td>
<td>Diamond $[3 \mu m]$ Suspension</td>
<td>3</td>
</tr>
<tr>
<td>Diamond</td>
<td>1</td>
<td>Diamond $[1 \mu m]$ Suspension</td>
<td>7</td>
</tr>
</tbody>
</table>

5.1 Microscopy

The epoxy samples were embedded into a polyester resin (EpoKwick, Buehler Ltd., Illinois, USA). The epoxy resin (20-8136-128) was mixed with the hardener (20-8138-032) at a ratio of 5:1 in mass; the mixture was stirred slowly, to avoid creating bubbles, until it turned clear. Clips were used to hold the samples in the bottom of some moulds, and the epoxy mixture was poured over them. The resin was left to cure in a fume cupboard for 24 hours at room temperature before being polished [180].

Resin-bonded silicon carbide and diamond grinding discs (also Buehler Ltd.) were used for polishing, at a force of 5 LBF per sample and a speed of 150 rpm. Specimens were first ground using a water medium and silicon carbide grinding discs, and then a diamond suspension (MetaDi, Buehler Ltd.) with diamond grinding discs, to obtain scratch and void-free surface finishes, as shown in table 5.1.

After polishing, the epoxy specimens were examined under an optical microscope. The ZEISS light microscope 1022447263 1/1, with the AxioCam ERc5s, controlled by the
AxioVision Rel. 4.8 software, was used.

Scotchcast 8 does not contain any micro-inclusions and is completely translucent. On the other hand, the Stycast 1090, shown in figure 5.2, contains micro-balloons, with a range of diameters between 5 - 160 µm.

Mix M173 is also a translucent epoxy, whilst Mix M207F contains irregular crystals of alumina filler, see figure 5.3.

To further study the microstructure of the different epoxies, some other samples were mounted on carbon stubs. The EMITECH K550 was used to coat the specimens with gold. The samples were then studied using a JEOL JSM 5610LV scanning electron microscope.

Even under higher magnifications, there are still no micro-inclusions present in the translucent epoxies Scotchcast 8 and Mix M173, though from figures 5.4 and 5.5 it can be seen that, whilst both materials are amorphous, Scotchcast 8 is far more homogenous than Mix M173. In addition, figure 5.6 highlights the presence of micro-balloons in Stycast 1090.

Figure 5.2: Stycast 1090 at 20x magnification.
Figure 5.3: Mix M207F at 50x magnification.

Figure 5.4: Scotchcast 8 at 400x magnification.
Figure 5.5: Mix M173 at 400x magnification.

Figure 5.6: Stycast 1090 at 300x magnification.
Table 5.2: Aspect ratios for samples of 5 mm diameter and varying thickness.

<table>
<thead>
<tr>
<th>Sample Thickness [mm]</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.25</td>
</tr>
<tr>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>3.75</td>
<td>0.75</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>6.25</td>
<td>1.25</td>
</tr>
<tr>
<td>7.5</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>1.8</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
</tr>
</tbody>
</table>

5.2 Aspect Ratio Compression Effects

Following on from compression experiments done on a range of materials of varying aspect ratio (see Chapter 4), it was decided to repeat those same experiments on two of the polymers, Mixes M173 and M207F, to compare and contrast their behaviour, particularly as the only polymer studied at those compression rates was polycarbonate.

As, when these particular epoxies were cast, the moulds were slightly larger, the diameters of these samples were actually \(\sim 5\) mm in diameter. As such, the thicknesses of the samples needed to be larger in order to reach the same aspect ratios as those attained in the previous chapter. These new thicknesses are shown in table 5.2.

5.2.1 Low Strain Rate Effects

A compression rate of \(0.001\) mm s\(^{-1}\) was adopted, resulting in strain rates as low as \(10^{-5}\) s\(^{-1}\). In addition, temperature effects on Mix M173 and M207F samples of varying aspect ratios at this compression rate were also studied. The temperatures chosen were \(-20^\circ\)C, \(+20^\circ\)C, and \(+80^\circ\)C.

As can be seen from figure 5.7, except for the M173 samples with aspect ratio 0.5 and lower, Mix M173 appears to consistently yield at \(~0.05\) strain. The gradient of the stress-strain curve up to the yield point clearly decreases with decreasing aspect ratio, such that the yield point generally decreases, except for those samples of thickness 2.5 mm and lower.

It is clear from this figure that the behaviour of M173 is as would be expected from a typical polymer; after yielding, the samples, regardless of aspect ratio, experience post-yield softening over a short period of strain, after which they are strain-hardened.

Figure 5.8 demonstrates the very dissimilar behaviour of the alumina-loaded epoxy, Mix M207F, to the Mix M173. Samples of Mix M207F generally yield at a lower strain than identically geometric samples of Mix M173, except for samples of aspect ratio 0.5 and lower.
Figure 5.7: Quasi-static stress-strain data for Mix M173 at a compression rate of 0.001 mm s$^{-1}$ and at +20°C.

Figure 5.8: Quasi-static stress-strain data for Mix M207F at a compression rate of 0.001 mm s$^{-1}$ and at +20°C.

Mix M207F is able to support almost three times the stresses of Mix M173, but its behaviour under compression is starkly different. Only samples with aspect ratio of 0.75 and lower appear to experience any form of strain-hardening; all other samples simply yield.

The apparent increase in stress for a given strain for samples of aspect ratio 0.25 (for Mix M173) and of 0.5 and lower (for Mix M207F) can be explained due to an increase in the effects of frictional confinement between the anvils and the thin specimens. Friction at the interfaces restricts both elastic and plastic expansion, introducing transverse stresses that increase the apparent axial stiffness of the specimen (see Sec. 4.5 for a more in-depth discussion of these effects).

Figure 5.9: Quasi-static stress-strain data for Mix M207F at a compression rate of 0.001 mm s$^{-1}$ and at +80°C.

Figure 5.10: Quasi-static stress-strain data for Mix M173 at a compression rate of 0.001 mm s$^{-1}$ and at +80°C.

Increasing the temperature at which the samples are compressed, to +80°C, we see
that Mix M207F now strain-hardens, across all aspect ratios, though the thinnest sample of aspect ratio 1 does not even reach yield, as demonstrated in figure 5.9.

Mix M173, upon heating, no longer yielded but fractured, though at much higher strains than identical samples at ambient temperature, see figure 5.10.

In addition, heating the samples meant that the epoxies’ ability to support higher stresses was decreased, such that Mix M207F yielded at lower stresses, and at lower strains, and Mix M173 fractured at even lower stresses. In addition, the thinnest samples were still affected by friction at these elevated temperatures.

Cooling the samples to \(-20^\circ\text{C}\) increases both the stresses and strains at which both epoxies yield. Mix M173 (see figure 5.11) continues to exhibit typical polymeric behaviour,
yielding and strain-hardening. For Mix M207F (see figure 5.12) on the other hand, yielding does not occur in the lowest aspect ratio sample, and strain-hardening is observed in samples with thicknesses of 2.5 and 3.75 mm, but not in any of the other samples, as at ambient temperature.

Comparing stress-strain behaviour for samples with identical aspect ratios across the temperature range, figures 5.13 and 5.14 highlight the different material behaviour for samples of Mix M207F of very low aspect ratios compared with samples of higher thicknesses. We see strain-hardening across all temperatures for samples of aspect ratio 0.5, but only yielding in samples of 6.25 mm thickness. In addition, the stress-strain behaviour for the lower aspect ratio is comparable for sub-zero and ambient temperatures, but significantly different at elevated temperatures. This trend diverges at higher aspect ratios, see figure 5.14, and we see that, whilst the shape of the stress-strain curves across the different temperatures is similar, the stress values are widely different.

Contrasting this behaviour with that of Mix M173 (see figures 5.15 and 5.16), we see that, regardless of aspect ratio, this epoxy’s material behaviour remains polymeric. Yielding and strain-hardening is observed for ambient and low temperatures, whilst heating the sample significantly reduces the stresses the sample can support.

Based on these low strain rate tests, it has been observed that the alumina-loaded epoxy, Mix M207F, is able to support far larger stresses than the clearer, purer epoxy, Mix M173, but lower strains. In addition, its ability to support large stresses is less affected by temperature as compared with the pure epoxy, but the material behaviour of the pure epoxy is less affected by the geometric size of the sample as compared with the epoxy containing filler. Adding a filler appears to increase the strength of the material, but decrease its polymeric behaviour.
5.2.2 Drop-Weight Testing

The impact mass used in these experiments was \( \sim 7 \text{ kg} \), and an impact velocity of \( \sim 3 \text{ m s}^{-1} \) was adopted. A high-speed video camera, the Phantom V12.1, was used to observe the deformation behaviour of the specimens.

From these experiments, at these higher strain rates, it is seen that Mix M207F is able to support larger stresses than Mix M173 (see figure 5.17), but that Mix M173 is able to support stress for a longer period of time, as shown in figure 5.18; in other words, Mix M173 is able to accommodate a much larger degree of strain than Mix M207F.

At the strain rates experienced in these drop-weight experiments, Mix M173 undergoes a number of different failure mechanisms depending on the aspect ratio of the specimen being compressed. Samples with aspect ratios \( \leq 1 \) suffer linear crack formation in the direction of the applied load (see figure 5.19), most probably resulting from the excessive tensile friction generated between the sample and the contact surfaces of the drop-weight anvils at maximum strain.

Comparing the high-speed images with the stress-time data obtained for a Mix M173 specimen of 5 mm thickness, we can observe that elastic deformation occurs until a yield stress of \( \sim 200 \text{ MPa} \) (just before point \( b \) as shown in figure 5.20). Between \( b - e \), the sample

![Figure 5.17: Stress-time data for Mix M207F, obtained during drop-weight impact experiments (mass \( \sim 7 \text{ kg} \), impact velocity \( \sim 3 \text{ m s}^{-1} \)).](image)

![Figure 5.18: Stress-time data for Mix M173, obtained during drop-weight impact experiments (mass \( \sim 7 \text{ kg} \), impact velocity \( \sim 3 \text{ m s}^{-1} \)).](image)

![Figure 5.19: Drop-weight sequence showing the compressive behaviour of a cylinder of Mix M173, aspect ratio 1 (diameter = height = 5 mm), during impact (mass \( \sim 7 \text{ kg} \), impact velocity \( \sim 3 \text{ m s}^{-1} \)).](image)
undergoes plastic deformation until \( \sim 1.05 \) ms, where the samples then begin to fracture parallel to the impact direction.

![Figure 5.20: Stress-time data for a cylinder of Mix M173, aspect ratio 1 (diameter = height = 5 mm), during impact (mass \( \sim 7 \) kg, impact velocity \( \sim 3 \) m s\(^{-1}\)).](image)

![Figure 5.21: Stress-time data for a cylinder of Mix M173, aspect ratio 1.5 (diameter = 5, height = 7.5 mm), during impact (mass \( \sim 7 \) kg, impact velocity \( \sim 3 \) m s\(^{-1}\)).](image)

Samples of Mix M173 with aspect ratios 1.25 and 1.5 experience plastic deformation (see figure 5.22), and the samples are able to be recovered.

Comparing the high-speed images with the stress-time data obtained for a Mix M173 specimen of 7.5 mm thickness, in figure 5.21, we can observe that elastic deformation occurs until a yield stress of \( \sim 270 \) MPa, at point \( b \), after which the material undergoes strain-hardening, as expected for an unloaded polymer.

Samples of Mix M173 with aspect ratios of 1.8 and larger buckle (see figure 5.24), which corresponds to the behaviour of the polymer polycarbonate at these same strain rates, see Sec. 4.3. In addition, comparing the high-speed images with the stress-time data, we observe elastic deformation until just after 0.29 ms, point \( b \) as shown in figure 5.23, after which the sample begins to buckle.

Mix M207F, on the other hand, experiences brittle fracture (see figure 5.25) for all aspect ratios but 3, where we observe shear bands acting at 45° to the direction of

![Figure 5.22: Drop-weight sequence showing the compressive behaviour of a cylinder of Mix M173, aspect ratio 1.5 (diameter = 5, height = 7.5 mm), during impact (mass \( \sim 7 \) kg, impact velocity \( \sim 3 \) m s\(^{-1}\)).](image)

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Figure 5.23: Stress-time data for a cylinder of Mix M173, aspect ratio 2 (diameter = 5, height = 10 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s$^{-1}$).

Figure 5.24: Drop-weight sequence showing the compressive behaviour of a cylinder of Mix M173, aspect ratio 2 (diameter = 5, height = 10 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s$^{-1}$).

Figure 5.25: Drop-weight sequence showing the compressive behaviour of a cylinder of Mix M207F, aspect ratio 0.5 (diameter = 5, height = 2.5 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s$^{-1}$).
applied load (see figure 5.26). It appears that the presence of alumina filler causes the predominant mode of failure in this epoxy to be that of failure before yielding, with cracks in the direction of the applied load.

Comparing the high-speed images with the stress-time data obtained for a 2.5 mm thick sample of Mix M207F, in figure 5.27, we observe that the sample undergoes elastic deformation until yielding at a stress of \(\sim 420\) MPa. Very soon after, in time and in strain, the sample begins to fracture in a brittle manner. It is also clear from the images that the sample actually supports very little strain.

Comparing the stress-time data for a 15 mm thick sample of Mix M207F with the corresponding high-speed images, we see that the sample yields at a stress just below 500 MPa, and that the sample continues to accommodate some strain before failing, at point \(d\) in figure 5.28.
Table 5.3: Impact velocities attained using different firing pressures.

<table>
<thead>
<tr>
<th>Firing Pressure [bar]</th>
<th>Impact Velocity [m s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>(\sim 4)</td>
</tr>
<tr>
<td>0.5</td>
<td>(\sim 6)</td>
</tr>
<tr>
<td>0.75</td>
<td>(\sim 8)</td>
</tr>
<tr>
<td>1.0</td>
<td>(\sim 9)</td>
</tr>
</tbody>
</table>

5.2.3 Split Hopkinson Pressure Bars

The results presented here are from experiments carried out on a Split Hopkinson Pressure Bar system (see Sec. 3.4) with Inconel 718 bars; the striker bar length was 228 mm. The firing pressures used were 0.25, 0.5, 0.75, and 1.0 bar, resulting in impact velocities of 3.7 - 9.2 m s\(^{-1}\) (see table 5.3) and strain rates between 250 - 6930 s\(^{-1}\). Due to interference from a power rail, some of the data presented here has some noisy traces.

![Stress-time data for Mix M173, at impact velocities of \(\sim 4\) m s\(^{-1}\).](image)

![Stress-time data for Mix M173, at impact velocities of \(\sim 9\) m s\(^{-1}\).](image)

Figures 5.29 and 5.30 show the stress-time behaviour of Mix M173 samples of all aspect ratios at the lowest and highest impact velocities respectively. At first glance, it appears that the stress-time relationship is quite varied for Mix M173, and indeed, the peak stresses experienced by the different samples are quite varied, though the spread is largest at the lowest firing pressure (figure 5.29).

However, it is possible to extract some trends. Across all the impact velocities, as the aspect ratio is increased, the stress supported by the sample decreases. In addition, at the lowest firing pressures, peak pressure for all the aspect ratios was reached between 70 - 80 \(\mu\)s. As the impact velocities were increased, the time at which the peak pressure was reached decreased for all the aspect ratios except 3, i.e. the samples of thickness 15 mm. This trend is most noticeable for aspect ratios \(\leq 0.75\).

Figures 5.31 and 5.32 show the stress-time behaviour of Mix M207F samples of all aspect ratios at the lowest and highest impact velocities respectively. The peak stresses
reached in the Mix M207F samples are almost double those experienced by the Mix M173 samples. The stress-time behaviour is also quite varied, even more than of Mix M173, and it is far more difficult to pick out any trends.

Looking instead at the stress-strain behaviour of the samples, we see that this behaviour is far more consistent across the strain rates for Mix M173. Indeed, at the two higher velocities (figures 5.33 and 5.34), the material behaviour is very similar, with similar stresses and strains being experienced for the same aspect ratios. Overall, we can see that peak stresses are reached within each sample at a higher strain as the aspect ratio is decreased, and that the peak stresses increase as the thickness of the samples decreases, except for samples of the lowest aspect ratio.

Contrasting the stress-strain behaviour of the Mix M173 with that experienced by the Mix M207F samples (see figures 5.35 and 5.36), we see that the material behaviour of the M207F samples is still highly varied, particularly at the lowest impact velocity (see
Figure 5.35: Stress-strain data for Mix M207F, at impact velocities of \( \sim 4 \text{ m s}^{-1} \).

Figure 5.36: Stress-strain data for Mix M207F, at impact velocities of \( \sim 9 \text{ m s}^{-1} \).

Figure 5.37: Stress-strain data for Mix M173, aspect ratio 1.

Figure 5.38: Stress-strain data for Mix M207F, aspect ratio 1.

Figures 5.37 and 5.38 demonstrate the more consistent stress-strain behaviour of samples of Mix M173, and the more varying material behaviour of Mix M207F, across the different strain rates respectively.

From these experiments, it is clear that the presence of alumina filler appears to add inconsistencies and an element of unpredictability to the experimental data, and it is far more difficult to draw obvious relationships. Far more experiments need to be carried out, if more material and time were to be available.
5.3 Strain Rate and Temperature Effects

Experiments were carried out at a range of strain rates and temperatures between −20°C and +80°C, on samples of ∼3 mm thickness and ∼5 mm diameter of Scotchcast 8 and Stycast 1090. These results were compared with results from similar samples of Mixes M173 and M207F under the same loading conditions. These experiments also enabled us to evaluate different methods of achieving a range of temperatures for the Split Hopkinson Pressure Bar system.

5.3.1 Low Strain Rate Effects

Compression rates between 0.001 - 3.0 mm s\(^{-1}\) were adopted, resulting in strain rates as low as \(10^{-4}\) s\(^{-1}\). These experiments were carried out at ambient temperature (+20°C), sub-zero temperatures (−20°C), and at elevated temperatures (+80°C).

Figures 5.39 and 5.40 show the effects of temperature on the mechanical response of Scotchcast 8 at compression rates of 1.0 mm s\(^{-1}\) and 0.1 mm s\(^{-1}\) respectively. As can be seen, the amount of stress generated within the Scotchcast 8 specimen, as well as the yield stress, increases as the temperature decreases. This is most probably because, as the sample is cooled, the ability of the polymeric chains, which make up the material, to move and re-arrange themselves under compression is reduced. This trend was observed across all the employed compression rates for the Scotchcast 8.

![Figure 5.39: Temperature effects on Scotchcast 8 at a compression rate of 1.0 mm s\(^{-1}\).](image1)

![Figure 5.40: Temperature effects on Scotchcast 8 at a compression rate of 0.1 mm s\(^{-1}\).](image2)

Whilst the material yielded at both ambient and reduced temperatures, at elevated temperatures, significant strain-hardening was observed, particularly at compression rates equal to and greater than 1.0 mm s\(^{-1}\), as can be seen in figure 5.39, suggesting a shift in the glass transition temperature of the material at higher strain rates (see Sec. 5.4). This trend agrees with observations made by others [138] who have examined the rate-dependent elastic-plastic deformation of glassy polymers from low to high strain rates.
As can be seen in figures 5.41 and 5.42, Stycast 1090 behaves with temperature in much the same way as Scotchcast 8, i.e. as the temperature is decreased, the stress levels generated in the material increase. However, unlike Scotchcast 8, Stycast 1090 does not appear to strain-harden at higher temperatures (see figure 5.43). Instead, the material appears to flow; a ductile and fluid-like response is observed. It thus appears that we do not observe a shift in the glass transition temperature of Stycast 1090 at these conditions.

The difference in the mechanical behaviour of the two materials may be attributed to the difference in their material make-up. As mentioned at the beginning, the Stycast 1090 is a syntactic foam, and is therefore made of an epoxy filled with micro-balloons, whereas the Scotchcast 8 is a pure epoxy resin. Thus, it appears that reducing the percentage of epoxy in the material has a significant effect on the strain-hardening response of the materials.
A greater degree of post-yield softening is observed within Stycast 1090 than Scotch-cast 8 at compression rates ranging from 0.001 to 1.0 mm s\(^{-1}\). At 3.0 mm s\(^{-1}\) however, the degree of post-yield softening appears to more closely match the smoothed response of Scotchcast 8 at equivalent temperature and applied rate of compression. The degree to which temperature influences mechanical response appears to be significantly greater within Scotchcast 8 than Stycast 1090, i.e. a much larger difference in accumulated stress is observed within Scotchcast 8 than Stycast 1090 under identical loading conditions.

![Figure 5.45: Scotchcast 8 and Stycast 1090 at a compression rate of 0.001 mm s\(^{-1}\) and temperature of +20°C.](image)

![Figure 5.46: Scotchcast 8 and Stycast 1090 at a compression rate of 3.0 mm s\(^{-1}\) and temperature of +20°C.](image)

As can be seen from figure 5.44, the mechanical response of both polymers is very similar at compression rates above 1.0 mm s\(^{-1}\); both the elastic response and the yield strength are roughly equivalent. However, as the compression rates are decreased, this similarity diverges, as can be seen in figure 5.45. This suggests that the mechanical behaviour of Scotchcast 8 is also far more strain rate sensitive than Stycast 1090 at room temperature.

It can be seen at 3.0 mm s\(^{-1}\) (figure 5.46) that the elastic response of both materials at room temperature is highly similar. The yield strength of the two materials is also roughly equivalent. However, this response is not echoed at lower rates of compression (see, for example, figure 5.44). The data presented here suggests that Scotchcast 8 is much more sensitive to strain rate than Stycast 1090 at room temperature, i.e. the overall response of Scotchcast 8 is seen to alter with the rate of applied load while that of Stycast 1090 is not.

As can be seen in figure 5.47, at −20°C, Scotchcast 8 experienced a yield stress significantly higher than observed in Stycast 1090. This trend was consistent across all the compression rates; the difference between the yield stresses of the two materials also appears to increase with increasing compression rate. Despite this, the initial elastic response was actually comparable for both materials; this could be due to the presence
Figure 5.47: Scotchcast 8 and Stycast 1090 at a compression rate of 1.0 mm s\(^{-1}\) and temperature of \(-20^\circ\text{C}\).

Figure 5.48: Scotchcast 8 and Stycast 1090 at a compression rate of 3.0 mm s\(^{-1}\) and temperature of \(+80^\circ\text{C}\).

of the epoxy in both materials being more significant at lower applied strains, but the micro-balloons in the Stycast 1090 having a larger effect at greater applied strains. This elastic modulus for both materials appears not to be affected by the rate of applied load.

Figure 5.49: Scotchcast 8 and Stycast 1090 at a compression rate of 0.001 mm s\(^{-1}\) and temperature of \(+80^\circ\text{C}\).

Figure 5.50: Scotchcast 8, Stycast 1090 and Mixes M173 and M207F at a compression rate of 0.001 mm s\(^{-1}\) and temperature of \(+80^\circ\text{C}\).

As was previously discussed, the effects of heating upon Stycast 1090 cause a significant reduction in the levels of accumulated stress, irrespective of strain rate. However, strain-hardening was seen to occur in heated Scotchcast 8 samples during both high and low compression rate testing. Further, significant, strain-hardening occurs within Scotchcast 8 at 3.0 mm s\(^{-1}\) (see figures 5.48 and 5.49).

Comparing the stress-strain behaviour of these two epoxies with the stress-strain behaviour of Mixes M173 and M207F, for compression rates of 0.001 mm s\(^{-1}\), and for the
Figure 5.51: Scotchcast 8, Stycast 1090 and Mixes M173 and M207F at a compression rate of 0.001 mm s\(^{-1}\) and temperature of +20°C.

Figure 5.52: Scotchcast 8, Stycast 1090 and Mixes M173 and M207F at a compression rate of 0.001 mm s\(^{-1}\) and temperature of −20°C.

different temperatures (+80°C, +20°C, and −20°C, in figures 5.50, 5.51, and 5.52 respectively), we can see that M207F accommodates much larger stresses than the other three epoxies. This can be attributed to the presence of the alumina filler. The mechanical behaviour of the pure epoxy M173 is comparable to that of the Scotchcast 8, also a pure epoxy, both at elevated and sub-zero temperatures.

Figure 5.53: Stress-strain data for Scotchcast 8 across all temperatures and compression rates.

Figure 5.54: Stress-strain data for Stycast 1090 across all temperatures and compression rates.

Figures 5.53 and 5.54 show quasi-static stress-strain data for Scotchcast 8 and Stycast 1090 respectively, across all the tested compression rates and temperatures. As the strain rate is increased, we see an increase in the applied strain, as well as higher stresses supported before the materials yield. There is a far larger spread observed in the data for Scotchcast 8 than for Stycast 1090, regardless of the experimental temperature.
At room temperature, the stresses supported by both materials are comparable, though slightly higher in Stycast 1090. Scotchcast 8, however, yields at slightly higher strains. At elevated temperatures, Stycast 1090 behaves in a similar fashion regardless of loading rate. As to be expected at these high temperatures, very little stress is supported by either polymer.

At sub-zero temperatures, it is noted that Scotchcast 8 is able to support far higher stresses than Stycast 1090. In addition, Stycast 1090 yields at lower strains than Scotchcast 8.

### 5.3.2 Drop-Weight Testing

![Figure 5.55: Scotchcast 8 at peak strain, experiencing tensile crack propagation.](image)

![Figure 5.56: Relaxation following peak strain in Scotchcast 8.](image)

Drop-weight experiments, carried out at ambient temperature and humidity, were performed on 10 x 10 mm cylindrical samples of both Scotchcast 8 and Stycast 1090. The impact mass used was \( \sim 7 \text{ kg} \), and the impact velocities were between \( 1 - 5 \text{ m s}^{-1} \). High speed images of the differing failure modes of these two epoxies are presented in figures 5.55 and 5.56, and 5.57.

Failure was seen to occur within the Stycast 1090 at both 3 and 5 m s\(^{-1}\), initiated by shear bands acting at 45 degrees to the direction of the applied load (see figure 5.57). This failure mechanism has been shown to occur in syntactic foams by others [126], who showed that the inclusion of microspheres in an epoxy resin sample aided the mitigation of impact stress.

The Stycast 1090 which was subjected to a 1 m s\(^{-1}\) impact was recovered largely intact, though the beginning of fracture was detected, both in the high-speed video, and by the decrease in the stress-time history at \( \sim 0.6 \text{ ms} \), see figure 5.58. Notably, a lower peak
Figure 5.57: Shear banding at $45^\circ$ to the direction of applied load in Stycast 1090.

force was generated during this lower velocity impact as compared to the higher impact velocities. However, a greater initial peak stress was achieved in the $3 \text{ m s}^{-1}$ impact event as compared to the $5 \text{ m s}^{-1}$ impact event. This suggests that the rate of applied load has influence upon the maximum stress permitted by the sample prior to shear-induced failure.

Figure 5.58: Stress-time data for Stycast 1090.

Figure 5.59: Stress-time data for Scotchcast 8.

At impacts of 3 and 5 m s$^{-1}$, at these higher strain rates, Scotchcast 8 is able to accommodate a much larger degree of strain than Stycast 1090 before failure, see figure 5.59. This is also apparent in the Split Hopkinson Pressure Bar data (discussed in Sec. 5.3.3).

The two materials appear to fail in different ways. The failure mechanism in Scotchcast 8 was that of linear crack formation parallel to the direction of the applied load (see figures 5.55 and 5.56), and most probably due to the excessive (tensile) friction generated at maximum strain at the surfaces between the sample and the drop-weight anvils (see Sec. 5.2.2).

Comparing this behaviour with that observed for drop-weight impact experiments on Mixes M173 and M207F (see Sec. 5.2.2), the material failure behaviour is quite coherent; the pure epoxies (M173 and Scotchcast 8) failed predominantly due to linear crack forma-
Table 5.4: Impact velocities attained using different firing pressures.

<table>
<thead>
<tr>
<th>Firing Pressure [bar]</th>
<th>Impact Velocity [m s$^{-1}$]</th>
<th>Strain Rate [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>~2.5</td>
<td>~830</td>
</tr>
<tr>
<td>0.2</td>
<td>~3.4</td>
<td>~1130</td>
</tr>
<tr>
<td>0.25</td>
<td>~4</td>
<td>~1330</td>
</tr>
<tr>
<td>0.5</td>
<td>~6.8</td>
<td>~2270</td>
</tr>
<tr>
<td>0.75</td>
<td>~8.7</td>
<td>~2900</td>
</tr>
<tr>
<td>1.0</td>
<td>~10</td>
<td>~3330</td>
</tr>
<tr>
<td>1.25</td>
<td>~11.5</td>
<td>~3830</td>
</tr>
</tbody>
</table>

ination, and the epoxies with micro-inclusions (M207F and Stycast 1090) experienced shear banding at 45° to the direction of applied load.

5.3.3 Split Hopkinson Pressure Bars

Inconel 718 bars were used, with a striker bar of length 181 mm, to dynamically load samples of ~3 mm thickness and ~5 mm diameter of Scotchcast 8 and Stycast 1090. The firing pressures ranged from 0.15 - 1.25 bar, resulting in velocities from 2.5 - 11.5 m s$^{-1}$ (see table 5.4). Strain rates of between 800 - 4000 s$^{-1}$ were achieved. These experiments were carried out at ambient temperature (~20°C), low temperatures (~−20±3°C), and at elevated temperatures (~+45±1.5°C).

![Figure 5.60](image1.png)

Figure 5.60: Stress-strain data for Scotchcast 8, at a temperature of +20°C and strain rates between 1130 - 3830 s$^{-1}$ (from firing pressures between 0.2 - 1.25 bar).

![Figure 5.61](image2.png)

Figure 5.61: Stress-strain data for Stycast 1090, at a temperature of +20°C and strain rates between 1130 - 3300 s$^{-1}$ (from firing pressures between 0.2 - 1.25 bar).

As can be seen from figure 5.60, and this is to be expected since Scotchcast 8 is a pure epoxy, the mechanical behaviour of the material at room temperature most resembles that of a viscoelastic material when subjected to short compressive pulses. After testing at room temperature, all the Scotchcast 8 samples were recovered but for those that were subjected to the highest (1.25 bar) firing pressures.
We can see that, generally, at the higher strain rates (>3000 s\(^{-1}\), attained from impact velocities of 10 m s\(^{-1}\) and greater), the yield stress is reached at a lower strain, \(\sim 0.05\), and that this yield stress is almost 20 MPa lower than the yield stresses reached at the lower impact velocities.

In contrast, for the epoxy resin containing micro-balloons, Stycast 1090, at room temperature, we obtain almost identical strain to peak stress relationships, regardless of the rate of applied strain (see figure 5.61). In addition, all the Stycast 1090 samples, but those impacted with the lowest firing pressure (0.15 bar, strain rate of \(\sim 800\) s\(^{-1}\)), fractured. This material failure is suggested at by the significant, almost identical, rate of reduction in the measured stress after a strain of \(\sim 0.05\), and this complements the minimal strain-to-failure behaviour observed for this epoxy during drop-weight impact tests (see Sec. 5.3.2).

![Figure 5.62: Stress-strain data for Scotchcast 8, at a temperature of +45°C and strain rates between 830 - 3300 s\(^{-1}\) (from firing pressures between 0.15 - 1.0 bar).](image)

![Figure 5.63: Stress-strain data for Stycast 1090, at a temperature of +45°C and strain rates between 830 - 3300 s\(^{-1}\) (from firing pressures between 0.15 - 1.0 bar).](image)

Figures 5.62 and 5.63 demonstrate the material response of Scotchcast 8 and Stycast 1090 respectively, at elevated temperatures of +45°C. It appears that, as a result of heating, the material behaviour of Scotchcast 8 now no longer appears to be affected by the rate of applied strain. However, the material response of the Stycast 1090 across the range of strain rates appears unaffected, though we do observe an increase in the amount of strain imparted to the syntactic foam.

In addition, though, at room temperature, the stresses supported by the two epoxies was comparable, after heating, Scotchcast 8 can no longer support these same high stresses, though Stycast 1090 remains unaffected.

Figures 5.64 and 5.65 show the effect of cooling on the mechanical behaviour of the Scotchcast 8 and Stycast 1090 samples respectively. Both materials were seen to fracture at strain rates >2400 s\(^{-1}\).
Scotchcast 8 now yields at a higher strain as compared to samples at room temperature, and can also support higher stresses. The samples are again, as at room temperature, affected by strain rate. As the rate of applied strain increases, the strain at which the samples yield increases, and a higher yield stress is reached. Indeed, at strain rates above 1130 s$^{-1}$, the yield stresses are significantly higher than those observed in samples subjected to the same loading rates but at room temperature.

The material behaviour of Stycast 1090 appears to be unaffected - a similar strain to peak stress, yield stress, and rate of reduction in the measured stress, as at room temperature are observed, regardless of impact velocity. However, cooling appears to now result in observable differences caused by the rate of applied load on the peak stresses reached within the samples - increasing the strain rate increases the observed peak stress.

Following on from these results, and then comparing the stress-strain behaviour across the tested temperature range for a firing pressure of 0.75 bar (strain rate of $\sim$2900 s$^{-1}$) for both Scotchcast 8 and Stycast 1090 (figures 5.66 and 5.67 respectively), it is clear that the material response of Scotchcast 8 is highly dependent on temperature and loading rate, but that the material behaviour of Stycast 1090 is far less affected by varying either temperature or strain rate. This behaviour is true across all strain rates achieved using Split Hopkinson Pressure Bars, as well as at the low compression rates achieved using quasi-static Instron loading (see Sec. 5.3.1).

Comparing the stress-strain behaviour of these two epoxies with the stress-strain behaviour of Mixes M173 and M207F (see Sec. 5.2) for temperatures of $+20^\circ$C and $-20^\circ$C, in figures 5.68 and 5.69 respectively, we see that M207F consistently supports far larger stresses than the other three epoxies, as at quasi-static strain rates, see Sec. 5.3.1. In addition, the stress-strain behaviour of M173 is comparable to that of Scotchcast 8, again
as observed at the lowest compression rates.

Whilst the yield stresses experienced by M173 were similar regardless of temperature, it was observed that both Scotchcast 8 and Stycast 1090 were able to support higher stresses at sub-zero temperatures, whereas this ability was reduced in M207F.

Regardless, the mechanical behaviour of Stycast 1090 was comparable across temperature, with a peak stress at a strain of $\sim 0.05$ and then a rapid decrease in the stress supported, whereas cooling the other epoxies increased the strain at which they yielded.

![Figure 5.66: Stress-strain data for Scotchcast 8, across the tested temperature range for a strain rate of $\sim 2900$ s$^{-1}$ (from firing pressures of $\sim 0.75$ bar).](image)

![Figure 5.67: Stress-strain data for Stycast 1090, across the tested temperature range for a strain rate of $\sim 2900$ s$^{-1}$ (from firing pressures of $\sim 0.75$ bar).](image)

![Figure 5.68: Scotchcast 8, Stycast 1090 and Mixes M173 and M207F at strain rates of $\sim 2900$ s$^{-1}$ (from firing pressures of $\sim 0.75$ bar) and a temperature of +20°C.](image)

![Figure 5.69: Scotchcast 8, Stycast 1090 and Mixes M173 and M207F at strain rates of $\sim 2900$ s$^{-1}$ (from firing pressures of $\sim 0.75$ bar) and a temperature of −20°C.](image)

Figures 5.70, 5.71, 5.72, and 5.73 show Split Hopkinson Pressure Bar stress-strain data for Scotchcast 8, Stycast 1090, and Mixes M207F and M173 respectively, across all the temperatures tested.

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tested compression rates and temperatures.

Scotchcast 8 (figure 5.70) demonstrates a clear trend in the stress-strain behaviour of the samples across the temperature range. Increasing the temperature from sub-zero values to elevated temperatures reduces the stresses supported by the samples, regardless of strain rate. As the temperature decreases, there is an increase in the strain at which the sample yields. Temperature has a more pronounced effect on the stress-strain behaviour of Scotchcast 8 than the strain rate. There is no clear strain rate effect on its mechanical behaviour, though the largest differences in the stress-strain behaviour are shown at room temperature.

Cooling Stycast 1090 (see figure 5.71) also increases the amount of stress supported by the sample, though there is more of a spread in the stress-strain data at these lower temperatures. The mechanical behaviour of Stycast 1090 at room and elevated temperatures is highly comparable, and the overall behaviour across all temperatures follows the same trend; a rapid decrease in stress after yield is observed. It is possible to see a more strain rate-dependent trend for Stycast 1090; as the applied strain rate is increased, the peak stresses reached by the samples are also increased.

Unlike the other three epoxies described here, Mix M207F supports the highest stresses at elevated temperatures (see figure 5.72), though there is a larger spread across the stress-strain behaviour at these temperatures than at any lower temperatures. Generally, the sub-zero and room temperature behaviour of Mix M207F is quite similar, though cooling the samples decreases the amount of stress they are able to support. As compared with Mix M173, Mix M207F is able to support higher stresses overall, though there is more of a spread in the yield stresses and strains attained by it.

Finally, figure 5.73 shows that Mix M173 demonstrates no clear strain rate dependence, though the spread in the stress-strain behaviour is most significant at elevated temperatures. Heating decreases the amount of stress the samples are able to support, but the material behaviour at sub-zero and room temperatures is comparable.
5.4 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) of Scotchcast 8 and Stycast 1090 in tension was performed using a Tritec 2000 manufactured by Lacerta Technology (formerly Triton Technology).

DMA is typically used to study and characterise the viscoelastic behaviour of polymers. A sinusoidal stress is applied to a sample, and the strain in the material measured, allowing determination of the dynamic modulus. Both temperature and the applied frequency of the stress can affect the dynamic modulus; as such, varying these parameters can help locate the glass transition temperature of the material, as well as to identify transitions corresponding to other molecular motions [138].

The glass transition temperature is the point at which an amorphous material tran-
sitions from a glass-like brittle state to a viscous or rubbery state as the temperature is increased [123].

This analysis was performed over a temperature range of \(-100^\circ\text{C} +120/ +140^\circ\text{C}\). The temperatures were reached using liquid nitrogen cooling and then a programme which raised the temperature from \(-100^\circ\text{C} +20^\circ\text{C}\) at 5°C min\(^{-1}\) before an increase to \(+120/ +140^\circ\text{C}\) at 2°C min\(^{-1}\).

The samples used in this analysis were 100 mm in length, 3 mm wide, and 1.5 mm thick. Frequencies of 1 and 50 Hz were investigated. In addition, analysis at 100 Hz was attempted, but this led to failure of the material.

Both \(\alpha\) and \(\beta\) transitions were observed during these tests. The \(\alpha\) transition is the primary glass transition, where long chain segmental motion occurs within the main polymer chain, while the \(\beta\) transition refers to local motion within segments of the chain.

![Figure 5.74: DMA data from Scotchcast 8 at 1 and 50 Hz.](image)

![Figure 5.75: DMA data from Stycast 1090 at 1 and 50 Hz.](image)

Figures 5.74 and 5.75 show the material response from analysis performed at two frequencies on Scotchcast 8 and Stycast 1090 respectively. Both graphs show evidence of a glass (\(\alpha\)) transition, through which the storage modulus significantly reduces. A shift in the position of this \(\alpha\) transition to higher temperatures with increased vibrational frequency was observed in both materials. For both materials, the \(\alpha\) transition is associated with restricted rotations and translations of the polymer main chains.

Figure 5.74 shows \(\alpha\) transition peaks centred at \(+58.7^\circ\text{C}\) and \(+79^\circ\text{C}\) for frequencies of 1 Hz and 50 Hz respectively. As the vibrational frequency was increased, there was an increase in the temperature at which a significant reduction in the storage modulus was observed.

As figure 5.75 shows, both \(\alpha\) (\(+66.7^\circ\text{C}\)) and \(\beta\) (\(-35^\circ\text{C}\)) transitions were observed at 1 Hz; however, this secondary \(\beta\) viscoelastic transition was less apparent in the analysis at 50 Hz. In addition, a reduction of storage modulus at this frequency began at \(\sim +50^\circ\text{C}\). A notable shift in the central position of the \(\alpha\) transition from \(+66.7^\circ\text{C}\) to \(+70^\circ\text{C}\) was
seen to result from the increased vibrational frequency. This result corresponds well with the rate-dependent shift of the transition observed in other polymers [138].

In addition, as can be seen from both figures 5.74 and 5.75, the $\alpha$ transitions for Scotchcast 8 are centred around higher values than for Stycast 1090 at corresponding vibrational frequencies.

5.5 Discussion

A characteristic feature of polymers is the manner in which they respond to an applied stress or strain depending on the rate, temperature, or time period of loading. If a polymer is subjected to a rapid change in strain, it appears stiffer than if the strain were applied at a slower rate [123].

Polymeric mechanical properties change dramatically with temperature, from glass-like brittle behaviour at low temperatures, to a rubber-like behaviour at elevated temperatures. In general, decreasing the strain rate, or increasing the temperature, makes polymers softer and more ductile [123].

![Figure 5.76: Yield stress for Scotchcast 8 as a function of temperature and strain rate.](image)

![Figure 5.77: Yield stress for Stycast 1090 as a function of temperature and strain rate.](image)

Figures 5.76 and 5.77 show the yield stresses of Scotchcast 8 and Stycast 1090 respectively, as a function of both temperature and strain rate. At elevated temperatures, these stresses are higher for Scotchcast 8 than for Stycast 1090 at the lowest strain rates, but lower at the higher strain rates. At ambient temperature, the stresses increase more steeply at the lowest strain rates for Scotchcast 8, and are higher at the highest strain rates. At sub-zero temperatures, for both the lower and higher strain rates, the yield stresses are higher in Scotchcast 8 than in Stycast 1090.

It is clear that more data is needed to identify specific transition points, although this experimental data does indicate the existence of transitions in the nature of the rate
dependence of the material yield behaviour. This is most clear in Scotchcast 8 and Stycast 1090 at elevated temperatures (see figures 5.76 and 5.77 respectively); beyond a transition threshold, the materials exhibit an increased sensitivity to strain rate. This transition threshold is determined by both temperature and strain rate. This same phenomenon has been observed in the yield behaviour of a variety of amorphous polymers, though the transition threshold, as well as the degree of strain rate sensitivity before and after the transition, is unique to the particular polymer [138].

A bilinear dependence of the yield stress on the logarithm of strain rate is to be expected [181]. At the lowest strain rates, the yield stress is found to increase linearly with the logarithm of strain rate (see figures 5.76 and 5.77), indicating that yield behaviour in this regime could be accurately explained and/or predicted in terms of a single activated process [138]. At the higher strain rates, the yield strength is again found to increase in an approximately linear manner with the logarithm of the strain rate. However, the slope of the data line is much steeper in this high-rate regime. It is thus clear that both Scotchcast 8 and Stycast 1090 undergo a significant material transition as the strain rate is increased beyond a certain, critical level, beyond the test capabilities of the apparatus used here.

It is well known that the mechanical response of polymers is highly dependent on the applied loading frequency. It is therefore not sufficient to use properties measured under static loads in the analysis of dynamic tests. In addition, the frequency dependence is not constant, but is greatest over the range(s) of frequencies corresponding to any particular polymer’s transition(s) at the test temperature. Furthermore, the effects of frequency and temperature are interlinked through the time-temperature superposition principle: changes in one can be related to changes in the other. This means that the variation in the mechanical properties observed at a single frequency or loading rate at various transition temperatures will also be observed at a single temperature at various frequencies [132][133].

Relating this principle to the data reproduced in this chapter, we can see, from figures 5.74 and 5.75, that increasing the temperature, whilst keeping the applied vibrational frequency constant, leads to a material transition, which is shifted to higher temperatures if the applied frequency is increased. Figures 5.76 and 5.77 demonstrate that increasing the strain rate increases the yield stress, regardless of temperature. However, beyond a certain strain rate, between 10 - 1000 s\(^{-1}\), the materials exhibit an increased sensitivity to strain rate. This too shows that a material transition must have occurred, this time not due to temperature, but due to strain rate.

Indeed, others have observed for some polymers that the dependence of yield stress on strain rate is greater at high rates. This bilinear relationship between the stress and strain rate has been explained due to the different molecular relaxations in the materials [182]. In addition to high strain rates, low temperatures also increase the observed strength of
the materials (see figures 5.76 and 5.77).

The time temperature superposition principle states that temperature and frequency (strain rate) are interlinked. However, in this case, more studies at intermediate temperatures and strain rates are needed in order to provide a suitable mapping function, such as the one described by the Williams-Landel-Ferry (WLF) equation (see Sec. 2.6.1.1). A significant weakness in the methods employed here was that two different types of apparatus were used: an Instron machine was used for the quasi-static experiments, whilst a Split Hopkinson Pressure Bar was used for the experiments at the higher strain rates. Unfortunately, the bilinearity in the material behaviour was observed to occur at the same strain rate as the change of apparatus.

With further experiments, at more temperature and strain rate intervals, it would be possible, by comparing the stress-strain results with results from DMA tests (see Sec. 5.4), to link specific relaxations within the materials to the dependence of the yield stress on both strain rate and temperature. In addition, compressive stress-strain curves at different strain rates could be correlated to those at different temperatures, via a simple mapping that relates temperature to the logarithm of the strain rate [182].

This assumption is possible due to the same underlying microstructural processes. The universal function for temperature dependence of viscosity, and mechanical and electrical relaxations, in amorphous polymers and other, super-cooled, glass-forming liquids, arises because the rates of all these processes depend predominantly on temperature, through their dependence on free volume [132][133][134].

This feature of polymers allows data interpretation through time-temperature superposition. By performing experiments over a range of temperatures at a single strain rate, and over a range of strain rates at a single temperature, and noting that increasing log(strain rate) is equivalent to decreasing temperature, the data at fixed temperatures can be mapped onto those at fixed strain rates, and vice versa. These mapped results can then be compared to other methods for measuring the thermo-mechanical response of polymers, for example, dynamic mechanical thermal analysis [132][133].

Because the range of strain rates which can be accessed experimentally is much smaller when compared to the equivalent range of temperatures, it is difficult to observe the effects of more than one transition in a single polymer through strain rate alone. As such, a related approach has been used very successfully to develop models for high rate behaviour [132][133][138].
5.6 Summary

This chapter presents the effects of temperature and strain rate upon the compressive response of the epoxies Scotchcast 8 (a pure epoxy), Stycast 1090 (a syntactic foam), and Mixes M173 (a clear epoxy) and M207F (an epoxy with alumina filler). Experimental procedure involved an Instron Universal Testing Machine, a drop-weight tower, and a Split Hopkinson Pressure Bar system to achieve a range of strain rates. Specially adapted environmental chambers were used to achieve a range of temperatures.

Conducting different types of loading experiments on metals does not generally present a significant problem due to their homogeneity and isotropy; conversely, repeating these experiments on polymers can often throw up problems due to their inhomogeneity and anisotropy.

The pure epoxies were shown to behave significantly differently from both the syntactic foam and the epoxy with the alumina filler. Mix M207F, the epoxy with the alumina filler, was shown to be able to accommodate by far the largest amount of stress, with the pure epoxies supporting comparable stress to each other, and Stycast 1090 less able to support large stresses. Furthermore, the pure epoxies were able to accommodate a much greater degree of strain than the loaded epoxies.

In addition, the ability of the loaded epoxies (Mix M207F and Stycast 1090) to support large stresses was less affected by temperature and strain rate as compared with the pure epoxies (M173 and Scotchcast 8). However, the material behaviour of the pure epoxy M173 was less affected by the geometric size of the sample as compared with the epoxy containing filler (M207F).

High-speed images taken from the drop-weight impact experiments demonstrated the different modes of failure for the epoxy encapsulants. The pure epoxies (M173 and Scotchcast 8) failed predominantly due to linear crack formation, while the loaded epoxies (M207F and Stycast 1090) experienced shear banding at 45° to the direction of applied load.

Dynamic Mechanical Analysis can be used to characterise the viscoelastic behaviour of polymeric materials, with a focus on the rate-dependent shift of material transition temperatures, whilst uniaxial compression testing can be used to characterise the rate-dependent yield behaviour of these materials. For the Scotchcast 8 and Stycast 1090 studied here, it was observed that the yield transition shifted to a higher strain rate with increased temperature. The time-temperature superposition principle can be applied to the collected data to show that glass (α) and β transitions were the cause of the bilinear dependence of yield stress on strain rate of the materials.

Considering the wide usage of these epoxies, it is important to consider the benefits and disadvantages of these different material behaviours, in particular for force mitigation. For example, the fact that Stycast 1090 fails at such low strains when subjected to high
compression rates significantly reduces the amount of transmitted stresses. This property would be useful for an application where one was trying to protect and mitigate force. However, the structural integrity of any system manufactured from such a material would be lost following a single high impact incident.
Chapter 6

Electromechanical Response of PZT 95/5

PZT 95/5 (95% lead zirconate, 5% lead titanate, with no added dopants) is a piezoceramic, and also both pyroelectric (affected by temperature) and, upon poling, ferroelectric (has spontaneous polarisation) (see Sec. 2.1.2).

A number of compression experiments were carried out on poled and unpoled PZT 95/5 samples of varying porosity and geometry, across a range of temperatures.

Strain rates between $10^{-4} - 10^4$ s$^{-1}$ were achieved using quasi-static testing equipment, drop-weight towers, and Split Hopkinson Pressure Bars.

Temperature was controlled for the quasi-static compression equipment and the Split Hopkinson Pressure Bar system, using purpose-built environmental chambers; temperatures between $-20^\circ$C - $+80^\circ$C were achieved.

In addition, the generated voltage output was measured for both drop-weight impact experiments and Split Hopkinson Pressure Bar compression on poled PZT 95/5 samples, using the electrode setup described in Sec. 3.5.1.

In this chapter, the data is displayed in each section in increasing order of applied loading rate, from quasi-static loading through drop-weight impacts to Split Hopkinson Pressure Bars.
6.1 Preparation of PZT 95/5 Samples

Unpoled billets of two differing porosities, and therefore densities, in addition to polished, unpoled square samples, were provided for these experiments by AWE Aldermaston. The denser PZT material was known to contain natural porosity attained during production; the more porous PZT was generated as a result of the addition of a poreformer (see Sec. 2.3.2).

The square samples were of \(\sim 3\) mm thickness, and lengths and widths of \(\sim 7.5\) mm. The billets were of \(\sim 12\) mm thickness, with lengths between 46 - 55 mm, and widths between 24 - 30 mm. The billet material therefore needed to undergo a number of processes in order to be of suitable size and shape for the compression experiments.

First, the billets were mounted onto a holder using a wax. Each billet was warmed using a heating plate, and a layer of wax melted onto one face. A metal block was then attached to this face and pressure applied as the wax cooled, allowing the billet to adhere to the metal block. This metal block was then screwed into place above a diamond saw.

A diamond wafering blade, 152 x 0.50 x 12.7 mm, 15 LC from Buehler Ltd., Illinois, USA, was used to slice the billets into different thicknesses; these thicknesses would be the thicknesses of the samples to be compressed. The samples were then polished using diamond grinding discs and suspensions (see Sec. 5.1). The resulting thicknesses were between 0.8 - 4.3 mm.

These unpoled slices then needed to be poled. To this end, a thin coat of silver was put on either side of the polished surfaces. A high voltage power supply was used to generate an electric field across each slice, and ramped up to the relevant voltages needed to ensure a field of \(\sim 2\) kV mm\(^{-1}\) across the different slices, ensuring that they were now poled; i.e. for a sample of 2 mm thickness, the voltage applied would need to be 4 kV. For comparison, some slices were left unpoled but were still bored.

Finally, samples of diameter 4.3 - 4.8 mm were bored out from all the slices and were now ready to be subjected to compression loading.

6.1.1 Density Measurements

In order to quantify the density of the PZT 95/5 as a result of its two different porosities, in addition to simple size and weight measurements of the billets, a Micromeritics Pycnometer AccuPyc 1330, linked to the program Monypyc, was used. Ten runs with ten purges were carried out at \(+22.9\)°C. Helium gas was pumped into the sample holder at 0.111 psig. This method for determining material density by measuring the pressure change of helium is most effective if the solids are dry.

The skeletal density of the less porous, more dense, PZT 95/5 was found to be \(\sim 8.38 \pm 0.03\) g cm\(^{-3}\), and will henceforth be described as ‘standard PZT’, or simply ‘PZT’. The density of the PZT 95/5 with the added poreformer, making it more porous and there-
Table 6.1: Average values attained for Vickers hardness tests on samples of PZT and pPZT.

<table>
<thead>
<tr>
<th>PZT</th>
<th>Vickers Pyramid Number</th>
<th>Hardness [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>298HV20/30</td>
<td>2.9</td>
</tr>
<tr>
<td>Standard</td>
<td>339HV20/45</td>
<td>3.3</td>
</tr>
<tr>
<td>Porous</td>
<td>175HV20/30</td>
<td>1.7</td>
</tr>
<tr>
<td>Porous</td>
<td>207HV20/45</td>
<td>2.0</td>
</tr>
</tbody>
</table>

fore less dense, was found to be $\sim 7.81 \pm 0.03$ g cm$^{-3}$, and will henceforth be described as ‘porous PZT’ or ‘pPZT’, with the prefix ‘p’ representing ‘porous’. These values compare well to those determined by simple billet-weighing measurements (8.35 g cm$^{-3}$ and 7.78 g cm$^{-3}$ respectively).

As described in Sec. 2.5.1, it is expected that an increase in porosity will lead to a decrease in the observed mechanical properties, such as strength and elastic modulus. The materials should fail by vertical slabbing under axial compression, where the failure planes will form vertically parallel to the loading direction (see Sec. 2.5.0.1 for a more detailed discussion).

### 6.2 Deformation Behaviour of PZT

#### 6.2.1 Hardness Testing

The Vickers hardness test was carried out on several unpoled samples of both the porous and standard PZT in order to help characterise the materials’ resistance to deformation and fracture. A Zwick Roell Indentec, linked to the program Indentec C.A.M.S. testing system by Newage, was used. This method was chosen primarily because the diamond indenter can be used for a range of materials regardless of hardness, and the hardness calculations are independent of the size of the indenter [49].

The unit of hardness is known as the Vickers Pyramid Number (HV), and can be converted into units of pascals. However, it is not the same as pressure, as it is determined by the load over the surface area of the indentation and not the area normal to the force. It can also be converted to yield stress under certain conditions. Toughness measurements are made by measuring the average length of the radial cracks emanating from the hardness impression.

Vickers hardness numbers are reported as xxxHVyy/zz, where xxx represents the hardness number, HV the hardness scale (in this case, Vickers), yy the load used in kgf (kilogram-force), and zz the loading time.

Table 6.1 shows the extremes of the range of hardness values for standard and porous PZT samples, in GPa. Values for PZT were found to be between 2.922 - 3.325 GPa, whereas the values for pPZT were found to be between 1.716 - 2.030 GPa, significantly
Table 6.2: Hardness values of well-known materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Vickers Pyramid Number</th>
<th>Hardness [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless Steel</td>
<td>140 - 180HV30</td>
<td>1.373 - 1.765</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>55 - 120HV5</td>
<td>0.5394 - 1.177</td>
</tr>
<tr>
<td>Iron</td>
<td>30 - 80HV5</td>
<td>0.2942 - 0.7846</td>
</tr>
<tr>
<td>Diamond</td>
<td>10000HV</td>
<td>98.1</td>
</tr>
</tbody>
</table>

Figure 6.1: Drop-weight sequence showing the fracture of a standard, unpoled PZT 95/5 sample; impact mass 7 kg, velocity 5 m s\(^{-1}\).

We can compare these values with those for other, well-known materials, shown in table 6.2. From this, we can see that even the porous PZT appears to be harder than stainless steel.

### 6.2.2 Fracture Behaviour of PZT

Drop-weight impact tests were carried out on PZT at ambient temperature and humidity, accompanied with high-speed imaging, in order to observe the deformation behaviour of PZT samples. The impact mass used in these experiments was \(\sim\) 7 kg, and the impact velocity 5 m s\(^{-1}\).

Both the standard and the porous unpoled PZT samples fractured along the axis of impact, as expected from the brittle failure of ceramics (see Sec. 2.5.0.1), and shown in figures 6.1 and 6.2. The specimens in these experiments fractured along vertical failure planes where the tensile stresses were maximum.

Relating the high-speed images to stress-time data collected for these same specimens, shown in figure 6.3, we can see that at \(a\) represents the beginning of the experiment, whilst at \(b\) the sample is still able to increase the stress it is supporting. At \(c\), we can see that material fracture has begun and, as such, the stress the sample is able to support has decreased. Image \(d\) shows complete failure of the sample, where sample stresses have decreased.

Figure 6.2: Drop-weight sequence showing the fracture of a porous, unpoled PZT 95/5 sample; impact mass 7 kg, velocity 5 m s\(^{-1}\).
decreased to zero. Peak stress was reached in the standard and the porous unpoled PZT samples at a similar time, at \( \sim 0.052 \text{ ms} \), and at a similar strain (\( \sim 0.08 \)), though the peak stresses were different. Stress within the standard PZT sample reached a peak stress of \( \sim 858 \text{ MPa} \), and only \( \sim 812 \text{ MPa} \) in the porous PZT sample. This is to be expected, as an increase in porosity decreases the amount of stress a ceramic specimen is able to support (see Sec. 2.5.1). Figure 6.4 shows the remaining fractured pieces of standard PZT after a drop-weight experiment.

Figure 6.3: Stress-time results from drop-weight experiments on standard and porous PZT (aspect ratio: 0.7); impact mass 7 kg, velocity 5 m s\(^{-1}\).

Figure 6.4: Fractured, standard PZT after a drop-weight experiment. The silvery appearance of the ceramic is due to damage of the anvils.

### 6.2.3 Microscopy

A number of standard and porous PZT samples before and after different compression experiments were studied, under both optical and scanning electron microscopy, employing the same methods as described in Sec. 5.1.

The pores in the PZT proved to be larger than the diamond suspension used during polishing (see Sec. 5.1). As a result, the suspension seeped into the pores. However, this actually enables us to more clearly see the pores under an optical microscope, see figures 6.5 and 6.6.

It is clear that, not only does the less dense PZT have a higher density of pores than the standard PZT (\( \sim 18 \pm 3\% \) more), but that a substantial number of these pores are also significantly larger than those pores found in the standard PZT (\( \sim 9x \) larger), and more interconnected. This is seen even more clearly when examining the samples further using a scanning electron microscope, as seen in figures 6.7 and 6.8. During compression tests,
Figure 6.5: Standard PZT 95/5 at 20x magnification.

Figure 6.6: Porous PZT 95/5 at 20x magnification.
Figure 6.7: Standard PZT 95/5 at 430x magnification.

Figure 6.8: Porous PZT 95/5 at 430x magnification.
Figure 6.9: Recovered standard PZT 95/5 from a drop-weight experiment at 900x magnification.

Figure 6.10: Recovered porous PZT 95/5 from a drop-weight experiment at 900x magnification.
it is expected that these larger and more interlinked pores will aid fracture propagation, reducing the samples’ abilities to support significant stresses (see Sec. 2.5.0.1).

Figures 6.9 and 6.10 show, respectively, samples of standard and porous PZT that have been subjected to drop-weight impact tests. Both the samples experienced brittle material failure. It is clear from both images that the presence of pores aided fracture propagation. In addition, the cracks in the porous sample were wider than the the corresponding cracks in the standard PZT sample, which suggests that the pores acted as propagating channels for fractures (see Sec. 2.5.0.1).

6.2.4 Digital Image Correlation

Some of the Split Hopkinson Pressure Bar experiments on unpoled standard and porous PZT samples were recorded using high-speed imaging for the purpose of Digital Image Correlation (DIC). For this, one face of several standard and porous samples was each speckled using acrylic paint.

An airbrush with a mount was held 23 cm away from the sample, and fired at a pressure of 1 bar for 5 seconds in order to obtain an even coat and a good speckled surface. The pressure dictates the size of the globules of paint; the lower the pressure, the larger the globules obtained. The length of time affects the coverage of the surface, and therefore the darkness.

The high-speed videos from these experiments were analysed by the freely available DIC software package Ncorr. DIC is a non-contact technique for measuring material deformation, and has been successfully demonstrated on a range of materials, from biological samples to polymeric foams [183], but very few papers exist on the application of DIC on ceramics.

DIC tracks the relative displacements of points between a reference (e.g. an undeformed) image and a current (typically a deformed) image. The aim here is to identify regions of high stress, upon tracking of the strain fields.

Figure 6.11 shows the localisation of deformation through a porous PZT sample. The images are accompanied by the frames from the high-speed video. It is seen that the DIC is able to effectively track the increasing strain changes with high spatial resolution; the material fractured along where the strain was concentrated, and is far easier to see in the DIC images than the high-speed images, with the fracture only becoming apparent far later in the high-speed images.
6.3 Variability in Ceramic Behaviour

Brittle materials show perfectly elastic behaviour under compression, until failure occurs. Under these applied loadings, the data demonstrate substantial scatter. The difference in defect sizes, and their random distribution, within ceramic materials causes a difference in their mechanical properties because, unlike metals and polymers, ceramics cannot compensate for inner defects via plastic deformation.

How easily domains are able to move is dependent on the strains imposed by surrounding crystals, as well as on the crystal size itself. In a polycrystalline ceramic, domain reorientation is affected by the size of individual grains, by the presence of impurities and pores which prevent domain wall movement, by stresses imposed by surrounding grains, by the nature of the grain boundaries, and by the presence of second-phase particles. Thus, the microstructure, the purity of the initial starting materials, and the manufacturing and firing procedures all have a strong effect on resulting properties. As a result, products made by similar processes may have variations of as much as 15 - 20% in the measured material properties (see Sec. 2.4) [89].

Thus, it is not enough to simply state a failure load, but instead a failure or survival probability must be calculated [99]. Weibull statistics are often used to describe fracture in brittle materials (see Sec. 2.5.0.3 for more detail) [82][96].

According to Freudental’s proposition, the probability of occurrence of a critical defect decreases with smaller volumes and increases at larger ones. The Weibull modulus deals
with this divergence in results. Many previous studies on brittle materials have shown that glassy materials present strength values which are more random than in ceramics, citing Weibull moduli \(m\) \(\sim\) 5 for glassy materials as compared to moduli values between 10 - 20 for ceramics [184].

Under high loading rates, the strength of brittle materials has been seen to increase (up to two times greater than under static loading), but with more variation in the strength values than seen in ductile materials. Fracture of brittle materials under dynamic loading can be due to the multi-activation of defects and not simply fracture due to a critical defect, resulting in the failure of the whole material. There is significant disagreement in the available literature as to whether failure of these brittle materials under dynamic loading provides a lesser or greater scatter in the obtained strength values than those from static loading. Some studies show that brittle materials exhibit a single strength value if subjected to high loading rates, whilst others indicate that the scatter value for high velocity loading is greater than for static loading [184].

In order to analyse the scatter in the results presented in this chapter, the Coefficient of Variation (\(CV\)), for the statistical distribution of material properties, will be used. The \(CV\) is the ratio of the standard deviation, \(\sigma\), to the mean value, \(\mu\), as follows:

\[
CV = \frac{\sigma}{\mu} \quad (6.1)
\]

This relationship has been shown to simplify the calculation of statistical parameters, and can be used to evaluate the Weibull modulus \(m\) as follows [184]:

\[
CV = \frac{\sigma}{\mu} \approx m^{-0.93} \quad (6.2)
\]

In order to reduce the scatter in the strength results, where time and material allowed, as many repeats in each compression experiment were executed as were possible. For clarity, and to avoid making the graphs difficult to interpret, the data chosen in the graphs in this chapter will be from representative specimens. Additional data supporting the claims made in this chapter are included in Appendix C.

Figure 6.12 shows results obtained from quasi-static loading on standard, unpoled, square samples of PZT 95/5 with an aspect ratio of 0.70, at +20°C, and at a compression rate of 0.004 mm s\(^{-1}\). All the samples completely failed. The Weibull modulus from this data was \(\sim\) 15.

Figure 6.13 shows results obtained from drop-weight impacts (with a mass of 60.81 g) on standard, poled samples of PZT 95/5 with an aspect ratio of 1, at +20°C, and strain rates of \(\sim\) 650 s\(^{-1}\). The Weibull modulus from this data was \(\sim\) 77.

Despite the consistencies observed in the mechanical behaviour of PZT samples when subjected to the same applied loading rates, it was observed that the voltage output behaviour was not identical.
Figure 6.12: Stress-strain data for standard, unpoled samples of PZT 95/5 (aspect ratio: 0.7), at +20°C and a compression rate of 0.004 mm s\(^{-1}\).

Figure 6.13: Stress-strain data from drop-weight experiments on standard, poled samples of PZT 95/5 (aspect ratio: 1), at +20°C and strain rates of \(\sim 650\) s\(^{-1}\).

Figure 6.14 shows that, for samples compressed at strain rates \(\sim 860\) s\(^{-1}\), though the peak voltage behaviour with time was comparable, the actual voltages observed were highly variable.

This can be explained by the fact that ceramics are not identical on a microstructural level. Upon poling (see Sec. 2.1.3), all the domains within the samples might not have been completely aligned, whilst some domains may switch back to their initial states after the poling field is removed, leading to the observable differences in voltage output [185].

Further increasing the strain rate, Split Hopkinson Pressure Bar experiments were carried out on unpoled and poled PZT 95/5 samples. The specimens were subjected to impact velocities between 3.5 - 10.5 m s\(^{-1}\), resulting in strain rates of the order of \(\sim 10^3\) s\(^{-1}\).

Figures 6.15, 6.16, and 6.17 show the stress-time behaviour of some standard and porous PZT samples (both poled and unpoled) across a range of strain rates. The behaviour appears comparable for similar strain rates, independent of porosity. The peak stresses at each strain rate range were much the same, and increased with increasing strain rate.

The Weibull modulus from these Split Hopkinson Pressure Bar data sets was itself varied, but generally between 2 - 5, significantly lower than those observed from drop-weight impact loading tests and quasi-static experiments, indicating a reduction in the randomness of the resulting strength values as the applied loading rate was decreased.

The various scatter levels for the different loading conditions are compared using the Weibull distribution in figure 6.18. The experimental results show that an increase in the applied loading rate increases the randomness of the resulting strength values (i.e. as the applied loading decreases from dynamic to quasi-static, \(m \to \infty\)).
supported by additional experiments, the data of which can be found in Appendix C, and has also been observed by other authors [184].

In compression, cracks at an angle to the compression axis propagate stably, requiring a progressive increase in load to make them propagate further. In addition, they twist and bend out of their original orientation to run parallel to the compression axis [82]. Fracture is not caused by the rapid, unstable propagation of one crack, but the slow extension of many cracks to form a crushed zone [81]. The stress-strain curve rises and reaches a maximum when the density of cracks is so large that they link to give a general crumbling of the material. It is not the size of the largest crack that counts, but that of the average [82]. Therefore, a brittle material’s strength in compression is, on average, a whole order of magnitude larger than its strength under tensile stress [90].
The Weibull modulus for quasi-static, drop-weight, and Split Hopkinson Pressure Bar test results on PZT 95/5.

The results here show an increased strength variation under higher loading rates, resulting in a greater scatter value for higher velocity loading than for static loads. It is believed [184] that at the lowest compression rates, failure of the specimens is due to maximum tensile stress failure originating at a critical defect, whilst under dynamic loading, there is a simultaneous activation of the majority of flaws by the propagation of the compressive stress pulse in the specimen.

Under quasi-static compressive loads, brittle solids such as ceramics normally undergo very little inelastic deformation. Under high strain rate dynamic compressive loads, on the other hand, they may undergo extensive micro-cracking and inelastic deformation [186]. In addition, as the strain rate increases, the fragment size decreases as a result of the coalescence of compression-induced tension cracks emanating from smaller flaws [187]. Thus, the fracture of brittle materials under dynamic loading can be due to the multi-activation of defects and not simply fracture due to a critical defect, and thus be more varied [184].
6.3.1 Degradation Behaviour of PZT

Figure 6.19: Stress-time data from drop-weight experiments on standard, poled PZT, aspect ratio 1 (diameter = thickness = 4.3); strain rates $\sim 470 \text{ s}^{-1}$.

Figure 6.20: Voltage-time data from drop-weight experiments on standard, poled PZT, aspect ratio 1 (diameter = thickness = 4.3); strain rates $\sim 470 \text{ s}^{-1}$.

In addition to studying variability across a range of samples, it was desired to determine whether there was any form of degradation within each of the PZT samples upon low rate impacts, and whether there was any obvious variation in the charge output if the sample was repeatedly recovered and re-impacted.

To this end, a poled, standard PZT sample, of aspect ratio 1 (i.e. diameter = thickness = 4.3 mm) was impacted at least 18 times with a mass of 70 g, and from a height of $\sim 26.5$ cm, resulting in an impact velocity of $\sim 2.3 \text{ m s}^{-1}$. The strain rates achieved for all impacts were comparable, at $\sim 470 \text{ s}^{-1}$.

Figures 6.19 and 6.20 show the stress-time and voltage-time data for the drop-weight impacts on the same sample of poled PZT. Both profiles are comparable; the peak stresses experienced by the sample are within 20 MPa of each other, the peak voltages within 5 V. Though there is some variation in these results, the later impact tests on the sample show a decrease in stress supported by the sample, coupled with a decrease in the voltage output. Because a critical fracture stress has not been reached, the sample does not fail. Crack growth in compression is stable; final failure requires the simultaneous growth and interaction, under increasing load, of many cracks, which does not occur at these lower impact rates (see Sec. 2.5.0.2) [106].

Because of the variation in these results, the degradation of the sample is not completely obvious. However, upon studying the charge-time relationships for each of these impacts, it does appear that the sample experienced degeneration upon repeated impacts. Figure 6.21 shows this as a reduction in the charge output upon increasing impact.

This is further supported upon comparison of the charge-strain data (figure 6.22). Peak voltage output (as well as peak stress) is reached at $\sim 0.005$ strain, and the sample
then experiences a comparable decrease in stress with strain (again, additional data can be found in Appendix C). Figure 6.22 shows that there is an overall decrease in charge output of \( \sim 15 \mu C \) from the initial impacts to the final impacts.

Thus, the results here show that, even if a sample does not completely fail under compressive loading, there will still be a degradation in the electromechanical behaviour of the material. This results in a noticeable decrease in the charge output by the sample, most probably due to misalignment of the dipoles within the specimen as a result of mechanical stress (see Sec. 2.1.3.1) [188].

6.4 Aspect Ratio Compression Effects on the Mechanical Behaviour of PZT 95/5

Following on from compression experiments done on both polymers and metals of varying aspect ratio, the experiments were repeated on the piezoelectric ceramic PZT 95/5. The range of strain rates examined here, between \( 10^{-4} \) - \( 10^4 \) s\(^{-1} \), were achieved using quasi-static, drop-weight tower, and Split Hopkinson Pressure Bar techniques. All the experiments were carried out on both poled and unpoled, porous and standard samples, at ambient temperature and humidity, sub-zero temperatures of \(-20^\circ C\), and elevated temperatures of \(+80^\circ C\). Some of the engineering stress-strain relationships obtained are compared and discussed, with additional data included in Appendix C.

Due to the brittle nature of the PZT samples, in all the quasi-static experiments, the material fractured before either of the mechanical limits discussed in Sec. 3.2 were reached. As such, all the quasi-static data plotted in this chapter will be until the specimen failed.

Figures 6.23 and 6.24 show some data from quasi-static compression tests on poled
samples of PZT 95/5 at both elevated and sub-zero temperatures respectively. The sample thicknesses ranged from ~0.8 mm to ~4.3 mm, resulting in aspect ratios of 0.2 - 1. (Note In Sec. 4.6 it was recommended that the lowest aspect ratio that should be used in these experiments was 0.25). It can be seen that, regardless of temperature, very thin samples, i.e. those of aspect ratio 0.2, appear to support unusually high stresses and strains as compared to samples of all other thicknesses.

In addition, decreasing the thickness of the sample, from an aspect ratio of 1 down to an aspect ratio of 0.5, we see that the strain supported by the samples increases; however, there is no clear stress dependence on the sample thickness.

Next, drop-weight impact tests, using a mass of 60.81 g, were carried out on samples with aspect ratios between 0.4 - 1.0. The samples were impacted at ~3.7 m s$^{-1}$.

Figure 6.25 shows the stress-strain relationships of standard, poled, PZT samples of varying thicknesses, and therefore aspect ratios, when impacted at the same velocity. It can be observed that all the samples reach comparable stresses (between 250 - 275 MPa) at comparable strains (~0.025), but that samples of decreasing aspect ratio support increasing strain, as seen in samples under quasi-static compression. In addition, the release of the stress is more rapid as the aspect ratios of the samples increase. Despite these observable differences in the stress-release behaviour of the samples, aspect ratio does not appear to affect the peak stress-strain behaviour at these loading conditions.

Further increasing the strain rate, Split Hopkinson Pressure Bar experiments were carried out on poled PZT 95/5 samples of varying thicknesses. The specimens were subjected to impact velocities between 3.5 - 10.5 m s$^{-1}$, resulting in strain rates as high as ~10$^4$ s$^{-1}$.

Figures 6.26 and 6.27 show the stress-strain behaviour of standard, poled PZT samples of varying thicknesses, and therefore aspect ratios, at two different Split Hopkinson
Figure 6.25: Stress-strain data from drop-weight experiments on standard, poled PZT 95/5, of varying aspect ratios, and at an impact velocity $\sim 3.7 \text{ m s}^{-1}$.

Figure 6.26: Stress-strain results for poled, standard PZT (varying aspect ratios), at firing pressures $\sim 0.25 \text{ bar}$ and impact velocities $\sim 3.7 \text{ m s}^{-1}$.

As seen at all lower loading rates, as the aspect ratio is increased, the strain accommodated decreases. In addition, as seen previously, all the peak stresses before failure are comparable for each loading rate, and thus independent of aspect ratio.

This is true across all loading rates, except for samples with the lowest aspect ratio of 0.2. As seen under quasi-static compression, samples with an aspect ratio of 0.2 display a higher apparent stress than expected, an example of which is shown in figure 6.28.

Thus, it has been observed that, regardless of applied loading rate (and indeed temperature), very thin samples, i.e. those of aspect ratio 0.2, appear to support unusually high strains as compared to samples of all other thicknesses.

The reasons for these apparent high stresses and strains in the thinnest samples have been discussed in detail in Sec. 4.5. Friction at the interfaces between the material specimen and the rigid platens causes the ends of a thin sample to be constrained against free expansion, creating a state of non-uniform triaxial stress in the specimen, and resulting in an increase of the apparent axial stiffness of the specimen. In addition, confinement effects are responsible for the increased ability of a sample to support strain (see Sec. 4.5).

This validates the claim made in Sec. 4.6 that the smallest aspect ratios should be no lower than 0.25. As such, data taken from PZT samples of the lowest thickness will be disregarded from now on, and not used to draw conclusions on the electromechanical behaviour of PZT 95/5.
Figure 6.27: Stress-strain results for poled, standard PZT (varying aspect ratios), at firing pressures \( \sim 1.00 \) bar and impact velocities \( \sim 9.4 \) m s\(^{-1}\).

Figure 6.28: Stress-strain results for poled, standard PZT (varying aspect ratios), at firing pressures \( \sim 0.75 \) bar and impact velocities \( \sim 8.0 \) m s\(^{-1}\).

6.5 Strain Rate Effects on the Mechanical Behaviour of PZT 95/5

Quasi-static compression rates between 0.001 - 0.004 mm s\(^{-1}\) were adopted, resulting in strain rates as low as \( 10^{-4} \) s\(^{-1}\).

Figure 6.29: Quasi-static compression results for standard, unpoled PZT 95/5 (aspect ratio: 0.7) at +20°C.

Figure 6.30: Quasi-static compression results for porous, unpoled PZT 95/5 (aspect ratio: 0.7) at +20°C.

Figure 6.29 shows some results from quasi-static compression experiments on unpoled samples of standard PZT 95/5. As the compression rate was increased, the PZT samples consistently displayed a higher modulus. In addition, as the compression rate was reduced, a higher strain was supported by the PZT samples but a lower stress. This trend is also observed in the unpoled porous PZT 95/5 samples, as shown in figure 6.30.
Next, using drop-weight loading, poled, standard PZT samples of aspect ratio 1 (diameter = thickness = 4.3 mm) were impacted with a mass of 60.81 g from different impact heights (between 40 and 80 cm), resulting in impact velocities between 2.8 and 4.0 m s$^{-1}$ and strain rates between 650 and 930 s$^{-1}$.

Figure 6.31 shows that the stress-strain modulus behaviour is comparable regardless of impact velocity, and the decrease in stress with strain after peak stress is also analogous. However, as to be expected, the peak stress which the samples reach is increased with increasing impact velocity, as well as the supported strain.

Figure 6.31: Stress-strain data from drop-weight experiments, from different heights, on standard, poled PZT (aspect ratio: 1); strain rates between 650 - 930 s$^{-1}$.

Further increasing the strain rate, Split Hopkinson Pressure Bar experiments were carried out on poled, standard PZT 95/5 samples. The specimens were subjected to impact velocities between 3.5 - 10.5 m s$^{-1}$, resulting in strain rates as high as $\sim 10^4$ s$^{-1}$.

The dataset in figure 6.32 is from compression experiments carried out on poled, standard, PZT 95/5 samples of aspect ratio 0.25 (other examples are available in Appendix C). The stress-strain behaviour highlights the increase in peak stress with increasing strain rate, as well as an increase in the strain to failure, and this was true for all the aspect ratios above and including 0.25.

Failure of brittle materials is generally due to the generation, dynamic growth, and then coalescence, of compression-induced tensile micro-cracks. Experimental observations seem to indicate that a sample’s compressive failure stress, and the resulting fragment sizes, depends on the applied strain rate, as well as the stress state [187].

Tensile micro-cracks are observed to nucleate at pre-existing defects, such as grain boundaries and cavities, where a local tensile field is generated by inhomogeneous local deformation of the material in the vicinity of the defects. Compression failure is then due to the unstable growth of these compression-induced tension cracks. It has been shown...
that these compression-induced tension cracks grow at limited speeds in the direction of maximum overall compression [186].

Due to rate effects, these cracks can continue to grow even after unloading. Hence, crack coalescence may also occur during unloading, in which case the failure stress at crack coalescence is smaller than the failure stress when the load continues to increase at its initial rate [187].

Thus, in order to understand the observed change in the compressive failure stress with increasing strain rate, one must consider the interaction between these tension cracks.

The orientation of micro-flaws and wing-cracks within brittle materials is generally random, and changes in their spacing can affect the growth of cracks. If the spacing between the wing-cracks is very large, interaction between them will be negligible. These tension cracks will cease to grow soon after unloading begins. As this flaw spacing is reduced, the tension cracks will grow faster, and therefore be larger. Decreasing interactions between the tension cracks means fewer micro-cracks will coalesce, resulting in a much higher failure stress. This is especially significant at the lowest strain rates [187].

It has been seen that the maximum flaw spacing generally increases with increasing flaw size. However, during high strain rate loadings, this maximum flaw spacing first increases, but then decreases, with increasing flaw size. This reduction is due to material inertia during crack growth. In addition, it has been shown that the crack length decreases as the frictional resistance of pre-existing micro-flaws on tension crack growth increases [186].

As the spacing between micro-flaws is increased, the failure stress increases with a decreasing strain rate. Increasing the size of the micro-flaws results in the failure stress decreasing at low strain rates, and increasing at high strain rates. The observed decrease at low strain rates is due to the decrease of the fracture toughness as the length of the flaw is increased. On the other hand, the increase at high strain rates is mainly due to material inertia effects during crack growth. This material inertia during crack growth can prevent larger flaws from coalescing under high strain rate loadings, depending on the spacings between the flaws [187].

At the higher strain rates, the growth of compression-induced tension cracks is restrained by the presence of lateral confinement. In addition, the maximum flaw spacing decreases with increasing lateral confinement. Thus, the overall axial failure stress is increased, and the fragment size decreased [187].
6.6 Porosity Effects on the Mechanical Behaviour of PZT 95/5

Quasi-static compression rates between 0.001 - 0.004 mm s\(^{-1}\) were adopted, resulting in strain rates as low as \(10^{-4}\) s\(^{-1}\), on both standard and porous samples of PZT 95/5. In addition, drop-weight impact tests were carried out at ambient temperature and humidity. The impact mass used in these experiments was \(\sim 7\) kg, and the impact velocity 5 m s\(^{-1}\).

![Figure 6.33: Quasi-static compression results for unpoled PZT 95/5 (aspect ratio: 0.7) at +20°C.](image)

![Figure 6.34: Stress-time results from drop-weight experiments on PZT 95/5 (aspect ratio: 0.7); impact mass 7 kg, velocity 5 m s\(^{-1}\).](image)

As can be seen from figure 6.33, the modulus displayed at each compression rate was comparable for both the standard and the porous PZT samples, but the porous PZT samples completely and consistently failed at a lower strain, and lower stress, than the standard PZT samples.

Increasing the loading rate using drop-weight impacts resulted in both the standard and porous samples experiencing higher stresses but lower strains than observed in the quasi-static experiments (see figure 6.34). In addition, the differences in the yield stress observed between the standard and the porous PZT samples was lower than seen in the results from the quasi-static experiments.

The peak stresses reached within the porous samples was consistently lower than those experienced by the more dense, standard PZT samples, regardless of loading rate. This is to be expected, as an increase in porosity decreases the amount of stress a ceramic specimen is able to support (see Sec. 2.5.1).

Having established that aspect ratio did not affect the peak stress-strain behaviour under the smaller drop-weight loading conditions (see Sec. 6.4), these next experiments were carried out to determine the effect of varying porosity on the mechanical behaviour of PZT. Both standard and porous PZT were subjected to the same impact loading
conditions. In this case, the impact mass was 112.82 g and the drop height 70 cm, resulting in impact velocities of $\sim$3.7 m s$^{-1}$.

Figures 6.35 and 6.36 both show that the PZT samples, regardless of sample porosity, support comparable stresses. In addition, it is shown that, as the aspect ratio of both standard and porous samples decreases, the strain supported is increased, and the rate of release of the stress in the sample is decreased, as shown from other experiments (described in Sec. 6.4).

Further increasing the strain rate, Split Hopkinson Pressure Bar experiments were carried out on both unpoled and poled, standard and porous PZT 95/5 samples. The specimens were subjected to impact velocities between 3.5 - 10.5 m s$^{-1}$, resulting in strain rates as high as $\sim 10^4$ s$^{-1}$.

The stress-strain behaviour demonstrated in figure 6.37 highlights the increase in peak stress with increasing strain rate, as expected (see Sec. 6.5), regardless of porosity of the unpoled samples. The more porous PZT samples appear to fail at shorter strains as compared with their more dense equivalents, although the peak stresses before failure are comparable. This is also shown for the poled PZT samples, regardless of aspect ratio or impact rate, an example of which is given in figure 6.38.

Stable pore collapse is often observed during static compression of porous, brittle materials. This is perhaps the reason for the observed differences in peak stress before fracture observed in the quasi-static regime [189]. Indeed, it has been found that more porous materials exhibit lower fracture toughness at low strain rates [12].

Under higher loading rates however, it is far more likely that the pores will act as stress concentrators, not collapsing but rather promoting axial crack nucleation. This in turn would result in anomalously large tensile strains, coincident with failure, resulting in the shorter strains to failure observed under the dynamic loading rates [189].
For the most part, the effect of porosity does not appear to be significant in the compressive stress-strain behaviour of PZT 95/5. However, the increase in porosity is only $\sim 7\%$. As such, it is difficult to make conclusive statements about the overall behaviour of less dense ceramics, and further tests on a wider range of porosities are needed.

## 6.7 Temperature Effects on the Mechanical Behaviour of PZT 95/5

The temperature effects on both poled and unpoled samples of standard and porous PZT (of varying thicknesses) at $-20^\circ$C, $+20^\circ$C, and $+80^\circ$C were studied, under both quasi-static loading and Split Hopkinson Pressure Bar rates.

Figure 6.39 shows some results from quasi-static compression experiments on unpoled samples of both standard and porous PZT 95/5, at a compression rate of 0.004 mm s$^{-1}$, and at both ambient ($+20^\circ$C) and elevated ($+80^\circ$C) temperatures.

As can be seen, the modulus at each temperature is comparable for the standard and the porous samples, but is clearly affected by temperature. Increasing the temperature decreases the modulus values, but appreciably increases the strain supported by the samples, as seen by others [190]. In addition, heating significantly increases the stress supported by the porous samples, but decreases that supported by the standard samples. As such, the difference in the stress at failure was significantly larger at room temperature than at the higher temperature.

Whilst the standard, non-porous PZT shows complete failure at an engineering strain of $\sim 0.32$, some initial cracking was observed from an engineering strain of $\sim 0.23$. Some cracking was indeed heard from this point, however the standard, non-porous PZT was...
still able to withstand further stress until complete failure of the specimen at $\sim 550$ MPa.

Figure 6.40 plots a number of data sets across aspect ratios and temperatures, at a compression rate of 0.001 mm s$^{-1}$. It is clear that increasing the aspect ratio of the standard poled PZT sample increases the value of the stress-strain modulus, as well as decreasing the strain at which the sample fails, as described earlier (see Sec. 6.4). The modulus values are comparable across the temperature range for each aspect ratio, and samples of each aspect ratio generally fail within a strain range of $\sim 0.03$ of each other, although at different stresses.

Samples at elevated temperatures were least able to support high stresses, and samples that were cooled to sub-zero temperatures were generally able to support the highest stresses.

Increasing the applied loading rate, using the Split Hopkinson Pressure Bar, standard and porous poled PZT samples of diameters 4.3 - 4.8 mm were subjected to firing pressures between 0.25 - 1.0 bar using an Inconel 718 striker bar of length 22.8 cm. This resulted in impact velocities between 3 - 12 m s$^{-1}$, and strain rates between the orders of $10^2$ - $10^4$ s$^{-1}$. Temperatures again ranged between $-20^\circ\text{C}$ - $+80^\circ\text{C}$.

Figure 6.41 shows some stress-strain data for samples of poled, standard PZT 95/5 (aspect ratio: 1), subjected to firing pressures $\sim 0.25$ bar. Samples at room temperature were able to support the largest stresses, whilst both heating and cooling reduced the ability of the specimens to accommodate comparable stresses. Indeed this was seen for most of the standard PZT samples, regardless of applied loading rate or aspect ratio, see Appendix C.

On analysing the stress-time behaviour of PZT samples subjected to strain rates between 5000 - 6000 s$^{-1}$ at different temperatures (see figure 6.42), we see that, at room
temperature, peak stress is reached at a similar time and that the overall stress-time behaviour is comparable. In addition, as compared to samples exposed to non-ambient temperatures, the peak stresses reached are relatively high. At elevated temperatures at these strain rates, the peak stress experienced is almost halved as compared to at room temperature. Furthermore, there is now more variability with regards to the time that the peak stress is reached, but the overall profiles are still comparable. Contrasting this with the stress-time behaviour at sub-zero temperatures, we see a much larger variation in both the time to peak stress, as well as the value of the peak stress itself. It appears that exposure to extreme temperature conditions negatively affects the ability of the PZT ceramic to bear high stresses at these higher strain rates.

In addition, it was seen that as the applied loading rates were increased on samples with...
the same aspect ratio, and across all the temperatures, the difference in the peak stresses reached at room temperature to those reached at extreme temperatures was increased. An example of this is shown in figures 6.43 and 6.44, which show the stress-strain behaviour of poled, standard, PZT samples of aspect ratio 0.5, at firing pressures of 0.5 bar and 1.0 bar respectively.

Although earlier experiments suggested that the level of porosity present in this PZT material does not significantly affect the mechanical behaviour of the ceramic under applied loading (see Sec. 6.6), subjecting the samples to extreme temperature environments appears to induce a large variation in the peak stress-strain behaviour of the more porous samples. Figures 6.45 and 6.46 show stress-strain data from porous and standard samples respectively. The samples were of the same aspect ratio and subjected to the same applied loading rates. It is seen that there is more scatter in the peak stress behaviour in the porous samples across the different loading rates as compared with the standard samples.

Study of the dynamic fracture of ceramics at extreme temperatures is still in its early days. Indeed, literature on impact studies of ceramics, which are designed for use in heat engines(!), is limited to testing at room temperature. This is primarily due to the lack of suitable testing procedures for both sub-zero and elevated temperatures [109].

It has been seen that ceramics exhibit cleavage fracture at both room temperature and elevated temperatures [109]. The research presented here shows that the piezoelectric ceramic 95/5 also fractures at sub-zero temperatures, and that the failure stress is reduced at both low and high temperatures, as compared with those observed at room temperature.

It is well-known that ceramics are rigid and brittle, as they are incapable of noticeable plastic deformation (see Sec. 2.5.0.1). However, their properties depend on both temperature and on the amount of crystallinity, since crystalline and non-crystalline phases behave differently at different temperatures. At the highest temperatures, crystalline

![Figure 6.45: Stress-strain data for poled, porous PZT (aspect ratio: 0.6) at two different strain rates, across all temperatures.](image)

![Figure 6.46: Stress-strain data for poled, standard PZT (aspect ratio: 0.6) at two different strain rates, across all temperatures.](image)
phases continue to be brittle, but non-crystalline phases are ductile. In addition, the plastic deformation of ceramic materials by diffusional creep is significant at temperatures close to their melting point, where the rate of diffusion is high [191].

Plastic deformation of crystalline solids occurs by the movement of lattice dislocations and/or diffusional creep. Materials with immobile lattice dislocations are brittle at low temperatures. Indeed, at low temperatures, both crystalline and non-crystalline phases are brittle. Lower temperatures and higher crystallinity content tend to increase the modulus and the brittleness of ceramics. Crystalline materials at room temperature can stiffen on cooling, absorbing less energy. This reduction in energy can result in the contraction of materials, widening cracks and other defects, which can then become critical starting points for failure [191].

An increase in the temperature of a material can lead to mechanical instability and the localisation of deformation [158]. In addition, the motion of domains within the polycrystalline material with temperature can induce internal stresses. This is especially true after samples have been electrically poled, since the anisotropic thermal strain from both linear expansion and transformational strains is greater [192].

It has been reported that an increase in the test temperature leads to an increase in the creep deformation rate under the same applied stress level [49][96]. Increasing the temperature of a brittle material decreases its strength [9]. In addition, the elastic constants of many piezocrystals, as well as the ultimate strength of many brittle materials, generally decrease slowly as the temperature is increased [63][112]. It has also been found that increasing the applied temperature decreases the fracture initiation toughness values, and that the compressive strength of ceramics varies with temperature [109]. All this is most probably because, as the temperature is increased, so too is the rate of crack growth [94].

6.8 Poling Effects on the Mechanical Behaviour of PZT 95/5

Compression rates of 0.001 mm s$^{-1}$ were adopted, resulting in strain rates as low as $10^{-4}$ s$^{-1}$. In addition, temperature effects on both poled and unpoled samples of standard and porous PZT at $-20^\circ$C, $+20^\circ$C, and $+80^\circ$C were studied.

Figure 6.47 shows some results from quasi-static compression experiments on unpoled and poled samples of standard PZT, at a temperature of $+20^\circ$C. The experiments were carried out on samples of a similar thickness ($\sim$3 mm), which experienced a comparable strain rate of $\sim$0.0003 s$^{-1}$.

As can be seen, the stresses at which the samples fractured completely were comparable, between 355 - 370 MPa; however, the poled sample failed at almost half the
Comparing unpoled and poled standard PZT under the same loading conditions, (in figure 6.48, where samples had an aspect ratio of 0.5, and were at +80°C), it can be seen that the modulus is comparable, but the unpoled sample is able to support a slightly higher stress as compared with the poled sample.

Further increasing the strain rate, Split Hopkinson Pressure Bar experiments were carried out on unpoled and poled, standard PZT 95/5 samples. The specimens were subjected to firing pressures between 0.25 - 0.75 bar, resulting in strain rates of the order of $\sim 10^3$ s$^{-1}$.

Figure 6.49 shows the stress-time behaviour of unpoled and poled, standard PZT samples at two different firing pressures. As the firing pressure was increased, and thus the impact velocity and the resulting strain rates, there was an increase in the peak stress experienced by the samples. In addition, as was observed at the lower quasi-static and drop-weight loading rates, the unpoled samples were able to support higher stresses than the poled samples, though the amount of strain accommodated was comparable.

These observations are possibly due to an increase in defects within the poled samples, which could have been generated as a result of the extra preparation they underwent, as compared to the unpoled samples. In addition, the motion of domains within the polycrystalline material during poling can induce internal stresses [185][192].
Figure 6.49: Stress-time data for unpoled and poled, standard PZT at two different firing pressures.

Figure 6.50: Normalised voltage-time data from drop-weight (impact mass 112.82 g) experiments on standard, unpoled and poled PZT 95/5, at an impact velocity \( \sim 3.7 \text{ m s}^{-1} \).

6.9 Electromechanical Behaviour of PZT 95/5

Figure 6.51: Normalised voltage-time data from drop-weight (impact mass 70 g) experiments on standard, poled PZT 95/5, of varying aspect ratios, and at an impact velocity \( \sim 3.7 \text{ m s}^{-1} \).

Figure 6.52: Normalised voltage-time data from drop-weight (impact mass 112.82 g) experiments on standard and porous poled PZT 95/5, impact velocities \( \sim 3.7 \text{ m s}^{-1} \).

Compression of poled PZT 95/5 piezoelectric ceramics results in a measurable voltage output, see Sec. 2.1.1. Unpoled samples are unable to produce any detectable voltage, as shown in figure 6.50. This is because there is no preferred orientation for the ferroelectric domains, and hence no net polarisation change upon mechanical deformation [188].

Having seen that the mechanical behaviour is generally consistent for samples of identical geometric shapes under the same drop-weight loading conditions, as well as for samples that remain intact after impact and are then re-compressed (see Sec. 6.3), it was
then of interest to see what the voltage output behaviour was for samples (both porous and standard) subjected to the same loading rates but having different aspect ratios, i.e. changing the thickness of the samples but keeping their diameters the same. In order for better comparison, the voltages were normalised with respect to the varying sample thicknesses, i.e. the data plotted in figures 6.51 and 6.52 shows the voltage output per mm thickness of the samples, whilst the respective labels indicate the initial aspect ratio of the sample.

As shown in figure 6.51, the voltage output behaviour under drop-weight loading appears quite variable. Although the duration of the peak voltage pulse is comparable in time, as to be expected due to all the samples being loaded at the same velocity, there are considerable differences in the peak voltage output. Indeed, the average peak voltage has a value of $12.49 \pm 7.70$ V. This, as alluded to in Sec. 6.3, could be due to variability of domain alignment within each sample during poling.

Increasing the impact mass, and therefore the stress experienced by the samples, results in an increase in the peak voltage output, see figure 6.52. Despite the comparable stresses experienced by both standard and porous PZT samples under drop-weight loading (see Sec. 6.6), the standard PZT samples give a noticeably higher peak voltage output than the porous samples. The variation in the peak voltage outputs is lower at these higher stresses; the average peak voltage output by the standard samples was $43.10 \pm 4.13$ V, whilst that from the more porous samples was $19.83 \pm 7.58$ V.
Figure 6.53 gives an example of some raw voltage-time data obtained during a Split Hopkinson Pressure Bar experiment on a standard, poled PZT sample of diameter 4.3 mm and thickness 3.3 mm, at +80°C. As can be seen from the Output Bar voltage curve, very little stress was transmitted. The Piezo Voltage curve demonstrates a peak voltage of \( \sim 70 \) V upon initial compression; this curve decreases as the sample fractures.

To assess the effect of strain rate on the stress experienced by standard PZT samples, as well as the charge output, samples were all taken from one billet (see Sec. 6.1), and several impact tests were carried out at ambient temperature. In addition, these experiments allowed the differences of using brass shim or Inconel 718 as electrodes to be evaluated.

Figures 6.54 and 6.55 show stress-strain data obtained from Split Hopkinson Pressure Bar experiments on standard, poled PZT 95/5 at room temperature, using brass shim and Inconel 718 electrodes respectively in order to collect the piezoelectric voltage output upon compression from the PZT samples.

Using brass shim electrodes significantly decreases the amount of strain experienced by the PZT samples as compared to using Inconel 718 slices, but increases the amount of stress supported by the sandwiched samples. Increasing the strain rate whilst using brass shim electrodes results in a noticeable increase in the stress and strain accommodated by the samples, whilst using Inconel 718 electrodes only appears to affect the strain experienced by the PZT samples; the stresses experienced by samples sandwiched by Inconel 718 electrodes were not spread as widely as those reached within samples in-between the brass shim electrodes. Indeed, the range of stresses for those with Inconel 718 were all between 250 - 350 MPa, whilst those with brass shim were between a much larger range of 150 - 800 MPa.

Increasing the strain rate applied to the samples, as well as increasing the stress
experienced, increased the voltage output by the samples, an example of which is shown in figure 6.56. Unfortunately, as these were the first experiments to be carried out on poled PZT samples using the Split Hopkinson Pressure Bar, the oscilloscope settings to use in order to successfully obtain full voltage output-time graphs were not known. As such, for some of the samples, some of the peak voltage data was actually lost - this is shown by plateaus where there should be some form of peak.

Figure 6.57 shows an example of total charge output over strain. This highlights that the samples experienced higher strains at higher strain rates. It also shows that, although higher strain rates resulted in higher peak voltages, the pulses were shorter in duration as compared with the peak voltages at lower strain rates, so a lower amount of charge was actually released overall.

Following on from experiments into the degradation behaviour of PZT (see Sec. 6.3.1), Split Hopkinson Pressure Bar experiments were carried out on samples which had survived intact from drop-weight loading impacts, in order to determine how the voltage output and stress supported at these higher strain rates would compare with those attained at relatively lower strain rates. The electrodes used here were still of brass shim.

Figures 6.58 and 6.59 show, respectively, the stress-strain and voltage-time data from experiments on the Split Hopkinson Pressure Bar on various poled samples recovered from earlier drop-weight experiments. It is seen that both the stresses reached and the output voltages are significantly reduced as compared with those shown earlier in this section, from fresh, previously un-impacted samples. This is most possibly due to the development of crack defects within the samples, as well as depolarisation of the samples, during the drop-weight impacts, and implies that the charge flows observed during those drop-weight impact tests were as a result of impact depoling as opposed to a simple potential being...
developed across the samples (see Sec. 2.1.3.1).

Finally, in order to determine whether the overall electromechanical behaviour of poled standard and porous PZT was dependent on loading conditions, PZT samples of diameters 4.3 - 4.8 mm were subjected to firing pressures between 0.25 - 1.0 bar using an Inconel 718 striker bar of length 22.8 cm. This resulted in impact velocities between 3 - 12 m s$^{-1}$, and strain rates between the orders of $10^2$ - $10^4$ s$^{-1}$. Temperatures ranged between $-20^{\circ}C$ - $+80^{\circ}C$.

Inconel 718 was decided to be used as the electrode for the piezoelectric voltage-measurement temperature experiments, as brass shim deformed very easily and needed to be replaced between each compression test, whereas Inconel 718 was more resistant to deformation and could be repeatedly used for multiple loading experiments.

Upon analysing the voltage-time behaviour of these poled PZT samples, the first thing to observe is that some samples which had been poled did not appear to produce any recordable voltages. This is most possibly due to some form of breakdown within the sample during poling.

Increasing the applied strain rate, regardless of temperature, increases the peak stress, as described already (see Sec. 6.5). This is reflected in the voltage output - higher strain rates yield higher voltages, as demonstrated in figures 6.60 and 6.61. In addition, at room temperature, the peak voltage is generally reached sooner in time at higher strain rates when compared with lower strain rates.

Although there is a significant amount of variation in the observed peak voltages when the samples are subjected to different temperatures, both increasing and decreasing the applied temperatures results in an overall decrease in the output voltages, as shown in figures 6.62 and 6.63.
Comparing the behaviour of porous PZT with that of standard, denser PZT, at all temperatures, it appears that the overall voltage output behaviour is not directly dependent on the porosity of the samples, as shown in figures 6.64 and 6.65. However, upon focusing on just the peak voltage output, it is possible to observe a lower output from the more porous PZT samples (see Sec. 6.10). It is now deemed instructive to look at the overall electromechanical behaviour of the PZT 95/5, and discuss how the peak stresses and peak voltage outputs vary with strain rate, porosity, and temperature.
6.10 Discussion

Figure 6.66 shows the increase in peak strain before failure for Split Hopkinson Pressure Bar experiments on PZT with applied strain rate. Regardless of density, temperature, or polarisation, there is a linear relationship between increasing the strain rate and increasing the strain at which the samples fail. This figure also demonstrates the significant scatter observed across all the datasets, which is to be expected since failure in ceramics is known to vary widely [1].

Indeed, as described in Sec. 6.3, Weibull moduli for these datasets was calculated across all the compression rates. It was found that increasing the loading rate resulted in lower values for the Weibull modulus, indicating an increase in the scatter and randomness of the observed strength values. This behaviour has been reported by others [184]. Overall,
the values of the Weibull moduli were found to vary between 2 - 30 for the compression data described here. These values compare well with those presented in the available literature, which report values between 10 - 20 for ceramics [184].

Figure 6.67 demonstrates, for drop-weight impact experiments on poled PZT 95/5 at room temperature, that, as the applied strain rate is increased, the peak stress supported by the samples before failure also increases. This behaviour was seen across all loading rates, regardless of porosity, temperature, or polarisation. Peak strengths of PZT 95/5 were found to increase with increasing strain rate. For geometrically identical specimens, it was found that peak stresses at strain rates of $10^{-4} \text{s}^{-1}$ were approximately 470 MPa, whilst increasing the applied strain rates to $10^{4} \text{s}^{-1}$ resulted in peak stresses $\sim$650 MPa. This corresponds to about a 38% increase in strength with the eight-orders-of-magnitude increase in strain rate. Compressive strength values of 558 MPa at strain rates of $10^{-4} \text{s}^{-1}$, and 663 MPa at strain rates of $10^{-2} \text{s}^{-1}$, of niobium-doped PZT ceramics have previously been reported [13].

Another example of this increase in strength with strain rate is given in figure 6.68. In addition, this figure indicates that there is no clear difference between the mechanical behaviour of the porous samples and the standard PZT samples at the highest strain rates, achieved with Split Hopkinson Pressure Bar experiments.

![Figure 6.68: Failure stress vs strain rate for unpoled PZT under Split Hopkinson Pressure Bar compressive conditions (+20°C).](image1)

![Figure 6.69: Failure stress vs strain rate for unpoled PZT under quasi-static loading.](image2)

However, as shown in figure 6.69, at the lowest applied compression rates, achieved using quasi-static loading, there are noticeable differences between the peak stresses reached in the porous and the standard PZT samples. The more porous samples consistently failed at a lower stress (and indeed a lower strain) than the more dense samples, regardless of temperature.

It is well-known that fracture is rate-sensitive in all materials. The effective fracture properties depend on void formation, and crack growth rate and link-up, which are all
determined by loading rate. This is due to the fact that the rupture of interatomic and intermolecular bonds is a thermally activated process. In addition, the mechanical behaviour of porous materials is controlled by shear instabilities developing along planes of high pore content [193].

The strength of brittle materials has been seen to increase with an increase in the loading rate. Increasing the time to peak load, i.e. decreasing the loading rate, causes a shift towards higher brittleness in the material. The fracture toughness tends to decrease with an increase in time, resulting in a reduction in the strength of the material as the applied loading rate is reduced [193].

It is thus believed that the effect of loading time on fracture is analogous to the effect of extremely high temperature. Higher temperatures result in high creep behaviour of brittle materials, and the contribution of creep also becomes significant at the lowest loading rates [185][193]. In addition, stable pore collapse is often observed during static compression of porous, brittle materials [189]. This is perhaps the reason for the noticeably lower failure stresses observed in the more porous PZT samples in the quasi-static regime.

The lack of an obvious difference (see figure 6.70) between the failure stresses of the porous and standard PZT samples at the highest rates is also not wholly unexpected, once the expected variation in brittle material behaviour at high strain rates is taken into account, and noting that the difference in porosity is actually only $\sim 7\%$. Others have also found this to be the case, though the porosity of their samples varied by $\sim 4\%$ [72].

![Figure 6.70: Failure stress vs strain rate for PZT under Split Hopkinson Pressure Bar compressive conditions.](image)

![Figure 6.71: Peak voltage output vs strain rate for poled PZT under Split Hopkinson Pressure Bar compressive conditions.](image)

Increasing the strain rate not only increases the peak stress reached in the samples, as well as the strain accommodated, for both poled and unpoled samples across all the temperatures, it also has the effect of increasing the voltage output from poled PZT samples, as shown in figure 6.71 for the highest compressive rates.

This effect is unsurprising, since the voltage output of a piezoelectric material is di-
directly dependent on the applied stress (see Sec. 2.1.3). When a non-centrosymmetric piezoelectric crystal is compressed or stretched, the ions in each unit cell are displaced, causing electric polarisation of the unit cell. Because of the material’s regular crystalline structure, the dipole moment appears in every unit cell in the crystal and the effects accumulate, resulting in the appearance of an electric potential across certain faces of the crystal. This pressure-generated electric charge is exactly proportional to the force acting on the crystal, and is measured in pico-coulombs (pC) [21][27]. For room temperature Split Hopkinson Pressure Bar experiments, it was found that applying stresses up to \( \sim 800 \) MPa resulted in peak voltages up to \( \sim 180 \) V. This generally linear increase fits well with values reported by others, who found that applying stresses between 600 - 4600 MPa on normally poled PZT 95/5 resulted in peak voltages between 30 - 3700 V [53].

Figure 6.72: Peak voltage output vs peak stress for poled, porous PZT under drop-weight loading at +20 \(^\circ\)C.

Figure 6.73: Peak voltage output vs peak stress for poled PZT under Split Hopkinson Pressure Bar compressive conditions.

This stress-dependence of the voltage output behaviour is clearly demonstrated for drop-weight impacts in figure 6.72, and more generally in figure 6.73 for Split Hopkinson Pressure Bar loading conditions. However, at these higher rates, we also see more spread across the data. This can be explained by the fact that ceramics are not identical on a microstructural level. Upon poling (see Sec. 2.1.3), all the domains within the samples might not have been completely aligned, whilst some domains may switch back to their initial states after the poling field is removed, leading to the observable differences in voltage output [185].

Subjecting PZT samples to variations in temperature affects their mechanical behaviour. Figure 6.74 shows the failure stress against the failure strain for standard samples of PZT across the full experimental temperature range. Despite the scatter, it is clear that both heating and cooling lead to a decrease in the stress supported by the samples. In addition, the failure of samples subjected to non-ambient temperatures was more catastrophic. This was highlighted when material was collected after the experiments. It
was seen that the mass of the ceramics that was able to be recovered after the elevated temperature and sub-zero experiments was $\sim 50\%$ of the material that was able to be recovered after room temperature experiments.

In addition, since the voltage output behaviour of poled PZT ceramics is dependent on the applied loading rate, and therefore the stresses supported by the samples, there is an observable decrease ($\sim 25\%$) in the voltages output by ceramics subjected to non-ambient temperature conditions, as shown in figure 6.75. Other authors have observed reductions in the voltage-stress behaviour of between 10 - 50% when heating and cooling PZT ceramics of different compositions to temperatures between $-150^\circ C$ and $+85^\circ C$ [7][16].

This is further highlighted in figures 6.76 and 6.77, which show, overall, lower peak

![Figure 6.74](image1.png)  
Figure 6.74: Failure stress-strain behaviour for poled, standard PZT under Split Hopkinson Pressure Bar compressive conditions.

![Figure 6.75](image2.png)  
Figure 6.75: Peak voltage output vs peak stress for poled, standard PZT under Split Hopkinson Pressure Bar compressive conditions.

![Figure 6.76](image3.png)  
Figure 6.76: Peak voltages observed across a range of strain rates, for poled PZT under Split Hopkinson Pressure Bar compressive conditions, at $-20^\circ C$.

![Figure 6.77](image4.png)  
Figure 6.77: Peak voltages observed across a range of strain rates, for poled PZT under Split Hopkinson Pressure Bar compressive conditions, at $+20^\circ C$. 

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voltages reached at the same strain rates upon cooling. In addition, the effect of porosity, whilst not appearing significant on the mechanical strength of the PZT specimens at the highest strain rates, is, however, observed to reduce the voltage output from PZT samples. This is to be expected, since the increase in porosity leads to a reduction in the volume fraction of the active piezoelectric ceramic phase [69], and has been observed by others [72].

The peak voltage outputs shown in figures 6.76 and 6.77 are lower for the porous samples as compared with the more dense samples, when being subjected to the same strain rates, although this difference is greater at room temperature than at sub-zero (and indeed elevated) temperatures. Since peak voltage output is dependent on strain rate and therefore peak stress, we can compare this with the differences in the stresses at failure observed between the porous and standard PZT samples during quasi-static loading, which were also significantly larger at room temperature than at higher temperatures (see Sec. 6.7).

Thus it appears that, overall, both the failure strength and voltage output behaviour of PZT are predominantly dependent on strain rate. The effect of porosity is significantly important on the mechanical behaviour of PZT samples at the lowest strain rates, and noticeably important on their voltage output at the higher rates. Extreme temperatures affect the strength of PZT samples across all compression rates.

6.11 Summary of the Electromechanical Behaviour of PZT 95/5

This chapter describes results from a large number of strain rate experiments conducted across a range of temperatures, on both poled and unpoled PZT 95/5 samples of two different densities.

The mechanical behaviour of PZT 95/5 was seen to have significant temperature and strain rate dependence. The failure stress was quite variable, sample to sample, as often found within brittle materials. It was also seen that significant processing decreased the strain to failure behaviour of the ceramic samples. This is most probably due to an increase in the defects within the samples, as well as the generation of extra internal stresses due to the movement of domains within the samples upon poling.

Increasing the strain rate increased the peak stress reached in the samples, as well as the strain accommodated, and this was true for both poled and unpoled samples across all temperatures studied. In addition, increasing the strain rate, and thus the peak stress, had the effect of increasing the voltage output, as well as decreasing the time at which the peak voltage was reached. This was again true across all temperatures.

If, after a compressive experiment, a sample was able to be recovered, it was seen to
support comparable levels of stress, though its charge output behaviour was degraded. This can be most attributed to the sample being damaged during loading, though this could be confirmed through further studies on the comparison between the released charge density and the remnant polarisation.

At the lowest loading rates, porous samples were less able to support stress than their standard counterparts whilst, at the highest strain rates, there were no clear differences between the standard and the porous samples with regards to their mechanical behaviour. However, at these higher strain rates, the effect of porosity was visible as a decrease in the peak voltages recorded across all temperatures as compared with the more dense PZT samples.

At the lowest compression rates, samples at elevated temperatures failed at lower stresses, whilst samples at sub-zero temperatures were able to reach higher stresses. However, at the highest strain rates, exposing the poled PZT samples to non-ambient temperatures completely reduced their ability to support stress.

In addition, Digital Image Correlation was carried out in conjunction with some Split Hopkinson Pressure Bar experiments. It was seen to be an effective method for mapping strain concentrations and fracture propagations through the ceramic samples.

Overall, it was seen that both the failure strength and voltage output behaviour of PZT are predominantly dependent on applied strain rate. Extreme temperatures affect the strength of PZT samples across all compression rates, whilst the effect of porosity is important on the mechanical behaviour of PZT samples at the lowest strain rates, and on their voltage output behaviour at the higher compression rates.
And that was Our argument which We gave Abraham against his people. We raise by degrees whom We will. Indeed, your Lord is Wise and Knowing.

Chapter 7

Conclusions

The predominant aim of this research was to obtain a better understanding of both the mechanical behaviour of the piezoelectric ceramic PZT 95/5, as well as its voltage output, when the material was subjected to a range of strain rates and temperatures. In addition, since, when PZT 95/5 is used in its various industrial applications, it is often coated with a sacrificial polymer, the mechanical behaviour of a number of polymers currently used in these industries at similar strain rates and temperatures was also studied.

To this end, a number of different projects were undertaken. The range of strain rates examined, between $10^{-4}$ - $10^4$ s$^{-1}$, were achieved using quasi-static compression, drop-weight towers, and Split Hopkinson Pressure Bars. Purpose-built environmental chambers were used to attain a range of temperatures between $-20^\circ$C and $+80^\circ$C. The stress-strain relationships obtained were compared and discussed.

7.1 Aspect Ratio Compression Effects

In order to establish the ideal specimen geometry to use under the desired applied loading rates, research was conducted on the effect of varying the thickness of samples of well-characterised materials. As such, polycarbonate 1000, aluminium 5083, copper 101, and titanium (Ti-6Al-4V) samples were chosen, of diameter $\sim$4 mm, and thicknesses varying between 1 - 12 mm, resulting in aspect ratios (length-to-diameter $l/d$) of 0.25 - 3.

Buckling was observed in the most slender specimens ($l/d > 1.8$) at the lowest strain rates, whilst the specimens with the lowest aspect ratios ($l/d < 0.25$) experienced the most variation in the initial peak stresses reached and the applied strains. This can be understood in terms of both the inertial and frictional forces experienced by the specimens.

Increasing the aspect ratio increases the time taken for a sample to reach stress equilibrium. However, if a sample is too short, it will suffer from inertial and frictional confinement, as well as errors in strain calculations due to end effects. Conversely, if a sample is too long, it will buckle.
For short, stubby samples, friction dominates the deformation, often resulting in a barrel shaped specimen. By lubricating the ends with a thin layer of grease, these frictional effects can be minimised. However, even when great care is taken to eliminate friction, the use of relatively short specimens will introduce an apparent increase in stress very similar to reported strain rate effects.

Thus, for experimental strain rates between $10^{-4}$ - $10^{4}$ s$^{-1}$, aspect ratios should be no lower than 0.25, and no higher than 1.5, in order that the observed stress-strain behaviour is consistent, repeatable, and coherent.

### 7.2 Polymers: Strain Rate and Temperature Effects

A number of experiments were carried out on four different polymers: Scotchcast 8, Stycast 1090, Mix M173, and Mix M207F. Investigations on these polymers enabled the design and evaluation of a number of different methods for cooling and heating samples prior to compression experiments. In addition, the piezoelectric ceramic PZT 95/5, when used as a component in an application, is often coated in a protective, sacrificial, layer of polymer, so it was important to understand the different types of polymers which exist and are currently used in these products.

For quasi-static compression testing, the temperature of the samples was controlled by use of a thermostatically-controlled environmental chamber, which encompassed both the steel column adapters and the sample mounted in-between the compression platens between the steel rods. Cold gas from a liquid nitrogen steel container was pumped through the enviro-chamber to achieve sub-zero temperatures, and the enviro-chamber had an in-built forced convection heating system, allowing higher temperatures to be attained.

A number of different heat exchange systems were developed to achieve the different (both high and low) temperatures required for the Split Hopkinson Pressure Bar experiments. The systems could achieve temperatures between the range of $-100^\circ$C and $+100^\circ$C.

Due to difficulties in securing liquid nitrogen regularly, two different systems needed to be devised for achieving sub-zero temperatures. The first involved cooling of the test specimens in-situ, with the sample held between the input and output bars. A chamber was built such that it fitted around the sample and the ends of the input and output bars, without impeding the movement of the bars. Gas from a Cryolab 20 liquid nitrogen dewar was passed through the enviro-chamber and around the sample, cooling it down. The entire chamber had been designed so that it could be securely mounted on a rail carriage, allowing for complete alignment with the rest of the SHPB system.

Perspex windows were added to the chamber, to enable use of high-speed imaging, which could then be used to further study dynamic compression and failure modes. This
setup also allowed for sample recovery for post-experimental analyses, such as scanning electron microscopy studies.

The second system, to be used when liquid nitrogen was unavailable, employed dry ice, but the specimens had to be cooled before being placed in the cooled SHPB system. A polystyrene box was filled with dry ice. A contraption was set up 1 cm above the dry ice, where preliminary experiments had shown the temperature of the air was at $-20^\circ$C. The samples were held for 20 minutes, as reasoned in Sec. 3, before being placed in the system, which itself was cooled down using pellets of dry ice to ensure that the sample would not heat up upon contact.

Both methods achieve the desired temperatures, but the liquid nitrogen cooling method is preferable as a greater degree of control can be exercised over the gas flow and in ensuring the samples are evenly cooled. Additionally, even lower temperatures can be reached if desired.

For achieving elevated temperatures, two different setups were also used. For the relatively lower temperatures of $+45^\circ$C, a 125 W ceramic band heater (connected to a thermostatic controller) was placed, non-contacting, on the ends of the input and output bars around the specimen sample. However, this system was found to be too inefficient for achieving higher temperatures as, despite the temperature rating of $+150^\circ$C on the ceramic band heater, it was not found to achieve much higher temperatures than $+50^\circ$C.

Therefore, a system making use of a heating plate and a hot air blower was devised. To achieve temperatures of $+80^\circ$C and heat the samples evenly, they were first placed on a heating plate at $+80^\circ$C for 20 minutes, being turned every five minutes to ensure thermal equilibrium throughout the sample. The sample was then transferred quickly to the nearby Split Hopkinson Pressure Bar system, whose ends were being heated by a hot air blower, positioned at 30 cm above the sample. Though this system was effective in attaining the desired temperatures, it required rapid transfer of the sample from one place to another, which is not ideal as samples can fall during movement. In addition, the hot air is not contained, so the risk of exposure to high heat is great. Finally, for some samples, there was a difference in temperature of $\sim1^\circ$C across the material closest to and furthest from the hot air blower.

An improved heating system is thus suggested, to contain flow of hot air around the sample in-situ and ensure an even heating of the sample, see figure 7.1. The enviro-chamber used for liquid nitrogen cooling of samples can be used for heating the samples in a similar manner. Helium gas will be passed through a copper coil placed in a pyrex beaker. The pyrex beaker is filled with oil, and placed on a heating plate, which will heat the oil, and therefore the gas, to the required temperature. The gas is then passed through the enviro-chamber which is positioned around the ends of the input and output bars of the Split Hopkinson Pressure Bar system, between which the sample is sandwiched. The sample is again held for 20 minutes, to ensure that it has reached thermal equilibrium.
Figure 7.1: Proposed enviro-chamber for achieving high temperatures using a Split Hopkinson Pressure Bar.

In addition, by regulating the gas flow, a wider range of temperatures will be able to be reached, as well as intermediate ones. A similar setup has been used by others [163].

In addition, in order to achieve full confidence in future tests, it is recommended that the use of thin film thermocouples be assessed for use with elevated Split Hopkinson Pressure Bar studies. Equally, such diagnostic technology may provide a greater degree of confidence in the data obtained from sub-zero temperature studies with the Split Hopkinson Pressure Bar system.

From the different loading experiments carried out on the various epoxies, it was observed that the mechanical behaviour of the pure epoxies was significantly different to the loaded epoxies. The epoxy containing alumina filler was able to accommodate the largest amounts of stress, and the syntactic foam the least, with the material strength of the pure epoxies comparable to each other and somewhere in-between the loaded epoxies. Moreover, the pure epoxies were able to accommodate a much greater degree of strain than the loaded epoxies.

In addition, the ability of the loaded epoxies to support large stresses was less affected by temperature and strain rate as compared with the pure epoxies. However, the material behaviour of the pure epoxy M173 was less dependent on the geometric size of the sample as compared with the epoxy containing alumina filler.

High-speed images taken from the drop-weight impact experiments showed the different modes of failure for the epoxy encapsulants. The pure epoxies failed predominantly due to linear crack formation, while the loaded epoxies experienced shear banding at 45°.
Finally, the time-temperature superposition principle was applied to the collected data to show that glass ($\alpha$) and $\beta$ transitions were the cause of the bilinear dependence of yield stress on strain rate of the materials.

### 7.3 Temperature and Strain Rate Effects on the Piezoelectric Ceramic PZT 95/5

In order to determine the strain rate, temperature, and porosity effects on unpoled and poled PZT 95/5 samples, a range of compression loading experiments were conducted. This research is important since, although ceramics such as PZT are used in extreme temperature environments, very little data exists on their electromechanical properties under these conditions. Much of the available literature focuses on single crystals or piezoelectric films, whilst the PZT used here was in its bulk form. Not only was the effect of porosity considered, but the ceramic was undoped PZT 95/5; most of the research by previous authors in this field has been performed on doped PZT materials, or on those close to the tetragonal-rhombohedral boundary, such as PZT 52/48.

The mechanical behaviour of PZT 95/5 was seen to have significant temperature and strain rate dependence. The failure stress was quite variable, sample to sample, as often found within brittle materials. It was also seen that significant processing decreased the strain to failure behaviour of the ceramic samples. This is most probably due to an increase in the defects within the samples due to specimen processing, as well as the generation of extra internal stresses due to the movement of domains within the samples upon poling.

Increasing the strain rate increased the peak stress reached in the samples, as well as the strain accommodated, and this was found to be true for both poled and unpoled samples across all the temperatures studied. In addition, increasing the strain rate, and thus the peak stress, had the effect of increasing the voltage output, as well as decreasing the time at which the peak voltage was reached. This was again true across all temperatures.

If, after a compressive experiment, a sample was able to be recovered, it was seen to support comparable levels of stress, though its charge output behaviour was degraded. This can be most attributed to the sample being damaged during loading, though this could be confirmed through further studies on the comparison between the released charge density and the remnant polarisation.

At the lowest loading rates, porous samples were less able to support stress than their standard counterparts whilst, at the highest strain rates, there were no clear differences between the standard and the porous samples with regards to their mechanical behaviour. However, at these higher strain rates, the effect of porosity was visible as a decrease in
the peak voltages recorded across all temperatures as compared with the more dense PZT samples.

At the lowest compression rates, samples at elevated temperatures failed at lower stresses, whilst samples at sub-zero temperatures were able to reach higher stresses. However, at the highest strain rates, exposing the poled PZT samples to non-ambient temperatures completely reduced their ability to support stress.

In addition, Digital Image Correlation was carried out in conjunction with some Split Hopkinson Pressure Bar experiments. It was seen to be an effective method for mapping strain concentrations and fracture propagations through the ceramic samples.

Overall, it was seen that both the failure strength and voltage output behaviour of PZT are predominantly dependent on applied strain rate. Extreme temperatures affect the strength of PZT samples across all compression rates, whilst the effect of porosity is important on the mechanical behaviour of PZT samples at the lowest strain rates, and on their voltage output behaviour at the higher strain rates.

Although several trends have been identified through this research, PZT is, in nature, a ceramic. Therefore its mechanical behaviour is highly variable, and significant sample processing further affects it. Failure in ceramics varies widely, and is often dominated by initiation. It is hoped that this research will go some way in improving the understanding of the electromechanical behaviour of the piezoelectric ceramic PZT 95/5, providing a significant, valuable, data source for others to compare and contrast both their experimental and simulated results.

In addition to employing the heating technique described above to ensure confidence in the attained temperatures, it is recommended that future research focus on a wider range of applied temperatures and porosities of PZT 95/5, coupled with some modelling. Use of an LCR meter to identify the electrical properties of PZT 95/5 specimens as functions of frequency, which can then be compared to the mechanical properties obtained from compression experiments, will further complement this research.
Bibliography


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Appendices
Appendix A

Chapter 4: Aspect Ratio Effects

The drop-weight sequences from experiments carried out on polycarbonate, aluminium, copper and aluminium have been synchronised with their respective stress-time data graphs. It is thus possible to determine the stress being experienced by the sample at different times during loading.

A.1 Polycarbonate

Figure A.1: Drop-weight sequence showing the compressive behaviour of a polycarbonate cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s\(^{-1}\)).
Figure A.2: Stress-time data for a polycarbonate cylinder with aspect ratio 1 during a drop-weight impact (see figure A.1).

Figure A.3: Stress-time data for a polycarbonate cylinder with aspect ratio 1.8 during a drop-weight impact (see figure A.4).

Figure A.4: Buckling in a polycarbonate cylinder, aspect ratio 1.8 (diameter = 4 mm, height = 7.2 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s\(^{-1}\)).

A.2 Aluminium

Figure A.5: Drop-weight sequence showing the compressive behaviour of an aluminium cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass ∼7 kg, impact velocity ∼3 m s\(^{-1}\)).
Figure A.6: Stress-time data for an aluminium cylinder with aspect ratio 1 during a drop-weight impact (see figure A.5).

Figure A.7: Stress-time data for an aluminium cylinder with aspect ratio 3 during a drop-weight impact (see figure A.8).

Figure A.8: Buckling in an aluminium cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass \( \sim 7 \) kg, impact velocity \( \sim 3 \) m s\(^{-1} \)).

### A.3 Copper
Figure A.9: Drop-weight sequence showing the compressive behaviour of a copper cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass $\sim$7 kg, impact velocity $\sim$3 m s$^{-1}$).

Figure A.10: Stress-time data for a copper cylinder with aspect ratio 1 during a drop-weight impact (see figure A.9).

Figure A.11: Stress-time data for a copper cylinder with aspect ratio 3 during a drop-weight impact (see figure A.12).

A.4 Titanium
Figure A.12: Buckling in a copper cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass $\sim 7$ kg, impact velocity $\sim 3$ m s$^{-1}$).

Figure A.13: Drop-weight sequence showing the compressive behaviour of a titanium cylinder, aspect ratio 1 (diameter = height = 4 mm), during impact (mass $\sim 7$ kg, impact velocity $\sim 3$ m s$^{-1}$).

Figure A.14: Stress-time data for a titanium cylinder with aspect ratio 1 during a drop-weight impact (see figure A.13).

Figure A.15: Stress-time data for a titanium cylinder with aspect ratio 3 during a drop-weight impact (see figure A.16).
Figure A.16: Drop-weight sequence showing the compressive behaviour of a titanium cylinder, aspect ratio 3 (diameter = 4 mm, height = 12 mm), during impact (mass $\sim$7 kg, impact velocity $\sim$3 m s$^{-1}$).
Appendix B

Chapter 5: Polymers

Each loading test was repeated three times in order to attempt to account for variability introduced by different material casts, examples of which are shown in the following figures (B.1 B.2 B.3 and B.4).

Figure B.1: Split Hopkinson Pressure Bar data for Scotchcast 8 (aspect ratio 0.6; height = 3 mm, diameter = 5 mm) at a temperature of +20°C, impact velocity ~6.8 m s$^{-1}$ and strain rate ~2270 s$^{-1}$.

Figure B.2: Split Hopkinson Pressure Bar data for Scotchcast 8 (aspect ratio 0.6; height = 3 mm, diameter = 5 mm) at a temperature of +20°C, impact velocity ~8.7 m s$^{-1}$ and strain rate ~2900 s$^{-1}$.
Figure B.3: Split Hopkinson Pressure Bar data for Scotchcast 8 (aspect ratio 0.6; height = 3 mm, diameter = 5 mm) at a temperature of +20°C, impact velocity $\sim$10 m s$^{-1}$ and strain rate $\sim$3330 s$^{-1}$.

Figure B.4: Split Hopkinson Pressure Bar data for Scotchcast 8 (aspect ratio 0.6; height = 3 mm, diameter = 5 mm) at a temperature of +20°C, impact velocity $\sim$11.5 m s$^{-1}$ and strain rate $\sim$3830 s$^{-1}$.

Figure B.5: Stress-time data for Mix M173, at impact velocities of $\sim$4 m s$^{-1}$.

Figure B.6: Stress-time data for Mix M173, at impact velocities of $\sim$6 m s$^{-1}$.
Figure B.7: Stress-time data for Mix M173, at impact velocities of $\sim7.8$ m s$^{-1}$.

Figure B.8: Stress-time data for Mix M173, at impact velocities of $\sim9$ m s$^{-1}$.

Figure B.9: Stress-time data for Mix M207F, at impact velocities of $\sim4$ m s$^{-1}$.

Figure B.10: Stress-time data for Mix M207F, at impact velocities of $\sim6$ m s$^{-1}$.

Figure B.11: Stress-time data for Mix M207F, at impact velocities of $\sim7.8$ m s$^{-1}$.

Figure B.12: Stress-time data for Mix M207F, at impact velocities of $\sim9$ m s$^{-1}$.
Figure B.13: Stress-strain data for Mix M173, at impact velocities of $\sim 4 \text{ m s}^{-1}$.

Figure B.14: Stress-strain data for Mix M173, at impact velocities of $\sim 6 \text{ m s}^{-1}$. 
Figure B.15: Stress-strain data for Mix M173, at impact velocities of $\sim 7.8$ m s$^{-1}$.

Figure B.16: Stress-strain data for Mix M173, at impact velocities of $\sim 9$ m s$^{-1}$.

Figure B.17: Stress-strain data for Mix M207F, at impact velocities of $\sim 4$ m s$^{-1}$.

Figure B.18: Stress-strain data for Mix M207F, at impact velocities of $\sim 6$ m s$^{-1}$.
Figure B.19: Stress-strain data for Mix M207F, at impact velocities of \( \sim 7.8 \text{ m s}^{-1} \).

Figure B.20: Stress-strain data for Mix M207F, at impact velocities of \( \sim 9 \text{ m s}^{-1} \).
Appendix C

Chapter 6: PZT 95/5

C.1 Variability in Ceramic Behaviour

Figure C.1: Stress-strain data for standard, unpoled, square samples of PZT 95/5 (aspect ratio: 0.70), at +20°C and a compression rate of 0.003 mm s\(^{-1}\) (Weibull modulus: \(~53\)).

Figure C.2: Stress-strain data for standard, unpoled, square samples of PZT 95/5 (aspect ratio: 0.70), at +20°C and a compression rate of 0.004 mm s\(^{-1}\) (Weibull modulus: \(~15\)).
C.2 Degradation Behaviour of Poled PZT

Figure C.3: Quasi-static compression results for standard PZT 95/5 at 0.001 mm s$^{-1}$ and +20°C.

Figure C.4: Stress-strain data from drop-weight experiments on standard, poled samples of PZT 95/5 (aspect ratio: 1), at +20°C and strain rates of $\sim$860 s$^{-1}$ (Weibull modulus: $\sim$35).
Figure C.5: Stress-strain data from drop-weight experiments on standard, poled samples of PZT 95/5 (aspect ratio: 1), at +20 °C and strain rates of $\sim 930 \text{ s}^{-1}$ (Weibull modulus: $\sim 184$).

Figure C.6: Stress-time data for unpoled standard and porous PZT at strain rates between 2000 - 2500 s$^{-1}$.

C.3 Aspect Ratio and Strain Rate Effects
C.4 Strain Rate Effects

Figures C.17 and C.18 show stress-strain data obtained at room temperature at differing strain rates on both standard and porous PZT. As the strain rate is increased, it is clear that much higher strains are supported, and much higher stresses are reached within the samples. However, there is no clear difference between the mechanical behaviour of standard and porous samples.
Figure C.11: Voltage-stress data from drop-weight experiments on standard, poled PZT, aspect ratio 1 (diameter = thickness = 4.3); strain rates $\sim 470 \text{ s}^{-1}$.

C.5 Porosity Effects

Figure C.12: Stress-strain data from drop-weight experiments on standard, poled PZT, aspect ratio 1 (diameter = thickness = 4.3), strain rates $\sim 470 \text{ s}^{-1}$.
C.6 Temperature Effects

As shown in figure C.23, for samples impacted at similar strain rates, the stress-time behaviour is quite consistent, for porous and standard samples.
Figure C.17: Stress-strain data for poled PZT at comparatively low strain rates, at +20°C.

Figure C.18: Stress-strain data for poled PZT at very high strain rates, at +20°C.

Figure C.19: Stress-strain for poled standard and porous PZT (aspect ratio: 0.50) at impact velocities ~3.7 s⁻¹.

Figure C.20: Stress-strain for poled standard and porous PZT (aspect ratio: 0.70) at impact velocities ~6.1 s⁻¹.
Figure C.21: Stress-strain for poled standard and porous PZT (aspect ratio: 0.50) at impact velocities \(\sim 7.8 \text{ s}^{-1}\).

Figure C.22: Quasi-static compression results for poled PZT 95/5 (aspect ratio: 0.2) at 0.001 mm s\(^{-1}\), across a temperature range of 100 °C.

Figure C.23: Stress-time data for poled PZT for strain rates between 5000 - 6000 s\(^{-1}\), at +20 °C.

Figure C.24: Stress-time data for poled PZT at strain rates between 5000 - 6000 s\(^{-1}\), and at +80 °C.
Figure C.25: Stress-time data for poled PZT at strain rates between 5000 - 6000 s\(^{-1}\), and at \(-20^\circ\text{C}\).

Figure C.26: Stress-strain data for poled, standard PZT (aspect ratio: 0.7) at strain rates \(\sim6280\) s\(^{-1}\) across all temperatures.

Figure C.27: Stress-strain data for poled, standard PZT (aspect ratio: 0.5) at strain rates \(\sim9260\) s\(^{-1}\) across all temperatures.

Figure C.28: Stress-strain data for poled, standard PZT (aspect ratio: 0.25) at strain rates \(\sim16710\) s\(^{-1}\) across all temperatures.

Figure C.29: Stress-strain data for poled PZT at very high strain rates, and at \(-20^\circ\text{C}\).

Figure C.30: Stress-strain data for poled PZT at very high strain rates, and at \(+80^\circ\text{C}\).
Figure C.31: Stress-strain data for poled PZT at comparatively lower strain rates, and $-20^\circ$C.

Figure C.32: Stress-strain data for poled PZT at comparatively lower strain rates, and $+80^\circ$C.

Figure C.33: Stress-strain data for poled PZT at impact velocities $\sim 3.7$ s$^{-1}$, and $-20^\circ$C.

Figure C.34: Stress-strain data for poled PZT at impact velocities $\sim 3.7$ s$^{-1}$, and $+20^\circ$C.
Figure C.35: Stress-strain data for poled PZT at impact velocities \( \sim 3.7 \text{ s}^{-1} \), and \( +80^\circ \text{C} \).

Figure C.36: Stress-strain data for poled PZT at impact velocities \( \sim 6.1 \text{ s}^{-1} \), and \( -20^\circ \text{C} \).

Figure C.37: Stress-strain data for poled PZT at impact velocities \( \sim 6.1 \text{ s}^{-1} \), and \( +20^\circ \text{C} \).

Figure C.38: Stress-strain data for poled PZT at impact velocities \( \sim 6.1 \text{ s}^{-1} \), and \( +80^\circ \text{C} \).
Figure C.39: Stress-strain data for poled PZT at impact velocities $\sim 7.8 \text{ s}^{-1}$, and $-20^\circ\text{C}$.

Figure C.40: Stress-strain data for poled PZT at impact velocities $\sim 7.8 \text{ s}^{-1}$, and $+20^\circ\text{C}$.

Figure C.41: Stress-strain data for poled PZT at impact velocities $\sim 7.8 \text{ s}^{-1}$, and $+80^\circ\text{C}$.

Figure C.42: Stress-strain data for poled PZT at impact velocities $\sim 9.3 \text{ s}^{-1}$, and $-20^\circ\text{C}$.
Figure C.43: Stress-strain data for poled PZT at impact velocities $\sim 9.3 \text{ s}^{-1}$, and $+20^\circ\text{C}$.

Figure C.44: Stress-strain data for poled PZT at impact velocities $\sim 9.3 \text{ s}^{-1}$, and $+80^\circ\text{C}$.

Figure C.45: Stress-strain data for poled PZT across varying strain rates, and at $+20^\circ\text{C}$.

Figure C.46: Stress-time data for poled PZT across varying strain rates, and at $+80^\circ\text{C}$.
Figure C.47: Stress-strain data for poled PZT across varying strain rates, and at $-20^\circ$C.

Figure C.48: Voltage-time data for poled PZT across varying strain rates, and at $-20^\circ$C.