XPS studies of Surface Ageing and Discharge Processes in Polymeric Insulators

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The ageing of polymer insulation occurs under long-term exposure to high electric fields and has attracted research due its relevance to high voltage insulation. In this work, polymers that have been electrically aged via a number of methods have been investigated using X-ray photoelectron spectroscopy (XPS). Despite some use in the investigation of outdoor insulation surfaces, XPS has not been used for investigations of polymer bulk electrical ageing before now. The first XPS measurements, using both small spot analysis and XPS imaging, are presented from the exposed inner surfaces of electrically aged artificial voids and electrical breakdown channels, as well as corona discharge aged surfaces and spark discharge by-products. XPS is shown to be a valuable technique for the investigation of polymer electrical ageing. Investigations into breakdown channels are supported by data acquired using X-ray photoemission electron microscopy (XPEEM) and scanning electron microscopy (SEM).

Results show that the chemistry present at these surfaces takes the form of significant oxidation over a wide area with localised production of graphitic carbon. C-O-, C=O, and O-C=O species are detected in all cases. It is found that similar ageing products are present regardless of the ageing process or material investigated. However, the level of oxidation and relative ratio of the species seen with XPS is shown to be highly dependant on oxygen availability. Greater intensity of carbon oxides, and a shift towards highly oxidised species, is observed when there is more oxygen in the system. XPS imaging of breakdown channels reveals that high concentrations of oxidised components form on the outer edges of the channel, with graphitic carbon forming in the central regions. In addition, evidence for degradation is seen to extend at least 300 µm from channels in XPS imaging and at least ~650 µm in XPS line scans.

Variation with the applied discharge energy was investigated for breakdown channels and spark discharge ageing. Evidence is seen for an energy dependence on the breakdown products, with higher energies producing relatively higher graphitic carbon and reduced oxidation products. Further, the relationship between the applied voltage and graphitic carbon concentration suggests an activated process with an energy barrier before graphitic carbon formation starts.

XPS observations are supported by confocal Raman microprobe spectroscopy (CRMS) results from artificial voids and electrical breakdown channels, which identify graphitic carbon on a fluorescent background as the main features. XPS data indicate oxidised species are the origin of the fluorescence seen and provides quantitative information on the levels, chemical states and spatial distribution of these species and of graphitic carbon.
Declaration

I, Patrick Lunt, declare that:

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Publications

Publications that have been made over the course of the Ph.D:


1. Introduction

High Voltage (HV) power transmission is of great importance in the efficient delivery of electricity across long distances. The UK national grid is made up of approximately 4500 miles of overhead lines and 420 miles of underground cables [1]. The industry relies on high quality, reliable and durable electrical insulation. In recent years, insulators are more frequently being created from composite polymeric materials as opposed to traditional ceramic, glass (for outdoor overhead power lines), oil or paper (for HV cabling) due to their favourable properties and low cost of manufacture [2]. However, polymers are more susceptible to chemical reactions and so are more vulnerable to long-term degradation. Failure of HV insulation in service can cause power outages and while such events are rare, it is of vital importance that insulators can be assessed during operation so they can be replaced without incident if they are deemed at risk of failure. Accurate assessment of the state of insulation requires a good understanding of the processes that lead to failure in order to develop effective techniques for diagnostics. As such, a considerable amount of research has been done on the properties and response to ageing [3-5] of composite polymer insulators. There is also much ongoing research into improving the materials with the aim of improving their reliability and useful lifetimes. Despite this there are still many unknowns in the field of electrical ageing, particularly in terms of the mechanisms behind ageing processes and the chemical changes that occur. This work aims to advance the knowledge in this area.

1.1 Electronic structure of insulators

Electrical insulators are distinguished from conductors by the availability of delocalized electrons for conduction. Allowed electron energy states in a periodic lattice potential, such as that in a crystalline solid, form distinct continuous bands with forbidden ‘band gaps’ between them. Electrons fill bands from the bottom. At $T = 0$ K the lowest filled state forms the top of the valence band with empty states forming the conduction band. Solids with partially filled bands (or in some cases bands which overlap) have many energy states
available to them at thermal energies, allowing for easy promotion to the empty states and thus allowing conduction to occur; such solids are metals. Solids with filled bands require enough thermal energy to excite electrons across the band gap for conduction to occur, the size of the band gap determines whether materials are semiconductors or insulators as shown in figure 1.1.

![Figure 1.1](image)

Figure 1.1. The size of the band gap, $E_g$, determines the conducting properties of a solid material. Adapted from [6]

The electrical properties of polymers are more complex as they do not have a strictly ordered crystalline lattice structure. A polymer consists of long chains of repeating identical molecular units, called a monomer, linked by covalent bonds. Available charge carriers can move along the ‘backbone’ of the chain and the band structures described in figure 1.1 are applicable in the sense of a polymer chain being a 1-dimensional crystal. In a saturated polymer chain all available electrons are tightly held in $\sigma$ bonds, rendering them electrically insulating. Separate chains are held together by Van Der Waals forces or by cross linking, where side branches form covalent bonds between chains. Charge transfer between chains requires a quantum tunneling process. In practice, the polymer chains are not perfect 1-dimensional crystals. Lattice irregularities, additives, impurities or chemical species intrinsic to the polymer lead to departures from the predicted band structure. Additional energy states may be present slightly below the conduction band or slightly above the valence band, known as trap states, depicted in figure 1.2. Traps may have energies distributed over several eV and are usually classified as ‘shallow’ or ‘deep’. For electron traps in
polyethylene (PE; a semi-crystalline polymer with chemical formula (-CH₂CH₂-)ₙ) deep traps (up to 1.5 eV below the conduction band) have been associated with low concentrations of chemical states and shallow traps (<0.3 eV below the conduction band) with a high concentration of lattice defects [7]. Deep traps are generally associated with the long-term trapping of charge whereas shallow traps may contribute to conduction effects [8].

![Diagram of band structure](image)

**Figure 1.2** Representation of the density of trapping states in the band structure of an insulating polymer. [8].

Charge that is injected into a dielectric is known as space charge. Because of the low conduction in insulators this charge may persist for a long time. This charge dissipates eventually due to drifting of the charge carriers to the electrodes or recombination with oppositely charged carriers. Deep traps may maintain space charge for even longer. The effects of space charge upon electrical treeing in insulation are discussed in section 1.3.

Carbon forms the backbone of most polymers with hydrogen, oxygen and nitrogen being among the most common additional elements. Often, additives or ‘filler’ materials are added during production to introduce various useful properties. Polymers may form crystalline or amorphous structures or, more commonly, a mixture of the two. Crystallinity in flexible polymers is a result of ‘lamella’ structures – polymer chains tightly back folded many times to form
blocks with the chain axis (parallel to the polymer backbone) perpendicular to the long axis of the lamella as shown in figure 1.3. In some cases polymers may contain spherulites, regions where many lamella regions branch radially outwards from a nucleation centre with amorphous material in the spaces between them. Changes in manufacturing conditions, such as temperature and the ratios of filler materials or the constituent monomers, can result in considerable variation in the macroscopic properties.

![Figure 1.3. Polymer chain folds in a crystalline lamella. Adapted from [9].](image)

1.2 Surface ageing

The properties of a polymer change over a period of time. A number of complex processes involving physical and chemical degradation contribute to this change, collectively termed ‘ageing’. Outdoor insulators are exposed in service to long-term environmental weathering and electrical stress. This form of degradation lends itself well to investigation by surface sensitive techniques such as X-ray Photoelectron Spectroscopy (XPS) [10-12], Fourier Transform Infra-Red (FTIR) [10, 11, 13-15] and Scanning Electron Microscopy (SEM) [11, 12] as it is generally limited to the outer surface of the material, with bulk properties largely unaffected. Investigation into the processes involved in degradation may lead to improvements to material manufacture and development of diagnostic techniques for evaluating the condition of insulators in service and predicting continued lifetimes.

An important property of outdoor insulation is hydrophobicity – the ability of a material to repel water. Chemical reactions resulting in the formation of oxygen-
containing functional groups on the surface are responsible for reducing hydrophobicity. Water accumulating on the surface can lead to arcing and flashovers (electrical discharges across the surface of an insulator under a high applied voltage) causing unexpected power outages and further damage to the insulator. Insulators investigated in service [10-16] show degradation from a combination of processes brought about by varying conditions of electrical stress, local contamination levels and material formulation.

Differences in the structure and chemical composition of insulating materials lead to variable responses to ageing. Two common polymeric insulators in use for outdoor HV applications are silicone rubber and EPDM (ethylene propylene diene monomer). EPDM is made from three monomers, ethylene, propylene and an unconjugated diene. Silicone rubbers are most often made using polydimethylsiloxane (PDMS) as the base polymer with a number of ‘filler’ materials added to improve properties such as tensile strength. PDMS contains an inorganic siloxane backbone of alternating Si-O atoms with organic methyl pendant groups. Common fillers include aluminium hydroxide (usually referred to as ATH), calcium carbonate and silica [17].

A visual asymmetry has been reported [10, 15, 16] in the degradation of outdoor insulation made from EPDM depending on which side of the insulator had more exposure to sunlight during service. Investigation showed that this asymmetry also manifests as greater surface damage and hydrophobicity reduction in sunlight exposed regions. This suggests that photo-oxidation plays an important role in the surface ageing of EPDM. This is attributed to UV radiation as although it is not sufficiently energetic to break C-H and C-C bonds, UV absorption has been associated with chromophoric impurities in the polymer [18]. UV exposure then causes the formation of highly reactive radicals, with subsequent chemical reactions in the presence of air resulting in a high degree of oxidation and chain scissions. XPS studies of EPDM under artificial weathering conditions [19-22] have shown that degradation proceeds predominantly by the oxidation of C-H bonds into hydroxyl and carbonyl groups and chain scissions resulting in loss of hydrophobicity and surface erosion. An example of a study of EPDM before and after 30 days of UV exposure is shown in figure 1.4. Changes in chemistry are attributed to the evolution of C-O-C and
C=O species. Studies of PDMS under accelerated UV conditions using FTIR and Raman have shown a limited oxidation of methyl groups tendency towards increased cross linking leading to increased surface hardness [23-25]. Studies with XPS concentrate on the silicon content and show the appearance of silica-like products [26, 27].

Figure 1.4. XPS spectra of the C 1s peak of EPDM exposed to corona discharge. a – unaged. b – aged for 30 days with UV radiation. New peaks are shown in b, attributed to C-O-C and C=O. Adapted from [22].

PDMS displays hydrophobic recovery over time. It is generally accepted that the dominant mechanism is due to the presence of low molecular weight oligomers that migrate to the surface, burying oxidised groups [28]. Toth et al. solvent extracted PDMS and characterised these oligomers by gas chromatography [29]. This was composed of predominantly cyclic dimethylsiloxane oligomers and some linear silicone oil components. They then showed by comparison to non-extracted PDMS that hydrophobic recovery after plasma treatment was significantly reduced. It has also been noted that the energy of rotation of the methyl groups about the backbone in PDMS is very low, allowing for reorientation to further bury oxidised groups [30]. It has been noted that electrical trees grown in silicone rubber may ‘degenerate’ during periods of non-growth [31], reducing the width and length of channels, possibly due to this mechanism allowing the diffusion of oligomers to fill the channel.

Corona discharge is a surface degradation phenomenon that occurs in regions with highly divergent electric fields such as that at a narrow needle tip electrode. Water droplets on hydrophobic surfaces may form with a small radius of
curvature and are sufficiently conducting to induce corona discharge on HV insulators [32]. Free electrons are accelerated to high energies causing excitation and impact ionisation of the molecules in the air surrounding the discharge region, generating more electrons, ions and photons, forming a hot plasma around the source of the high electric field. The generation and subsequent acceleration of more electrons causes a cascade effect known as a Townsend avalanche. Corona discharge subjects the surface to impact ionisation, generates UV radiation and produces chemicals such as ozone and nitrous acids [33]. This causes erosion and chemical degradation of the insulator surface. The energy involved is enough to cause breaking of chemical bonds. XPS and FTIR studies reveal a high degree of oxidation via the formation of polar groups C-OH, C=O and O-C=O [33-37]. In the case of silicone rubber this causes the formation of a brittle silica-like layer on the surface [28, 29, 35]. This layer reduces the rate of hydrophobic recovery, while cracks in the layer accelerate recovery [38], providing evidence that the recovery is caused by migration of low molecular weight components either intrinsic to the material or produced by the corona.

1.3 Electrical treeing

In addition to the external surface ageing of an insulator, degradation can occur within the bulk. This ageing is most commonly associated with partial discharges (PD) which occur in gas filled voids within insulation. These voids may be present in the polymer as a result of manufacturing conditions, physical and electrical stresses on the material [3, 39] or at the imperfect interface with another material, e.g. a metal-insulator contact [40]. A PD is an electrical discharge over only a portion of the insulator, such as a void, as shown in figure 1.5. PD activity occurs because while the applied electric field across the insulation is insufficient to cause a discharge in the polymer insulation itself, the electrical permittivity of the gas in the void is lower than that of the insulation and the electric field across the void may exceed the breakdown voltage of the gas. Like in corona discharge, partial discharges accelerate free electrons across the gap causing Townsend avalanches. These avalanches deposit charges (either electrons or ions) on the void walls, in such a way that they
reduce the electric field inside, stopping the discharge. These deposited charges affect the magnitude of subsequent discharges and the number of electrons available for the following discharge [41].

PDs across a gap such as a void or channel are governed by Paschen’s law, which states that under a uniform electric field the breakdown voltage \( V_b \) is dependant on the product of the size of the gap, \( d \), and the density of the gas, \( \rho \), i.e. \( V_b = f(d\rho) \). A Paschen curve for air is shown in figure 1.6. The formation of a discharge requires the ionization of gas molecules in order to form an avalanche of charged particles. For this to occur, the electron mean free path must be long enough for electrons to gain sufficient kinetic energy for ionization but no longer than the size of the gap. As such, there exists a minimum \( V_b \) at a certain \( \rho \) for a fixed gap size, with \( V_b \) rapidly increasing at higher and lower \( \rho \). The energy involved in partial discharges causes an increase in the local temperature in the void/channel, increasing the gas density and therefore, by Paschen’s law, \( V_b \) also increases until the discharge can no longer be sustained. The combination of these effects leads to physical and chemical erosion of the void in the direction of the applied field due to ion bombardment and the production of reactive chemicals in the gas.
The phenomenon of electrical treeing is commonly seen as a cause of electrical breakdown in polymeric insulators subject to a high electric field. Electrical trees are small, dendritic structures which form from impurities or voids in the polymer. The initiation of an electrical tree is associated with an inception time before which a void may grow to sufficient size to support PD activity. PDs then cause the extension of the void into a channel via erosion, the beginnings of an electrical tree. As such, PDs are firmly associated with electrical tree growth [43].

Electrical trees form fractal patterns, with a fractal dimension describing the proportion of space they fill and hence the extent of degradation to the material in a given volume [44]. High fractal dimensions (2-3) result in thick, highly branching ‘bush’ type trees whereas a low fractal dimension (1-2) is associated with ‘branch’ type trees such as that shown in figure 1.7. The form a tree takes has been shown to depend on the applied voltage during growth, with branch type trees forming at lower voltages, and bush type trees at higher voltages [45]. These forms are not discrete and there exist intermediate bush-branch forms, a comparison of bush and branch types is shown in figure 1.8. The form of an electrical tree is also influenced by a wide variety of material properties and experimental parameters. Once a tree crosses the insulator a conducting path may form, leading to complete failure, known as breakdown, leaving behind a breakdown channel. The inception of an electrical tree occurs in the
presence of highly divergent electric fields, similar to corona discharge. Such fields may be generated in voids, at conducting impurities and at the electrodes. For example high fields may be generated at the tips of pin electrodes inserted into insulation for growth of electrical trees in a controlled environment.

![Figure 1.7 An electrical tree grown from a needle tip through an insulating material. In this case a high field is created at the needle tip due to its geometry and the tree grows towards a plate contact a short distance from the tip. Image adapted from [46].](image1)

![Figure 1.8 An example of an (a) branch and (b) bush type tree. [47].](image2)

Much of the research in this area involves epoxy resins or polyethylene (PE) polymer materials which are commonly used in HV insulation such as underground cables. Material properties have a large influence over susceptibility to electrical treeing. The presence of impurities, degree of crystallinity and the size of spherulites in PE has been shown to affect the electrical treeing resistance [48] as well as temperature, electrode design and mechanical strain [49]. Under certain conditions two distinct types of electrical
trees may form, those from which PD activity is present throughout the tree, termed ‘non-conducting’ trees and those where PDs are confined to the tree tips, ‘conducting’ trees [50]. By conducting it is meant that the trees are not sufficiently insulating to allow PDs to occur. It has been found that branch type trees are more likely to form conducting trees and bush type trees are most likely to form non-conducting trees. The change in conditions required for formation of conducting or non-conducting trees may be as small as a temperature difference of 10 °C during growth [51]. Trees have been observed to switch from non-conducting to conducting in PE after a critical time [52]. In epoxy resins the crossover from conducting to non-conducting trees has been seen to depend on whether samples were above or below their glass transition temperature during growth [53].

1.3.1 Tree initiation

Electroluminescence (EL), which is the emission of light from a material either due to charge recombination or impact ionisation within the material, usually precedes the onset of measurable PD activity. Champion, Dodd and Stevens [54, 55] investigated EL in epoxy resins under AC fields. They asserted that EL was a result of Schottky or Fowler-Nordheim (F-N) emission, depending on the electric field at the pin electrode tip, and that no threshold field was required for the onset of this behaviour. In the Schottky emission regime, also called field enhanced thermionic emission, the electric field lowers the potential barrier at the electrode for an electron to enter the polymer via thermionic emission. F-N emission occurs at very high fields where the width of the potential barrier is reduced to the point where the quantum tunneling effect allows for appreciable numbers of electrons to get through.

In an AC field the current oscillates sinusoidally and may be split into four quadrants, Q1-4 illustrated in figure 1.9. Champion, Dodd and Stevens identified three different regimes of EL behaviour over time, termed types A, B and C. In type A emission, EL increases gradually in Q3, with little change in the other quadrants. The EL then drops sharply and gives way to highly fluctuating type B emission in Q1 and Q3 as shown in figure 1.9. Type B is accompanied by microchannel formation and low intensity discharges. Once a large channel
is formed type C emission, associated with PDs and tree formation begins. It was found that type A behaviour could be skipped in favour of immediate type B emission on the application of a sufficient electric field.

![Figure 1.9 The electroluminescence intensity over time of an epoxy resin sample subjected to a strong AC field in the first and third quadrants. The four quadrants of one period an AC signal are illustrated in the upper left corner [44].](image)

Teyssedre et al. [56] investigated the onset of EL under AC and DC fields for a variety of polymers and found agreement with Champion, Dodd and Stevens [54, 55] for AC fields but suggested that a threshold field exists for EL under DC conditions. The reasons for differences between DC and AC fields are due to the response of the field to charge injection and the build up of space charge.

In an AC field positive charge injection occurs on the positive half cycle (Q1 and 2), forming positive space charge which acts to reduce the injection current. At the onset of the negative half cycle (Q3) the polarity of the field is reversed, the positive space charge then acts to increase the total field, increasing injection. Electrons then recombine with the trapped positive charge producing an EL signal with some electrons becoming trapped and contributing to recombination in the next positive half cycle. Over time this results in a build up of net space charge. Observation has shown that EL is strongest in Q3. This may be due to differences in carrier mobilities or recombination rates [44]. Under DC fields no
such polarity reversal occurs; charge recombination relies on the field driven drift of carriers into the bulk [56].

In the model presented by Wu and Dissado for epoxy resins [57], some of the energy from recombination is used for EL with the rest being used to generate new traps. Over successive cycles this leads to increasing recombination and therefore the observed increase in EL. The transition to type B behaviour is attributed to connection of shallow traps into a ‘percolation cluster’ under the effects of increased field such as that present in Q3 of the AC cycle. This leads to an increase in the carrier mean free path and a transition to impact excitation and ionisation behaviour, leading to tree formation.

1.3.2 Tree propagation models

The propagation of an electrical tree is fundamentally different from that of other breakdown mechanisms, such as thermal runaway, where electrical power dissipation generates heat faster than the material can lose it. This increasing temperature leads to higher conductivity and therefore more electrical power dissipation so an exponential increase in breakdown rate is observed. Instead, electrical tree propagation rates may be seen to decrease over time [45]. The onset of tree propagation is characterised by the appearance of measurable PD pulses. PDs cause an avalanche of charged particles along a channel which acts to reduce the effective field inside. Such avalanches result in impact excitation or ionisation of molecules, potentially leading to bond breaking and further damage at the end of a channel, extending the tree.

There are multiple models that attempt to describe the mechanism by which electrical trees propagate and the reason for their branched, fractal structures. The earliest model used to simulate dielectric breakdowns was suggested by Niemeyer et al. [58]. It took the form of a statistical model whereby a stepwise extension to the tree length was governed by an electric-field-weighted probability. Subsequent alterations to the model, such as introduction of a minimum threshold field for breakdown, have served to improve it [59]. The simple model is able to reproduce electrical treeing patterns with success but relies on an arbitrary parameter for controlling the fractal dimension of the
produced tree which lacks physical basis. Deterministic breakdown models [45, 60] seek to reproduce treeing using processes known or assumed to be present in tree propagation such as the electron avalanches involved in PD activity. There are now models which use a completely deterministic process where instabilities in the spatial development of PDs replace the stochastic element [61, 62].

1.4 Chemical changes during electrical ageing

The processes involved in electrical treeing are not well understood, in particular there is limited knowledge of the breakdown products involved or the chemistry present in the walls of the electrical trees themselves. Gaseous degradation products from PDs have been identified via gas chromatography and mass spectrometry. CO, CO$_2$, CH$_4$ and H$_2$ are seen in a number of polymers [63]. Sekii subjected PE samples to PDs in the presence of N$_2$ + O$_2$ or a purely N$_2$ atmosphere and found that degradation was significantly affected by the presence of oxygen [64]. Oxidised carbonyl components and the release of CO$_2$ increased with oxygen concentration. In research on the gaseous products formed during corona discharge of low density polyethylene (LDPE), these products are also observed [65]. Thermogravimetric analysis (TGA) and FTIR studies of PDMS have shown the production of H$_2$O and CO$_2$ during ageing [66].

There are few studies on non-gaseous degradation products and their distribution on the inner surfaces of tree channels and voids. Under inspection with reflected light, conducting trees appear black, and non-conducting trees appear white. It is suggested that this is the result of carbonized degradation products in conducting trees [50]. Confocal Raman studies have found evidence of disordered sp$^2$ carbon in conducting trees with the presence of high fluorescence in non-conducting trees being attributed to unidentified degradation products [51]. After severe PD degradation, crystalline deposits form in PE and epoxy [5]. In the case of epoxy these crystals were identified as hydrated oxalic acid (C$_2$H$_2$O$_4$·2H$_2$O). There have been some XPS studies on corona discharges in artificial voids [67] and fractured surfaces of polyethylene cables [68, 69]. These studies do not investigate the spatial distribution of the chemical species, however, showing only single spot analysis. It is thought this
thesis contains the first studies on the inner surfaces of tree channels and voids using XPS imaging and line scans to investigate the spatial distribution of chemical breakdown products.

1.5 Aims

The aim of this project was to investigate changes in the physical and chemical composition of the surfaces of aged insulators using surface analysis techniques with an emphasis on X-ray photoelectron spectroscopy. The chemical species present on the inner surfaces of artificial voids and electrical tree breakdown channels generated in polymer insulators have been studied, along with corona discharged surfaces and breakdown products from spark ageing. These systems are in many ways analogous to the process of electrical treeing but produce features or products at sizes suitable for XPS analysis. While XPS has seen success in the investigation of aged insulator surfaces exposed to outdoor conditions, such as corona discharge, studies have not been performed on voids and channels before using XPS. These studies are presented in comparison with confocal Raman microprobe experiments of the same systems by partners at the University of Southampton.

The structure of the thesis is as follows: Chapter 1 gives an introduction to the electrical ageing of polymers as well as an overview of the existing literature on the subject of electrical ageing and the overall aims of the project. In chapter 2, information on the materials and explanations of the theory and methods for experimental techniques used in this thesis is presented. Chapter 3 contains the results and discussion of XPS investigations into electrically aged artificial voids in LDPE. Results and discussion of XPS, XPS imaging, X-ray photoemission electron microscopy (XPEEM) and SEM studies of electrical breakdown channels in polydimethylsiloxane (PDMS) created at a range of energies are presented in chapter 4. Chapter 5 contains an XPS study of corona discharge in LDPE surfaces in air and nitrogen atmospheres and an investigation into breakdown products from spark discharges in a number of liquid systems. Chapter 6 is the conclusions chapter, containing a summary of the investigations presented in this thesis and the overall conclusions from each chapter, along with an explanation of the direction of future work.
2. Experimental techniques

This chapter gives information on the different materials investigated in this thesis, an explanation of the techniques used to investigate them, namely XPS, XPEEM and SEM, and information on the XPS analysis.

2.1 Materials

All samples were produced by collaborators at the University of Southampton and analysed by Dr. Nicola Freebody using Raman spectroscopy before being sent to the University of Manchester for further analysis by XPS, XPEEM or SEM. Samples consisted of a number of polymer materials which had been degraded with varying methods in order to directly investigate or model the affect of electrical discharges on them, the details of which follow here.

2.1.1 PDMS

Silicone rubbers are a class of flexible materials based on polymers with an inorganic siloxane backbone of alternating Si-O atoms. Silicone rubbers used as dielectrics are most often made using PDMS as the base polymer, which consists of the Si-O backbone with methyl pendant groups, as shown in figure 2.1. They are commonly used in outdoor insulation due to favourable electrical and degradation resistant properties. PDMS consists of the Si-O backbone with organic methyl pendant groups. PDMS has a high resistance to degradation due to the high Si-O bond energy of 443 kJmol\(^{-1}\) [70]. As such it also does not absorb UVa in the 300-400 nm wavelength range and UV photons with shorter wavelengths (UVb and UVc) are strongly absorbed by the earth’s atmosphere – though they are produced during corona discharge and plasma treatment [28]. The Si-C bond has a lower energy of 326 kJmol\(^{-1}\) but the polar nature of the siloxane bond increases its stability [71]. It has also been noted that the energy of rotation of the methyl groups about the backbone in PDMS is very low, allowing for reorientation to bury oxidised groups [30].
Figure 2.1. The PDMS monomer, consisting of an alternating Si – O backbone with 2 \( \text{CH}_3 \) groups attached to each silicon atom.

Silicone rubbers commonly contain a high proportion of filler materials to improve properties such as physical strength. The samples used in this thesis are of pure PDMS without fillers in order to investigate the effects of electrical degradation on the polymer itself. The use of PDMS as a model material is advantageous for XPS and XPEEM as it has a nominal fixed stoichiometry of C:O:Si of 2:1:1. Departures from this ratio are clear in XPS spectra, allowing for easier interpretation than for a purely hydrocarbon-based polymer. PDMS elastomer is used for studies of electrical breakdown channels in chapter 4 and a shorter chain liquid PDMS oil is used in spark discharge investigations in chapter 5.

The PDMS elastomer samples received were produced using a Dow Corning Sylgard 184 silicone elastomer kit according to the manufacturer’s instructions, producing solid blocks of 6 x 10 x 15 mm. A plane electrode was fixed to one edge and a hypodermic needle inserted into the polymer perpendicular to the plane electrode with a separation of 2 mm between needle tip and electrode. Applying a high voltage to the needle causes rapid electrical tree growth. Electrical breakdown channels were produced using varying voltages and growth times by allowing an electrical tree to bridge the electrodes. Samples were then sectioned by Dr. Freebody prior to being sent to the University of Manchester using a RMC MT-7 ultra microtome equipped with a CR-21 cryo-system set at -120 °C in order to expose parts of the trees and channels on the surface. An example is shown in figure 2.2.
Figure 2.2 An electrical breakdown channel created using a voltage of 11 kV. The channel is visible across the centre of the sample and has a dark outer edge. Samples were marked with permanent marker to show the ‘top’ side as can be seen on the left. The scale bar is 1 mm.

2.1.2 LDPE

LDPE is a hydrocarbon thermoplastic polymer containing only C-C and C-H bonds, with a structure shown in figure 2.3. It is a semi crystalline polymer and forms regions containing spherulites surrounded by amorphous regions. It is widely used in HV cable insulation. The C-C bond energy is 347 kJmol\(^{-1}\), which is similar to the energy for Si-C in PDMS and considerably lower than the Si-O backbone. From this it can be expected that chain scission is more common in C-C based polymers and a greater vulnerability to UV radiation. LDPE was used in the investigations of artificial voids in chapter 3 and corona discharge in chapter 5. As with PDMS the samples investigated were free of the fillers commonly added to the final insulation.

![Chemical structure of PE](image)

Figure 2.3 The chemical structure of PE, a simple carbon chain with attached hydrogen atoms.
For the artificial voids discs of LDPE were produced using hot compression. Large voids were created in the polymer by mixing the polymer with a blowing agent, azodicarbonamide. Upon subsequent heating, the blowing agent decomposes into gaseous products, leaving empty voids. Gold electrodes were attached to the samples and a high voltage placed across them to produce partial discharges within the voids in order to simulate the process of electrical treeing on a larger scale.

The corona discharge LDPE samples were aged in a test cell which could be purged with nitrogen in order to create an oxygen depleted environment. The method is similar to production of electrical trees and breakdown channels except here the needle is not inserted into the polymer but instead held a fixed distance above it. Samples were provided from aging in both air and nitrogen atmospheres as well as an unaged reference sample.

2.1.3 Spark discharge ageing

During the course of their investigation into corona discharge, researchers at the University of Southampton noticed deposits forming on the tips of the needles used to produce the corona. As these deposits proved too small to investigate using XPS, the researchers devised a novel means of reproducing the deposits in larger quantities using a spark generator submerged in liquid systems. The deposits could be extracted from the liquid and washed using acetone to remove residue.

Samples were received of breakdown products formed from dodecane (DD), dodecylbenzene (DDB) and a liquid form of PDMS. Where possible, samples were provided at high and low discharge energies in order to investigate the effect of this on the resultant chemistry.

2.2 Ultra-high Vacuum (UHV)

The signal in an XPS, XPEEM or SEM experiment requires the unhindered passage of electrons between the sample and the analyser. Scattering from gas molecules present in this region results in a loss of useful information,
increasing the background noise. In order to reduce the chance of scattering, the electron inelastic mean free path in the residual vacuum, $\lambda$, must be increased. $\lambda$ is inversely proportional to the number density of gas molecules in the chamber, which is proportional to the pressure at constant temperature and volume. A long enough $\lambda$ for most purposes is achieved by pressures of $\sim 10^{-6}$ mbar. However, UHV pressures required for XPS and XPEEM are lower than this as it is necessary to increase the monolayer time – defined as the length of time taken to form a single layer of adsorbed gas on the surface of the sample. A long monolayer time keeps the surface cleaner from contaminants over the time in which a sample is being analysed. Typical UHV pressures are on the order of $10^{-10}$ mbar.

Gases adsorb onto all inner surfaces of a UHV chamber, producing a background pressure as they ‘outgas’ at low pressures with more porous materials increasing the residual pressure, greatly limiting the achievable pressure. To counter this issue, prior to use, the chamber is ‘baked’ at 150-200 °C for several hours while pumping in order to desorb gases from surfaces and remove them. Due to the high temperature, strength and vacuum level requirements, most components in a UHV chamber are made from high purity stainless steel.

### 2.2.1 UHV pumps

There are multiple types of pump capable of attaining and maintaining UHV conditions. It is common for a number of different pumps to be used on a single chamber. Commonly used pumps are described in this section.

#### 2.2.1.1 Rotary vane pumps

Rotary vane pumps contain a cylindrical chamber with a cylindrical rotor offset from the centre of the chamber such that it has an eccentric rotation. Vanes in the rotor maintain a seal with the chamber walls either through springs or centrifugal force. Fluid enters one side of the pump and is forced out at the other. These pumps are widely used as backing pumps and are capable of achieving pressures of about $10^{-3}$ mbar.
2.2.1.2 Turbomolecular pumps

These pumps contain angled blades which rotate at high speed providing an impulse to gas molecules in a particular direction, compressing them into a smaller volume. The higher pressure gas is then removed by a backing pump, usually a rotary vane pump.

2.2.1.3 Titanium sublimation pumps

A titanium filament is heated in the UHV chamber to a temperature at which it sublimes. A thin layer of reactive clean titanium coats the surrounding chamber walls, reacting with gas molecules incident upon it, forming stable solid compounds and effectively removing them from the system. Sublimation pumps are not run continuously; they are activated periodically to produce a fresh layer of titanium for enhanced pumping in combination with other pumps.

2.2.1.4 Sputter ion pumps

These pumps are operated under pressures of $10^{-3}$ mbar or better. Electrons are produced at an anode by electrical discharge and are accelerated in spiral paths around the filament by a strong magnetic field. They collide with gas particles, ionising them. Ions are then accelerated into the cathode implanting them deep within it.

2.2.1.5 Diffusion pumps

A fluid with a low vapour pressure is boiled by a heater in the bottom of the pump causing it to rise through a central column and be ejected through a number of jets. These jets are designed such that the vapour exits at supersonic speeds towards the bottom of the pump. Gas molecules are swept downwards and removed by a rotary vane backing pump. The walls of the pump are cooled so that the vapour condenses and runs back to the heater. The inlet from the UHV chamber may contain a liquid nitrogen cooled trap to prevent vapour from back streaming into the chamber.
2.2.2 Pressure gauges

The pressure in a system is proportional to the number density of molecules in the system. As such, most UHV pressure gauges work by measuring this number density.

2.2.2.1 Pirani gauge

Pirani gauges consist of a heated filament open to the chamber. They work in the medium pressure region (~1 – 10^{-3} mbar). In this region the thermal conductivity of the gas in the chamber is highly dependent on pressure as the mean free path of molecules approaches the diameter of the filament. Changes in pressure can be related to the rate of temperature change in the filament. This continues until the pressure drops and radiation becomes the dominant process governing thermal conductivity.

2.2.2.2 Ionisation gauge

There are 2 main types of ionisation gauge, hot cathode and cold cathode. Cold cathode gauges work on very similar principles to the sputter ion pump; as such they also pump gases out of the system. In hot cathode gauges a filament produces electrons by thermionic emission. In both cases electrons are accelerated in spiral paths around the filament by a magnetic field and collide with gas particles, ionising them. Ions are collected by the cathode producing a current which is directly proportional to the number density of gas molecules in the chamber and therefore allowing measurement of the pressure.

2.3 X-ray photoelectron spectroscopy

XPS, also called electron spectroscopy for chemical analysis (ESCA), is a surface sensitive technique which provides chemical state information about the top few nm of a sample [72]. Incident X-rays induce photoemission in a sample, electrons are collected and their kinetic energies measured. Spectra are then produced containing characteristic peaks which can be used to identify chemical species present on the sample surface. The technique must be carried out under UHV conditions in order to allow unscattered electrons from the sample to reach the detector.
2.3.1 Photoemission

Photons of sufficient energy incident on a material cause electrons to be ejected from the surface \textit{via} the photoelectric effect according to equation (2.1):

\[ E_\gamma = E_k - E_b - \phi , \]

where \( E_\gamma \) is the photon energy, \( E_k \) is the kinetic energy of the electron after being ejected, \( E_b \) is the binding energy of the electron in the material and \( \phi \) is the work function of the material. The work function is defined as the minimum energy required to remove an electron from the material, leaving it at rest in the vacuum. Typical work functions are on the order of a few eV whereas core electron binding energies can range from \(~10\) eV up to a few keV. Therefore soft X-rays (\(~200-2000\) eV) are commonly used to allow excitation of a range of orbitals in most elements. The process is illustrated in figure 2.4.

For a conducting sample in electrical contact with the analyser the Fermi levels of both are equal. In this case the work function in equation (2.1) corresponds to that of the analyser rather than the sample. For insulators or samples which cannot be grounded this is not the case. In order to achieve accurate binding energies reference peaks of well known energy can be used to calibrate the spectrometer.

![Figure 2.4. A schematic diagram of the photoelectric process. An incident photon causes an electron to be ejected from an atomic orbital according to eq. (2.1).](image)
The surface sensitivity of XPS is a consequence of the inelastic mean free path, $\lambda$, of electrons within a solid. Electrons travelling through a solid are attenuated according to the Beer-Lambert law,

$$I(x) = I_0 \exp\left(\frac{-x}{\lambda \cos \theta}\right), \quad (2.2)$$

where $I(x)$ is the intensity after travelling through distance $x$, $I_0$ is the initial intensity and $\theta$ is the angle from the surface normal at which the electrons exit the solid. $\lambda$ is also a function of the electron kinetic energy, as shown in figure 2.5. A simple calculation with equation (2.2) shows that approximately 95% of electrons leaving the surface originate from within $3\lambda$ of the surface. The depth of sample probed can be controlled by adjusting the angle between the sample and the analyser. Increasing the angle between the detector and the normal to the sample surface will increase the surface sensitivity. This technique, referred to as depth profiling, can be performed in order to characterise the chemical species present at varying depths into a sample surface.

Figure 2.5. The universal inelastic mean free path curve (given in atomic monolayers) for varying electron kinetic energy. In the soft X-ray region (~200-2000eV) $\lambda$ is ~1-10 monolayers, giving XPS a high surface sensitivity. Figure from [73].
2.3.2 Photoemission peaks

Peaks in an XPS spectrum take the form of Gaussian-Lorentzian curves with a peak width taken as the full width at half maximum (FWHM). The magnitude of the FWHM depends on a number of factors; the core hole lifetime, the energy resolution of the detector and the line width of the X-ray source being the main contributors. The relationship between FWHM and the core hole lifetime is a consequence of the Heisenberg uncertainty principle,

\[ \Delta E \leq \frac{\hbar}{2\Delta \tau} \quad (2.3) \]

where \( \Delta E \) is the FWHM in eV, \( \hbar \) is the reduced Plank’s constant in eV-seconds and \( \Delta \tau \) is the lifetime in seconds. This results in a Lorentzian peak shape whereas the shape due to the experimental factors is Gaussian in nature. A mixed convolution of a Gaussian and a Lorentzian line shape is produced with the relative contributions from the two being dependant on the experimental conditions. The individual contributions to the peak width are summed in quadrature to give the total FWHM.

2.3.3 Auger peaks

Photoemission induced by XPS leaves atoms in an excited state after the removal of core electrons. An electron from a higher orbital fills the core hole, releasing energy either by X-ray fluorescence or by Auger emission. In Auger emission the energy is transferred to a second electron which is then emitted from the sample. This results in peaks in the XPS spectrum much like photoemission with the exception that these peaks are independent of the X-ray source energy. As such these peaks may be identified by a change in the exciting X-ray energy; all photoelectron kinetic energies will shift by the energy difference whereas Auger peaks will remain unaltered.

2.3.4 Spin-orbit coupling

Electrons have a property called spin, with quantum number \( s = \frac{1}{2} \). In an atomic orbital the magnetic interaction between the spin state of the electron
and its orbital angular momentum, quantum number $l$, gives rise to spin-orbit coupling. $l$ can take positive integer values 0, 1, 2, 3 etc. which correspond to the s, p, d, and f orbitals respectively. For a single atomic orbital, the total angular momentum, $j$, is given by

$$j = |l \pm s|.$$  \hspace{1cm} (2.4)

For orbitals with $l > 0$ (i.e. p, d and f orbitals) $j$ will take 2 distinct values, e.g. for a p orbital $j$ can equal 1/2 or 3/2. This causes doublet peaks to form in XPS spectra. The ratio of the doublet peak areas is given by the degeneracy, $2j+1$, giving, for example, a 2:1 ratio for p orbital doublet areas.

### 2.3.5 Satellites

A non-monochromated X-ray source produces photons from a range of low intensity X-ray lines besides the principal line. Each line will produce photoelectron peaks at different energies resulting in low intensity peaks shifted by set values from the main peaks. These peaks are known as X-ray satellites and can be removed with data processing or by using a monochromated source. Other satellite features are produced by atomic relaxation following photoemission. The rearrangement of electrons may leave an electron in an excited state producing a ‘shake up’ satellite or it may ionize the atom producing a ‘shake off’ satellite.

### 2.3.6 Chemical shift

While XPS survey scans can identify the presence of elements and gain a measure of their relative abundances the technique can be taken further. Detailed scans of specific orbitals may reveal a number of convoluted peaks with different binding energies, a product of different chemical shifts as seen in figure 2.6. Chemical shift arises from the presence of atoms bonded in different chemical environments such as bonding to different elements or differing oxidation states. The spectra can be deconvoluted using data processing software to fit a number of Gaussian-Lorentzian peaks to reconstruct the data.
and the differing chemical environments can be identified according to the respective binding energies of these peaks.

2.3.7 Sample charging

When working with insulating samples it is often not possible to have the sample in electrical contact with the analyser. Electrons which leave the surface are not replaced, leading to sample charging. Charging can lead to significant shifts in expected peak positions as photoelectron energies are altered by the resulting electric field and can cause broadening or splitting of peaks if the charge of the sample surface is heterogeneous, known as differential charging. For spectrometers with a non-monochromated X-ray source the effects of charging are reduced somewhat by a steady flow of electrons from the anode but these electrons are not present when using a monochromator. Sample charging and methods for charge compensation are discussed further in section 2.3.11.

Figure 2.6. A narrow scan over a C 1s region showing chemically shifted components as a result of different bonding states with oxygen [13].
2.3.8 X-ray sources

In a typical X-ray gun, electrons are generated by a filament and accelerated towards an anode of the chosen target material. Core electrons are stripped from the anode and subsequent atomic relaxation results in the generation of an X-ray spectrum. As well as the characteristic lines, a broad Bremsstrahlung background is present. Bremsstrahlung radiation is produced when incident electrons make a close pass to an atomic nucleus. The resulting coulomb interaction imparts a large acceleration to the electron causing it to lose energy in the form of radiation. The range of possible interactions results in a continuous energy spectrum up to the initial electron kinetic energy.

The choice of anode material is dependant on the properties of the principal X-ray line, requiring both a high enough energy to produce photoelectrons from core levels in all elements and a linewidth narrow compared to the linewidth of the core-levels. Al Kα (1486.6 eV energy and 0.85 eV linewidth) and Mg Kα (1253.6 eV energy and 0.7 eV linewidth) [74] are the most commonly used sources that fit these criteria. The majority of the energy incident on the anode is converted to heat so X-ray guns are water cooled. Usually a ~2 µm thick Al window is placed between the anode and the sample to reduce the effects of excess Bremsstrahlung radiation and contamination on the sample.

Some spectrometers make use of dual anode X-ray guns, usually with Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) sources which are plated onto 2 sides of a conical anode arrangement. These sources allow the X-ray energy to be easily switched to facilitate, for example, identification of Auger peaks.

Anodes attached to a high speed rotating disc may be used to give enhanced cooling ability. Electrons are not incident on the entire anode at any time allowing it to cool partially before being exposed again thus allowing guns to run at higher energies – and therefore higher fluxes – without overheating.
2.3.9 X-ray monochromators

The removal of unwanted spectral lines and Bremsstrahlung radiation can be achieved using a monochromator resulting in a greatly increased signal to noise ratio. They also focus X-rays and reduce the characteristic X-ray linewidth, increasing spatial and energy resolution but at the expense of a reduction in intensity [74]. Typically Al Kα X-rays are reflected from a (1010) quartz crystal surface according to Bragg’s law,

\[ n\lambda = 2d \sin \theta , \]

where \( n \) is the diffraction order, \( \lambda \) is the X-ray wavelength, \( d \) is the crystal interatomic spacing and \( \theta \) is the angle of incidence. A typical monochromator is shown in figure 2.7. The sample and focusing points for the source and crystal form part of a Rowland circle. The Rowland circle has a diameter equal to the radius curvature of the quartz crystal being used. In order to maximize crystal surface contact with the circle and to reduce spherical aberration, the quartz crystal surface may be ground to the radius of the Rowland circle [75].

Figure 2.7. An electron analyser and X-ray monochromator based on a Rowland circle used as part of an electron spectrometer [73].
2.3.10 Electron energy measurement

Modern XPS instruments almost all make use of a concentric hemispherical analyser (CHA) to analyse the photoelectrons emitted from the sample. They consist of a pair of concentric hemispheres, one larger than the other, with a mean radius $R_0$ between them as shown in figure 2.8. Electrons are focused and retarded by an electrostatic lens before entering the analyser. The hemispheres are held at different potentials so as to deflect electrons between them. Electrons which enter with the correct energy are refocused at the other end of the analyser while others hit the inner or outer walls. There are two different operating modes, Constant Analyser Energy (CAE) or Fixed Retard Ratio (FRR). In CAE mode the hemisphere potentials are fixed to accept electrons at a set ‘pass’ energy. Different electron kinetic energies are scanned by altering the retarding voltage in the lens. Alternatively the hemisphere potentials may be scanned with the retarding voltage in FRR mode in order to maintain a constant ratio between the initial electron and pass energies. The energy resolution $\Delta E$ (i.e. the instrument contribution to the observed FWHM of XPS peaks) of the analyser is given by

$$\frac{\Delta E}{E} = \frac{W}{2R_0} + \frac{\theta^2}{4},$$  \hspace{1cm} (2.6)

where $E$ is the electron pass energy, $W$ is the entrance slit width and $\theta$ is the analyser acceptance angle. It can be seen that increasing $R_0$ and reducing $W$ will improve $\Delta E$. However, reducing the entrance slit width also reduces the signal intensity. Using CAE mode maintains a constant $\Delta E$ while FRR mode keeps $\Delta E / E$ fixed. Upon exiting the CHA electrons are multiplied by a channeltron or micro-channel plate in order to produce a large enough current to be detected.
Figure 2.8. Schematic diagram of electron paths through a CHA. $R_1$, $-V_1$, $R_2$ and $-V_2$ are the radii of and voltages applied to the inner and outer hemispheres respectively, $\delta\alpha$ is a small angle deviance of the entering electrons from the entrance normal. Figure from [73].

X-ray imaging requires that the relative spatial origin of electrons is preserved when they reach the detector. To this end a spherical mirror analyser may be used. This type of analyser is similar in form to a CHA; electrons enter two hemispheres as in a CHA but at an oblique angle to the electrostatic field, with voltages set up resulting in a mirrored image of the electron distribution.

2.3.11 Charge stabilization

The removal of photoelectrons from a sample can cause charging issues in insulating samples as described in section 2.3.7. For spectrometers with a non-monochromated X-ray source the effects of charging are reduced by a steady flow of electrons from the anode but these electrons are not present when using a monochromator so there is a need for charge compensation.

2.3.11.1 Electron flood gun

Electron flood guns flood the sample with low energy (< 10 eV) electrons in order to replace those lost to photoemission and prevent the build up of charge.
By adjusting the gun voltage the sample can be brought to a stable potential which allows for an accurate spectrum to be obtained following an energy correction.

2.3.11.2 Magnetic immersion lens

A magnetic immersion lens forms part of the lensing system on modern Kratos analytical spectrometers. With the addition of a charge balance plate above the sample, as shown in figure 2.9, low energy electrons produced by a filament may be trapped in the magnetic field, forming a dynamic equilibrium between the negatively biased charge plate and the sample. As the sample becomes more positively charged due to photoemission it will accept the electrons trapped in the field, producing a self compensating system that responds rapidly to changes in charging conditions [76].

![Diagram of magnetic immersion lens](image)

Figure 2.9. Charge stabilisation using a magnetic immersion lens. The filament is not in direct line of sight with the sample [76].

2.4 XPS facilities

2.4.1 Kratos AXIS ULTRA spectrometer

Kratos AXIS ULTRA spectrometers have been used to produce the majority of the XPS data presented here. Three different spectrometers were used, situated in the University of Manchester (pictured in figure 2.10), Cardiff
University and Nottingham University. The principles of their operation are the same but they differ slightly in the forms of their fast entry locks and preparation chambers. The spectrometer is capable of large and small spot spectroscopic analysis with a variety of aperture sizes using a hemispherical analyser and imaging of heterogeneous surfaces to produce 2D chemical state plots using a spherical mirror analyser. The analysers are combined such that the outer hemisphere of the hemispherical analyser forms the inner hemisphere of the mirror analyser (see figure 2.11). This allows both analysers to use the same detector. A monochromated Al Kα source and a hybrid magnetic and electrostatic lens system are used which can produce spatial resolutions in imaging mode on the order of 10 µm. For small spot analysis a 110 µm aperture was used, imaging scans used either an 800 x 800 µm or 400 x 400 µm field of view. In order to produce chemical state images scans in the imaging mode were taken in 0.1 eV energy steps. This results in a large data set where post-analysis each pixel in each image represents a unique spectrum over the defined energy range.

Figure 2.10. The Kratos AXIS ULTRA spectrometer based in The University of Manchester School of Materials.

Multiple samples can be mounted onto a single sample bar and introduced into the preparation chamber via a fast entry lock where they are outgassed until reaching a suitable pressure for analysis (< 5 x 10⁻⁹ mbar). Once inserted into
the main chamber a fixed camera allows for alignment of the sample positions. Sample position and charge compensation settings can be fully controlled using the Kratos Vision software; a user can pre-program sample positions and scan parameters allowing sets of data from multiple samples to be acquired more efficiently.

2.4.2 NCESS

The National Centre for Electron Spectroscopy and Surface Analysis (NCESS) at STFC Daresbury laboratory was an EPSRC funded facility which operated until 2011 with a Scienta ESCA300 spectrometer as shown in Figure 2.12.

![Figure 2.11. The combined analysers in the AXIS ULTRA spectrometer. In spectroscopy mode electrons are measured by a hemispherical analyser whereas imaging mode uses a spherical mirror analyser in which the spatial origin of the electrons is preserved. In both cases electrons are detected using a delay line detector (DLD) [77].](image-url)
Figure 2.12. The Scienta ESCA 300 spectrometer at STFC Daresbury laboratory.

A 300 mm radius hemispherical analyser with a multi-channel detector gives a potential instrument energy resolution of 0.3 eV [78]. The load lock, preparation and main chambers are capable of holding multiple samples at once, allowing time for samples to reach acceptable pressure while another is being analysed. Sample transfer involves a simple rack-and-pinion railway mechanism with wobble sticks used to transfer between chambers. Changing between samples must be done manually, preventing the level of automation possible with the AXIS Ultra spectrometer. Like the AXIS Ultra spectrometer, the Scienta is equipped with a monochromated Al Kα source and is capable of standard transmission scans and 1 dimensional spatial imaging.

In transmission mode signal is gathered from the full x-ray illuminated area, which forms a line ~ 0.5 mm x 6 mm along the sample [78]. This mode gives a high signal but a low spatial resolution. With the addition of a pre lens the spatial resolution may be improved at the cost of signal. In this mode the signal is dispersed in energy across the detector, forming a 2-dimensional image of binding energy against position along the x-ray line across the sample. This mode scans a smaller part of the x-ray area of 70 µm x 2.1 mm [78]. This produces images of binding energy against position, essentially a set of stacked
spectra from a top down view. The peak intensities are shown by a brightness scale. An example of what the images represent is shown in figure 2.13.

![Figure 2.13. An illustration of the NCESS imaging mode. The optical image on the left is of a void sample showing in blue the area analysed by the NCESS imaging mode. The corresponding image of the C 1s signal from the NCESS spectrometer is shown on the right. The position scale on this image is arbitrary. The bright regions show the position of the peak, which shifts with position across the void. The scale bar in black is 1 mm.](image)

### 2.5 XPEEM and synchrotron radiation sources

XPEEM is a parallel imaging technique which works somewhat analogously to an optical microscope, but using electrons to overcome the diffraction limit. As such it boasts a high spatial resolution in the 10s of nm [79]. Electrons are produced through photoemission and pass through an electron optics system before being incident on a channel plate followed by a screen. XPEEM is similar to XPS in that it requires a UHV system, an X-ray source and an electron energy analyser. A schematic of the XPEEM instrument is shown in figure 2.14. Photoelectrons produced from the sample form a magnified image at the objective, the image is then further magnified in a lensing column before being energy filtered by a hemispherical analyser after which they are detected with a phosphor coated microchannel plate, which then produces a real time image on a CCD. In order to reduce chromatic aberration the objective lens accelerates the photoelectrons up to energies of 10-15 keV. The combination of high spatial resolution and parallel imaging requires a very high brightness X-ray source which is not available in a laboratory setting and so XPEEM systems make use of synchrotron light sources instead.
A synchrotron is a type of particle accelerator which accelerates charged particles in a circuit to near the speed of light in order to produce intense radiation tangential to the particle path. The use of diffraction grating monochromators and insertion devices allows for a high intensity, variable energy source. The X-ray source for the data in this thesis is the MAX II synchrotron source based in MAX-lab in Lund, Sweden.

### 2.5.1 Synchrotrons

The layout of the MAX-Lab facility is shown in figure 2.16. Electrons are initially accelerated in a linear accelerator (the MAX Injector) before entering the storage rings, where they are accelerated up to a fixed energy for each ring by an applied electric field, while being curved along a circular path by dipole bending magnets. Once the final energy is reached the applied field is still required to replace energy lost to radiation. In the MAX II storage ring, electrons are accelerated up to a final energy of 1.5 GeV allowing the production of photons from the UV up to the hard X-ray region. The storage rings are kept in UHV conditions in order to lessen losses of electrons from the beam due to collisions but the beam current still decays over time and so injections are
performed every 12 hours. When this happens the remaining beam is ‘dumped’ and replaced.

2.5.1.1 Insertion devices

While the electrons produce radiation as they go around the ring due to the action of the bending magnets, greater intensities and photon energies can be achieved through the use of insertion devices positioned in straight sections of the ring. These come under 2 categories: wigglers and undulators.

Undulators are composed of a series of magnets with alternating polarity. As the electron beam passes through this causes rapid small sinusoidal oscillations producing a high intensity beam of light, as illustrated in figure 2.15. On its own this is not sufficient to produce photons in the X-ray regime as the emitted wavelength is directly proportional to the undulator period, L, and it is not practical to create undulators on such short length scales. However, the relativistic speed of the electrons increases the photon frequency into the X-ray range via a combination of Lorentz contraction and Doppler shift. Relativistic effects also result in an extremely small angular spread of photons, further increasing the source intensity. The relationship between the energy radiated, \( \Delta E \), by an electron and the radius of curvature, \( R \), of its path is

\[
\Delta E = \frac{4 \pi e^2 \gamma^4}{3R}, \quad (2.8)
\]

where \( e \) is the electronic charge and \( \gamma \) is the Lorentz factor. \( \gamma \) contains corrections for the relativistic effects mentioned above, it can be seen that as \( \gamma \) increases the energy radiated increases and therefore the wavelength is reduced. The radiation from successive undulations can interfere constructively or destructively, producing high intensity at certain wavelengths. The narrow wavelength band produced by the undulator due to this effect can be chosen, or scanned through, by adjusting the magnetic field. This is done by altering the gap between the magnet poles, with narrower gaps increasing the field and so reducing the radius of curvature, resulting in production of shorter wavelengths.
Wigglers function similarly to undulators but operate with higher magnetic fields and/or a smaller number of magnet periods. This results in larger undulations and produces a broad band emission similar to a series of bending magnets but shifted to smaller $\lambda$ due to the smaller radius. The larger radius also prevents the constructive interference present in undulators.

A number of ‘beamlines’ extend tangentially from the ring (see figure 2.16) and serve to channel photons produced in the insertion devices towards the end stations where experiments are performed. Before reaching the end stations the photons pass through a monochromator. These monochromators can be adjusted mechanically to select a broad range of photon energies.
2.5.2 Beamline I311

The work presented here was undertaken at the I311 beamline, a dual end station undulator beamline with one station designed for high resolution spectroscopy and the other dedicated to microscopy studies. The microscopy station is an Elmitech SPELEEM [82] multi-technique station capable of low energy electron microscopy (LEEM), XPEEM, photoelectron spectroscopy (PES) and photoelectron diffraction studies, shown in figure 2.17. In addition to the synchrotron-produced photon beam, there is a high flux electron gun and a UV lamp available.

In XPEEM, photoelectrons produced from the sample travel through a lensing column into a hemispherical analyser after which they are detected with a phosphor coated microchannel plate, which then produces an image on a CCD. The photon energy range available is from 43 – 650 eV [83], allowing investigation of most elements. This energy range is smaller than that available for more routine XPS studies due to the high photon flux requirements of the technique; higher energy photons are not produced with sufficient intensity at Max II. In XPEEM mode the spectrometer has a lateral resolution of 40 nm.
Samples may be held one at a time in the XPEEM chamber. Prior to this, the sample to be analysed is first placed into a load lock to pump down to an acceptable pressure. At this stage the samples may also be heated to promote degassing.

The photon energy is generally controlled such that the electron kinetic energy remains constant for all elements. This maintains a fixed mean free path for each element, making direct comparison between elements possible after intensity and cross section corrections.

There is no suitable charge compensation system available when using XPEEM, due to the much higher photon flux compared to lab based sources and the high voltage applied to the sample, as such sample charging is an issue [84], causing blurring and smearing if images and reducing signal intensity. In order to alleviate charge build-up a 400 mesh (a hole size of 37 µm) hexagonal Au TEM grid was fixed over the region of interest in two PDMS breakdown channel samples using a two part silver epoxy, as shown in figure 2.18.
2.6 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a real time imaging technique capable of producing high resolution surface topography images of a wide range of samples. It is well known for its large depth of field in comparison with other imaging techniques, allowing complex 3-D structures to be investigated in a single image [85].

Electrons are accelerated and focused into a tight spot on the sample surface; this spot is then rastered across the sample and emitted electrons are collected in order to produce an image. The main source of signal in a conventional SEM comes from secondary electrons, or secondaries, which have been ejected from the sample surface as a result of inelastic interactions with the primary electron beam, and backscattered electrons, primary beam electrons which have been elastically scattered through more than 90° before exiting the sample surface.

2.6.1 Scattering processes

Interaction between the sample and the electron beam occurs through the combination of elastic and inelastic scattering. Elastic scattering is a process in
which the kinetic energy of the interacting electron is conserved but the path of the electron is altered by the Coulomb interaction with a nearby atomic nucleus. The screened Rutherford equation can be used to calculate the cross section, \( \sigma(>\phi_0) \), for scattering angles greater than an angle \( \phi_0 \):

\[
\sigma(>\phi_0) = 1.62 \times 10^{-20} \frac{Z^2}{E^2} \cot^2 \frac{\phi_0}{2},
\]

where \( Z \) is the atomic number of the scattering atom and \( E \) is the incident electron energy (in keV). The angle of scattering can take any value from 0 to 180° but the cross section is heavily biased toward small angles. The \( Z \)-dependence allows for elemental contrast images, especially for high \( Z \) elements. Elastic scattering spreads electrons through the sample, degrading the spatial resolution while limiting the depth penetration.

Inelastic scattering removes kinetic energy from electrons transferring it to the environment via a number of different loss processes. As these processes reduce the kinetic energy of the incident electron beam they further limit the range electrons can travel into the sample. The most important process in terms of SEM imaging is that of secondary electron excitation. Inelastic scattering of the beam by valence band electrons can promote them into the conduction band and provide them with enough energy to travel through the sample, undergoing further scattering. With enough energy these electrons may overcome the material work function and escape the sample surface where they may be collected into a positively biased detector. The escape depth is described by the Beer-Lambert law and is independent of the excitation energy as in XPS (see section 2.3.1) but the kinetic energy of secondary electrons is defined as those under 50 eV resulting in a larger escape depth on the universal mean free path curve than in an XPS experiment. The sampling depth is further affected by secondary electrons produced as backscattered electrons leave the surface. Such secondaries will contain characteristics of the backscattering signal.
2.6.2 SEM instrumentation

A typical SEM can have many different detectors for the various signals generated but the most basic will consist of a UHV chamber, an electron source, the electron optics and a secondary electron detector.

There are two main types of electron gun in use: thermionic emission guns and field emission guns (FEGs). Thermionic emission guns involve emission from heating a filament such that electrons can overcome the work function and escape the surface. Tungsten or LaB$_6$ filaments are the most common. LaB$_6$ has a lower work function and so higher emission brightness than tungsten for similar operating conditions but it is chemically reactive at high temperatures and so has more stringent vacuum requirements. FEGs produce emission by lowering and narrowing the potential barrier using an extremely narrow tip to produce a high density electric field, resulting in a very high brightness source. An Everhart-Thornley detector is used to collect the electron signal. For a secondary electron image a positively biased grid collects the low energy electrons onto a scintillator attached to a photomultiplier tube and a CCD. This allows the output to generate real time images on a screen.

In a conventional SEM sample charging is an issue for insulating samples, causing streaking and distortion in images and so in order to investigate insulating samples it is common to coat them in a thin layer of carbon or gold, preventing subsequent analysis using surface sensitive techniques like XPS. The environmental SEM (ESEM) provides a way around this drawback by using differential pumping of the microscope column, allowing a low vacuum environment at the sample position. Charge is carried away by gas particles in the chamber and gases, such as water vapour, can be introduced in small amounts to improve the neutralisation. This allows insulating samples to be imaged without prior preparation.

SEM is complementary to XPS imaging analysis as it is also a surface sensitive technique but with a much greater spatial resolution. While optical microscopy can be misleading in transparent samples, causing ambiguity in sample alignment for XPS, SEM can be used effectively to identify regions of interest on
the sample surface for XPS analysis or as a follow up investigation of features seen in XPS imaging.

Samples were scanned using a Philips XL-30 ESEM based in the School of Earth, Atmospheric and Environmental Sciences at the University of Manchester. Samples were introduced in the as-presented state and images taken at an accelerating voltage of 20 kV.

2.7 Raman microprobe spectroscopy

At points in the results chapters of this thesis comparisons are made to Raman spectroscopy data produced from the samples by collaborators at the University of Southampton to prior them being received at the University of Manchester. Therefore it is pertinent to include a brief description of the technique.

Raman spectroscopy utilises monochromatic laser light to scatter light from the sample. The majority of photons undergo Rayleigh scattering, an elastic process which does not alter the incident photon wavelength. Raman scattering is a weak process which accounts for ~ $10^{-7}$ of the scattered light [86] but results in a measurable shift in photon wavelength.

A quantum-mechanical description accounts for the effect as an excitation of the scattering molecule into an excited virtual state. The interaction of a photon with a molecule causes a change in its vibrational state. If the molecule relaxes back to its initial state no energy is lost – resulting in Rayleigh scattering. Molecules which relax into a different vibrational state are said to have undergone Raman scattering, causing a shift in the photon energy equal to the energy of the vibrational state. If the molecule relaxes into a higher vibrational state the photon loses energy and this is called a Stokes shift. Alternatively an anti-Stokes shift is observed if the molecule is already in an excited state and relaxes to a lower state. These scattering processes are illustrated in figure 2.19. Typically Stokes shifts are measured as they occur with higher intensity than the corresponding anti-Stokes shift. As the Stokes shifts correspond to vibrational states of molecules present in the sample they can be used to characterise the chemical species present in a sample.
Confocal Raman Microprobe spectroscopy (CRMS) was used to collect the data shown in this thesis. In CRMS a pinhole is placed behind the objective lens in order to occlude photons generated far from the focal plane from reaching the detector. This greatly increases the depth resolution, allowing depth profiling of transparent samples [87].

2.8 XPS analysis

Data were analysed using the CasaXPS software [88]. For the data from NCESS the relative sensitivity factors held within the CasaXPS software were used. Custom relative sensitivity factors were provided for the Manchester Kratos spectrometer and these have been used for the data from the other Kratos spectrometers. A Shirley background [89] was used for all data and the narrow scan envelopes were fitted using either Gaussian - Lorentzian product or sum line shapes. Both types of line shape are approximations to a true Voigt function [90]. For the majority of data it was found a sum Gaussian lineshape resulted in a closer fit to the data. All data have been charge referenced setting the C-H component of the C 1s peak to 285.0 eV.

The polymers investigated contain primarily carbon and oxygen, with the addition of silicon for the case of PDMS. Reference values for the chemical
shifts associated with these elements are listed in table 2.1. It should be noted that some shifts are very similar, for example it is difficult to distinguish between C=O and O-C-O bonds in the C 1s peak as the binding energy ranges overlap completely.

<table>
<thead>
<tr>
<th>Core level</th>
<th>Species</th>
<th>Binding energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>C-O-C</td>
<td>286.5</td>
<td>[91]</td>
</tr>
<tr>
<td></td>
<td>C-OH</td>
<td>286.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C*-O-C=O</td>
<td>286.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>287.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-C-O</td>
<td>287.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-O-C*=O</td>
<td>289.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O=C-OH</td>
<td>289.2</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>C-O-C</td>
<td>532.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-OH</td>
<td>532.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-C-O</td>
<td>533.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C=O</td>
<td>532.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O*-C=O</td>
<td>533.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O-C=O*</td>
<td>532.2</td>
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<tr>
<td></td>
<td>Si-O-Si (PDMS)</td>
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<tr>
<td>Si 2p</td>
<td>PDMS (2p_{3/2})</td>
<td>102.4</td>
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<td>PDMS (2p_{1/2})</td>
<td>101.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO₂ (2p_{3/2})</td>
<td>103.0 – 103.8</td>
<td>[92]</td>
</tr>
</tbody>
</table>

Table 2.1. Binding energies of common species found in XPS of the investigated polymers. Values are relative to the saturated hydrocarbon C 1s peak at 285.0 eV and are given an error of ± 0.2 eV.

When the FWHM of peaks in the C 1s spectrum are ~1 eV or less, as is seen in much of the data presented here, asymmetry becomes visible in the C-H component. This is due to vibrational excitation of the C-H bond stretching [93, 94]. This effect can be modeled by a series of symmetrical peaks of decreasing intensity with equal FWHM and a constant energy separation corresponding to the energy of the C-H stretch – 0.39 eV. While a polymer such as LDPE would also be expected to show C-C vibrational excitation the energy of this stretch is much smaller and the C-H stretch dominates.
A sample of carbon black was analysed as a reference for the graphitic carbon expected in the samples. The peak shape of graphitic carbon in various forms has been shown to change only in the degree of asymmetry and the FWHM of the C 1s envelope, and these relate to how complete the graphite structure is [95, 96] and so carbon black is considered to be an acceptable starting point given the unknown form of the carbon produced from electrical discharge. The peak model created for this sample has been used to fit graphitic carbon peaks in the more complex C 1s peak shapes seen in the degraded samples. A survey spectrum identified the sample as containing carbon (99.1 ± 0.1 At %) and oxygen (0.9 ± 0.1 At %). The narrow scan of the carbon peak is shown in figure 2.20. The main peak attributed to graphitic carbon has been fitted at 284.5 eV [92] with an asymmetric line shape, the two other peaks in the fit correspond to a small oxide peak, consistent with the low oxygen content, and a broad π-π* shake up peak at 289.9 eV which accounts for ~6% of the graphite peak intensity. The peak shape and fitting agrees with the literature on graphitic forms of carbon [97, 98]. This peak shape has been used as a basis to fit the graphitic carbon peaks in subsequent data.

![Figure 2.20. C 1s narrow scan from carbon black. Inset is a magnification of the C-O- and π-π* components.](image-url)
Analysis of the XPS imaging data is more complex. It requires processing and noise reduction as the data are 256 x 256 pixels, each containing a spectrum. Such processing drastically reduces the required scanning times to acquire an acceptable signal-to-noise ratio. This is achieved using a non-linear iterative partial least squares (NIPALS) procedure. This is based on a principal component analysis (PCA) which states that any dataset can be fully described by a linear combination of components ordered by variance. The procedure sorts the dataset into a number of principal components, or abstract factors, such that the 1st abstract factor contains the greatest possible variance from the data. The 2nd abstract factor contains the greatest possible variance from the remaining data and so on. Eventually the higher factors contain only the noise in the data and can be discarded, improving the signal-to-noise level greatly. The remaining principal components are enough to completely reconstruct the original data minus the noise. The NIPALS procedure reduces the computational requirements of this process by allowing the calculation to be terminated once enough abstract factors have been determined. The number of abstract factors desired can be set in the CasaXPS software.

This method is used to generate atomic concentration images. Creating chemical component images requires classifying the pixels in an abstract factor by intensity, similar to separating elevations on a contour map by colour. This orders the data by the changes in the image, such as the pixel intensity or binding energy shifts. By summing the pixels in each classification spectra are created for pixels of similar chemistry. From these spectra peak models may be made in the same way as for standard transmission spectra. These peak models may then be applied to the noise-reduced spectra and converted back to the final chemical component images. An example of a classified abstract factor and the corresponding peak models is shown in figure 2.21.
Figure 2.21. (a) An XPS imaging abstract factor with pixels classified by intensity. Four colours have been chosen to represent the image, red being least intense and orange most intense. (b) The corresponding coloured spectra and peak model for the pixels summed from (a) Here, three components labelled O 1, 2 and 3 have been fitted to the data for each classification. The same peak model is used for each spectrum.
3. Artificial voids in LDPE

Artificial void samples were investigated with XPS using the NCESS facility and the Manchester and Cardiff based Kratos spectrometers. Samples were investigated with confocal Raman spectroscopy by Dr. Nicola Freebody prior to analysis with XPS. Samples were investigated in the as-received state subsequent to being cut down to an acceptable size. Many voids were investigated; however, most were not well suited for XPS analysis. Due to time constraints on access to XPS instruments efforts were concentrated on gaining higher quality results from two particular voids, the data from which is presented in this chapter.

3.1 Raman analysis

Raman spectra were taken from regions of interest in several voids, in a number of different materials. An optical image of a void in LDPE in which breakdown had occurred, is shown in figure 3.1, with labelled regions of interest. Position A denotes a region away from the void, position B is an area in the void centre, position C is towards the void edge and position D is on the void edge. The Raman spectra shown in figure 3.2 were taken from the corresponding regions of interest labelled in figure 3.1. Position A shows the Raman signal associated with undamaged LDPE. There are no signs of degradation outside the void. A reduced LDPE signal is seen in position B due to the focus of the Raman laser being in the centre of a hole; no signal would be expected here but it is possible for confocal Raman to receive signal from a significant distance above and below the focal point [99]. Position C features a rise in background signal on top of the LDPE associated with the presence of fluorescent chemical species. Position D shows no trace of the original polymer, it has been replaced by a large fluorescent background and 2 distinct bands at approximately 1250 and 1550 cm\(^{-1}\). These are the D and G bands attributed to the presence of sp\(^2\) hybridised carbon [100, 101] and so in this region the discharge energy involved in the breakdown was sufficient to cause chain scission of the polymer and reform it into a disordered graphite-like form, such as polyaromatic hydrocarbons (PAHs).
Figure 3.1. An optical image of a void in which electrical breakdown has occurred. Letters denote lateral positions from which the Raman spectra shown in figure 3.2 were taken [102].

Figure 3.2. Raman spectra of the lateral positions labelled in Figure 3.1. The intensity scale is arbitrary [102].
The features described here were common to all materials investigated – areas in which breakdown had occurred were blackened and the Raman spectra of these show the D and G bands associated with sp² carbon. These bands were associated with a dramatic rise in background signal due to fluorescence, often completely swamping the signal from the original polymer matrix. It is not possible to identify the chemical species responsible for the fluorescence using Raman spectroscopy.

3.2 XPS analysis

3.2.1 Void 1

This void sample was produced with a voltage of 10 kV and had broken down under the applied electric field; Raman studies had found evidence of disordered sp² carbon, which we aimed to find in the XPS spectra. A representation of the positions on the sample of two transmission scans and imaging scans is shown in figure 3.3. The void can be seen in the form of a channel across the surface, with a blackened region surrounding it. The central hole extends through the full thickness of the sample, exposing the carbon putty used for sample mounting. Survey spectra taken over and away from the void showed the presence of significant C 1s, O 1s and Si 2p peaks in both positions with a C:O:Si ratio of 12.4:1.7:1 over the void and 7.9:1.9:1 away from it. An increase of ~ 10% in carbon concentration is seen over the void. Traces of gold and iodine may also be seen along with significant silicon and oxygen peaks in both positions. Relative to the C 1s set to 285.0 eV, the Si 2p peak is positioned at 102.0 ± 0.5 eV and is associated with siloxane bonds. Given the 1:1 stoichiometry between Si and O in the siloxane bond the majority of the O 1s content is also accounted for in this assignment, leaving ~ 5 % unaccounted for.
Figure 3.3. An image of void 1 showing the estimated positions of the 0.5 mm x 6 mm X-ray beam for the transmission scans over (red) and away (green) from the void. The small blue area represents the 70 µm x 2.1 mm area of the imaging scans.

The imaging mode scans for C 1s, O 1s and Si 2p over the void, shown in figure 3.4, show two shifts towards higher binding energy across the void centre followed by a shift back towards the initial binding energy on the far side of the void. The shifts that are seen are not thought to be a result of a chemical shift as they are equal in magnitude in each element, and chemical shifts vary with element. Instead, it is likely that they highlight regions of differing conductivity in the void. Since charging shifts the peaks to higher binding energy these lower binding energy areas can be seen as having a higher electrical conductivity than the rest of the sample. This may be expected if the void contains a surface layer of carbonized breakdown products. Since the sample contains a hole in the centre, as seen in figure 3.3, the region of interest is considered to be the one giving rise to the first binding energy shift which represents the blackened breakdown region on the edges of the void.
Figure 3.4 Imaging mode scans of void 1 for C 1s, O 1s and Si 2p respectively. An intensity drop-off is seen in the oxygen and silicon signals in the sampled region, over the void, but this is not seen in the carbon signal. The red line shows the region sampled in the narrow scan shown in figure 3.6.

The transmission mode C 1s and O 1s narrow scans, shown in figure 3.5, are expected to contain an average of the data seen in the imaging scans. The C 1s data has been fitted with peaks with assignments according to table 2.1 in chapter 2 with C-H defined to be at 285.0 eV binding energy. C-O- is seen at 286.1 eV, C=O/O-C-O at 287.6 eV, O-C=O at 289.1 eV and a graphitic carbon peak at 284.4 eV. The presence of a peak associated with a π-π* transition at 293.5 eV binding energy provides further evidence for the presence of graphitic carbon. The O 1s and Si 2p scans show a small feature to high binding energy as a result of charging. The O 1s peak has been fitted with peaks corresponding to the oxide species in the C 1s spectra. The species concentrations from the O 1s peaks do not fully account for the corresponding peaks in the C 1s spectrum. One explanation for this discrepancy is that the sensitivity factors used in calculating the relative concentrations are universal factors from the CasaXPS
program, as opposed to empirically derived factors for the NCESS spectrometer which is the case for the Kratos spectrometer data. Alternatively, it may be seen that the peak position in figure 3.4 drifts with position and this may increase the signal intensity in the C 1s oxide region of the transmission scan, due to the signal being an average over a wider area than the imaging scan. A peak assigned to metal oxides, considered likely to be a result of the gold and iodine contamination is also seen.

A C 1s spectrum extracted from the region labelled in figure 3.4 is shown in figure 3.6. A graphitic carbon peak accounting for 24.7 ± 0.3 % of the total C 1s may be fitted to the C 1s data but there is no evidence of oxidised carbon components or of a π-π* shake-up peak. The binding energy window of the imaging scan does not extend to high enough energy to include the π-π* peak seen at 293.5 eV in figure 3.5. Other carbon spectra from the imaging scans show similar features and O 1s and Si 2p spectra show a single peak. These areas within the void do not show signs of the chemical changes seen in the transmission mode scans. The smaller analysis area involved causes a marked reduction in the signal-to-noise ratio, potentially burying small components. Alternatively, the oxidised components may lie further outside the void itself as the imaging signal comes from a smaller area than the transmission scans. The imaging mode scan shows an increase in graphitic content relative to the transmission mode scan. Again, this may be explained by way of the larger analysis area in transmission scans showing that the graphite is concentrated in the centre of the void. This agrees with Raman analysis, which found varying degrees of fluorescence surrounding localized areas of high graphitic carbon content. Fluorescence is either a result of fluorescent impurities or species introduced as a result of ageing. As fluorescence is a common feature of ageing in Raman spectra it is unlikely that impurities account for this. In the XPS analysis, areas of oxidised carbon frame regions of graphitic carbon and it is therefore possible that the fluorescence is associated with the presence of oxidised carbon components. C-O, C=O and O=C-OH groups have been shown to play a significant role in fluorescence of graphene oxide [103], which may support this.
Figure 3.5. Transmission mode narrow scans of the (a) C 1s and (b) O 1s peaks over the void for sample void 1. Oxidised components and a peak attributed to graphitic carbon are present. The inset data in (a) is a magnification of the $\pi-\pi^*$ transition peak associated with the graphitic carbon peak.
Figure 3.6. C 1s narrow scan integrated from the sampled region shown in figure 3.5. The data are taken from the region labeled -0.4 to -0.5 on the y axis. The peak shows no evidence for oxidised carbon components but shows the presence of a peak assigned to graphitic carbon.

The void 1 sample was also analysed using both a series of scans across a line and the 2d imaging mode at the Manchester Kratos spectrometer. The line scan consisted of four scans with a 110 µm spot size and a separation of 300 µm. The positions of the line and image scans on the sample are shown in figure 3.7. Imaging scans of the C 1s and Si 2p / Au 4f regions were taken in a 400 x 400 µm area.

Table 3.1 contains the elemental ratios of C:O:Si for the four positions shown in figure 3.7. The ratios for positions 1 and 2 are comparable and show the highest carbon and oxygen content relative to silicon. In position 3 the relative carbon content is lowest, before increasing again in position 4. The relative oxygen content in positions 3 and 4 is also reduced. The relative carbon content in all positions is less than that seen both over and away from the void from the NCESS data on this sample. This change is largely accounted for by a 2-fold increase in the Si concentration. As the Si is a contaminant this change may be
due to an increase in surface contamination in the time between the data sets were taken.

Figure 3.7. An image of the void 1 sample inside the analysis chamber of the Manchester Kratos spectrometer taken with an optical microscope attached to the spectrometer. Displayed in blue are the positions where the line scans were performed and square area over which the image scan was taken.

<table>
<thead>
<tr>
<th>Scan position</th>
<th>C:O:Si ratio (± 3%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5:1.5:1</td>
</tr>
<tr>
<td>2</td>
<td>5.2:1.4:1</td>
</tr>
<tr>
<td>3</td>
<td>4.1:1.2:1</td>
</tr>
<tr>
<td>4</td>
<td>4.7:1.3:1</td>
</tr>
</tbody>
</table>

Table 3.1. C:O:Si ratios for the 4 line scan positions across void 1. A drop in relative carbon content is seen in position 3, towards the centre of the void.

These ratios do not show evidence of increased carbon content towards the edges of the void as expected from Raman analysis; however, with a scan of
only four positions, it is probable that the line scan does not extend far enough beyond the void itself for a comparison to the undamaged polymer.

A comparison of the C 1s and O 1s narrow scans from the four positions is shown in figure 3.8, with associated component concentrations given in table 3.2. There is a graphitic carbon component present in all four positions. The concentration of this component varies across the void, accounting for 28.5% and 38% of the total C 1s signal in positions 1 and 4 respectively and peaking at 51.4% at position 3 in the void centre. A graphitic peak of 25.7% concentration is seen in position 2 within the void. Limited amounts of carbon oxidation can also be identified at all positions. The components in positions 1 and 2 show similar contributions associated with C=O and O-C=O groups with little contribution from C-O groups. Position 4 shows the most significant oxide component as C-O with only small traces of C=O and O-C=O. Position 3 shows the least evidence of oxidation with only small traces of oxide components and no peak present at ~530 eV. This peak, present in the other 3 positions, is in a region associated with metal oxides and while there are traces of metals detected in the survey scans there are insufficient amounts to account for this peak. As such, the presence of this peak may suggest some underlying issues in charge compensation. The main O 1s peak is attributed to various levels of oxidised silicon due to the silicon contamination; if this takes the form of surface debris then some differential charging may be expected.

<table>
<thead>
<tr>
<th>Position</th>
<th>C 1s At %</th>
<th>O 1s At %</th>
<th>C-O%</th>
<th>C=O%</th>
<th>O-C=O%</th>
<th>Graphitic carbon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>67.5 ± 0.9</td>
<td>18.0 ± 1.3</td>
<td>2.8 ± 0.4</td>
<td>0.3 ± 0.2</td>
<td>0.5 ± 0.2</td>
<td>38.4 ± 0.8</td>
</tr>
<tr>
<td>3</td>
<td>65.6 ± 0.5</td>
<td>18.5 ± 0.7</td>
<td>0.4 ± 0.2</td>
<td>0.8 ± 0.3</td>
<td>-</td>
<td>51.4 ± 1.1</td>
</tr>
<tr>
<td>2</td>
<td>68.2 ± 1.2</td>
<td>18.1 ± 1.7</td>
<td>-</td>
<td>1.6 ± 0.4</td>
<td>0.5 ± 0.2</td>
<td>25.7 ± 0.7</td>
</tr>
<tr>
<td>1</td>
<td>66.4 ± 1.1</td>
<td>19.9 ± 1.4</td>
<td>0.5 ± 0.2</td>
<td>1.4 ± 0.4</td>
<td>0.6 ± 0.2</td>
<td>24.5 ± 0.4</td>
</tr>
</tbody>
</table>

Table 3.2. The variation of C 1s and O 1s elemental concentration and C 1s species in a line across the degraded region of void 1. The components are given as a % of the total C 1s signal.
Figure 3.8. Narrow scans of the four points from the line scan of void 1 for (a) C 1s and (b) O 1s. Inset is a magnified view of the oxidised carbon components. The scan position is labelled at the right of each scan. Peak heights have been normalised to the main peak.
This data set compares favourably with that acquired with the NCESS spectrometer and shows a level of signal-to-noise and spatial resolution intermediate between the NCESS transmission and imaging scans. The higher signal-to-noise ratio with respect to the imaging scan in figure 3.6 allows for low levels of oxidised peaks to be identified as seen in the narrow scans in figure 3.5. This suggests that the low signal to noise in figure 3.6 may account for the lack of oxidised components. The level of oxidation is still less than is present in the transmission scans in figure 3.5. This suggests the oxidation is present in a larger area than that scanned with the line scan. The graphitic carbon concentration is comparable to that seen in the spatial imaging scan in figure 3.6 rather than that seen in figure 3.5, corroborating the evidence that graphitic carbon is concentrated within the void. This is a result of the greater spatial resolution compared to the narrow scans, allowing for higher sensitivity to the graphitic carbon in the void centre as seen in the imaging scan. It may be inferred from this that the oxidation occurs over a greater area than the production of graphitic carbon, and that localized regions of high graphitic content occur with little oxidation present.

Imaging scans, as seen in figure 3.9, were taken from the region highlighted in figure 3.7 for the C 1s, Si 2p and Au 4f regions. Time constraints prevented an O 1s image scan from being taken. An increase in carbon content can be seen over the void (in the top left of the image) with a corresponding decrease in silicon content and an almost total disappearance of the gold signal. This matches the findings of the NCESS data with a ~10% increase in C 1s content compared to Si 2p over the void. The presence of gold comes from the contacts used to create the breakdown and so it is not expected to be present within the void itself. Each pixel in the images represents an individual spectrum, and so it is possible to generate spectra from specific regions of interest. C 1s spectra created from the top left and bottom right regions (i.e. over and outside the void) showed no visible chemical differences beyond the increase in intensity.
3.2.2 Void 2

Void 2, like void 1, had broken down under the electric field applied. The data should therefore be comparable with those for void 1, although this void was produced at a higher voltage of 14 kV. It was studied using a 7-point line scan across the void. A 110 µm spot size with a 250 µm separation between positions was used. An image of the scanned region is shown in figure 3.10. Visually, this void appears less degraded than void 1, which was blackened throughout the void region. In this case the region of interest consists of a dark ring around a depression. Void 1 took the form of an extended channel, as opposed to the more circular void seen here.

The sample was found to contain oxygen and silicon with traces of gold and nitrogen. The elemental variation of O and C across the sample, seen in table 3.3, shows a decrease in the O:C ratio over the centre of the void. Also contained in table 3.3 is the concentration of the C 1s components. The 7 narrow scans of the C 1s peak, shown in figure 3.11, contain peaks associated with oxidised carbon components, and reflect the oxygen variation in a decrease in C-O, C=O/O-C=O and O-C=O oxidised carbon components in the void centre. The relative ratios of these components are quite stable; species with higher numbers of carbon-oxygen bonds appear with lesser intensity than
those with fewer. Small concentrations of graphitic carbon were observed across all positions, with increased concentrations seen in positions 6 and 7, at one edge of the void. The graphitic content in these two positions is 2-5 times larger than elsewhere in the void; these positions are on the darkened ring seen in figure 3.10 and so it is expected that graphitic content would be greater here.

![Figure 3.10. An optical image of void 2 showing the positions of the seven scans. Positions 1 and 7 are labelled. The dark region to the upper left is residual carbon tape on the sample underside from the sample mounting.](image)

<table>
<thead>
<tr>
<th>Scan position</th>
<th>C 1s At %</th>
<th>O 1s At %</th>
<th>C-O%</th>
<th>C=O%</th>
<th>O-C=O%</th>
<th>Graphitic carbon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>80.8 ± 1.0</td>
<td>11.5 ± 0.8</td>
<td>6.5</td>
<td>2.1</td>
<td>1.4</td>
<td>10.2</td>
</tr>
<tr>
<td>6</td>
<td>78.9 ± 1.1</td>
<td>11.5 ± 0.9</td>
<td>4.6</td>
<td>2.2</td>
<td>1.2</td>
<td>8.8</td>
</tr>
<tr>
<td>5</td>
<td>84.2 ± 0.9</td>
<td>8.3 ± 0.6</td>
<td>3.2</td>
<td>0.9</td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>84.1 ± 1.1</td>
<td>8.9 ± 1.0</td>
<td>1.8</td>
<td>1.3</td>
<td>0.1</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>80.6 ± 1.3</td>
<td>11.0 ± 1.2</td>
<td>2.2</td>
<td>1.7</td>
<td>0.6</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>78.5 ± 1.1</td>
<td>13.1 ± 1.0</td>
<td>4.3</td>
<td>1.7</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>1</td>
<td>79.0 ± 1.0</td>
<td>13.8 ± 0.9</td>
<td>6.7</td>
<td>2.1</td>
<td>1.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 3.3. The variation of C 1s and O 1s elemental concentration and C 1s species in a line across the degraded region of void 2.

As the void is a hollowed depression in the material it may be that the variation apparent here is simply a result of degradation being stronger closer to the electrodes. If the undamaged void is spheroid in shape then the edges parallel
to the electrodes will have a shorter gap between the void walls than in the centre, potentially resulting in a lower breakdown voltage and higher partial discharge activity, leading to greater degradation. This may explain why the breakdown appears as a dark ring around the void edge if this region has a higher electrical discharge activity. The increased graphitic component towards one sample edge is consistent with the position of this dark ring although it is unclear why this is not seen at both edges. The scan areas are smaller than the gap between scan positions and as such do not overlap, allowing for the possibility of this expected region of increased graphitic carbon being missed between two positions. A higher concentration of graphitic carbon towards the void edge is also consistent with the findings of Raman analysis.

In comparison with the void 1 sample, void 2 appears less visually degraded than void 1. The degradation shows differences in the extent of oxidation and graphitic carbon content. In void 2, oxide components account for up to ~10% of the total C 1s content, with the graphitic carbon accounting for an equal percentage. In the void 1 sample, graphitic carbon accounts for as much as 51.4% of the C 1s peak whereas oxide components only account for ~3.5% at most. Additionally in the void 1 sample, the oxidation is seen to be reduced in areas with increased graphitic content whereas in void 2 the opposite is observed. The two void samples were produced at differing applied voltages, with void 1 produced at 10 kV and void 2 at 14 kV, which may suggest an energy dependence on the products formed; more investigation at a range of energies would be required to confirm this. Although there is a larger degree of variation in void 1, in both samples there is a general trend for more highly oxidised species to occur in lesser concentrations - carbon singly bound to oxygen is, in general, seen in higher concentration than doubly bound species, which are, in turn, more abundant than triply bound groups. Both samples show that partial discharges followed by breakdown cause extensive departures from the base polymer chemistry via the production of oxidised species and localized regions of high graphitic carbon content.
Figure 3.11. Carbon 1s narrow scans for the void 2 line scan showing the components at the foot of the main peak. Inset is the full region of the C 1s peak from position 1. The scan position, 1 through 7, is labelled to the right. Peak intensities are normalised to the main peak at 285.0 eV. The concentration of oxidised carbon components is seen to decrease in the void centre and an increased graphitic component is seen in positions 6 and 7 on the edge of the void.

3.3 Conclusions

From the studies of these samples we may conclude that the process of electrical breakdown in the voids results in an increase in relative carbon content. This is accompanied by the appearance of C-O, C=O/O-C=O and O-C=O functional groups. Raman spectroscopy on these samples results in a large fluorescent background over the voids, likely to be contributed to by these components. Parts of the breakdown contain graphitic carbon, consistent with the findings of Raman spectroscopy. In void 2, larger concentrations of these degradation products are found towards the edges of the void, whereas in the data for void 1 the void centre shows a large graphitic component and small amounts of oxidised carbon components. Larger concentrations of oxide components are seen in large area transmission mode scans, suggesting that
the oxidised components may extend over a larger area than the void itself, which then give way to graphitic components in the centre. Again, this is largely consistent with the findings of the Raman spectroscopy, where fluorescence and graphite like carbon signals are found in greatest concentration at the edges of voids.
4. Breakdown channels in PDMS

Electrical tree breakdown channels are the end result of an electrical tree crossing an insulator and bridging the HV electrodes. Destructive currents may then flow, causing the insulator to fail. Breakdown channels are typically much larger than the trees that produce them. Tree channels are typically ~ 10 µm in diameter, on the limits of XPS imaging resolution, whereas breakdown channels may be 1-2 orders of magnitude larger. Raman spectra of breakdown channels, as explained in section 4.1, show analogous features to conducting tree channels but with increased intensity [102]. XPS may be used to identify As such, analysis of breakdown channels may be used to investigate the chemical products from the treeing process.

A series of breakdown channels in PDMS were produced at the University of Southampton by Dr Nicola Freebody as described in chapter 2; a hypodermic needle is inserted into a block of PDMS with a plane electrode attached to the opposite edge, a so called point-plane electrode setup, and a high voltage applied to the needle. This causes tree growth and eventual breakdown. In this chapter, data from four different samples are presented. The samples produced at differing discharge voltages on the needle of 10, 11, 14 and 15 kV in order to investigate the chemical products produced and the effect of the applied voltage upon these products. The samples were cut and sectioned using a cryomicrotome to produce samples of approximately 2 x 5 x 0.5 mm such that part of the inside of the channel is exposed and running along the surface. An optical image of a typical breakdown channel after sectioning is shown in figure 4.1. As in the data from chapter 3 these samples were then investigated by Dr Freebody with Raman spectroscopy prior to being sent to The University of Manchester for further analysis. Different samples were analysed using four methods, standard XPS line scans across the surface, XPS imaging of the breakdown channels, XPEEM and finally SEM imaging.
Figure 4.1. An image of a typical sectioned sample of PDMS containing a breakdown channel produced using an applied voltage of 11 kV. The channel can be seen towards the sample centre with blackened edges. The sample transparency obscures the fact that the inner channel surface is only exposed at the sample surface at certain points along its length. XPS analysis is only possible at these points as the rest of the channel is subsurface.

4.1 Raman analysis

Raman spectroscopy was used to investigate a breakdown channel formed using a 15 kV breakdown voltage as shown in figure 4.2. Four areas were scanned in and around the channel. The corresponding scans in figure 4.3 show evidence of the D and G bands of graphitic carbon at approximately 1250 and 1550 cm$^{-1}$ on a background of fluorescence mixed in with the signals for undamaged PDMS in the 500-800 cm$^{-1}$ region. The graphitic carbon content varies relative to the fluorescence and PDMS signal in each position. This variation is significant even in the three positions A, B and D within the breakdown channel, showing that the production of graphitic carbon is not constant through the channel. This suggests that either the graphitic coverage is incomplete across the surface or that the thickness of the graphitic layer is variable. As can be expected the smallest D and G bands are seen in position C, which is just outside the channel; however, these bands are still present and a large fluorescent background is seen, suggesting that degradation is occurring in a region outside of the channel. In order to produce the D and G bands seen in the LDPE voids in chapter 3 the reaction must involve chain
scission of the polymer. In the case of chain scission in PDMS the most common by product from the Si-O backbone would be SiO$_2$, and the presence of this would be detectable in Raman spectra from a band at 464 cm$^{-1}$. This band is not seen in any of the Raman spectra and therefore suggests that chain scission of PDMS is not occurring. It is likely that the energy involved in the partial discharges in the tree channel during formation are sufficient to break the Si-C (326 kJmol$^{-1}$) bonds of the side groups but insufficient to overcome the higher bond energy of the Si-O bonds of the backbone (443 kJmol$^{-1}$) [70].

![Figure 4.2](image.jpg)

Figure 4.2. An optical micrograph of a 15 kV breakdown channel in PDMS, with the dashed line showing the channel axis. The labelled regions correspond to scanned areas in figure 4.3. The line features outside the channel are a result of the microtoming process. Figure adapted from [102].
4.2 XPS Line scans

Line scans were performed in the same way as described in chapter 3; a 110 µm spot size was used with a 300 µm separation between scans. In order to find regions where the channels were exposed to the sample surface rough XPS imaging was used. This found regions within the channel area where the signal disappeared, signifying areas where deep channels out of the focal plane of the spectrometer were present. For this, the energy of the O 1s peak was used as it gave the greatest signal-to-noise ratio. Once the region of interest was identified for each sample, six scans were taken along a line parallel to the long axis of the sample approximately perpendicular to the breakdown channel with a total distance travelled of 1.5 mm across the surface of each sample. The scan end points were arranged such that the centre of the channel was halfway along the line scan, giving scans up to 0.75 mm either side of the channel centre. The spectra from the line scans of each sample are presented in figure 4.4 for ease of comparison, with discussion in the sections that follow.
Figure 4.4. C 1s line scans for PDMS breakdown channels produced using a voltage of (a) 10 kV, (b) 11 kV, (c) 14 kV, (d) 15 kV. Peaks are normalized to the C-H component. All images have the same scaling, except for (d) due to the large graphitic carbon components. The inset image in (d) shows a spectrum from the position indicated with an arrow. This spectrum has the same scaling as the other spectra.
4.2.1 10 kV channel

The survey spectra from a line scan across a 10 kV breakdown channel show the presence of C, O and Si only with < 2.5 atomic % concentration (at %) variation in composition across the surface. The average C:O:Si ratio is (1.65 ± 0.05):(1 ± 0.03):1 showing a carbon deficiency compared to unaged PDMS which has a 2:1:1 C:O:Si ratio. C 1s narrow scan spectra from the line scan across a 10 kV breakdown channel are shown in figure 4.4 (a). Components attributed to traces of oxidised species are seen; C-O- at 286.7 eV, C=O/C-O-C at 287.6 eV and O-C=O at 289.2 eV are all present though the C-O- component is only seen in one of the central positions. The quantities of these components are typically < 1 % of the total peak and the signal to noise ratio at this level is poor, leading to a 50-80% uncertainty in the concentrations. Traces of graphitic carbon have also been fitted to 3 positions. 2 components are present in the Si 2p spectra with Si 2p 3/2 peak positions of 102.3 eV and 103.5 eV. These are associated with Si-O- bonding and Si-Ox bonds respectively and are accounted for in the O 1s fits. The relative amount of these components is stable across the scanned region with the Si-O- component accounting for 78.2 ± 2.2 % of the total silicon. There is no pattern seen across the spectra; the oxidation in the C 1s and Si 2p signal is quite evenly distributed although it is unclear in the C 1s case if this is due to a true lack of variation in chemistry across the scanned region or if a clear pattern is obscured by the noise in the data.

4.2.2 11 kV channel

Survey spectra of the 11 kV breakdown channel show < 2 at % variation in composition across the surface and contain C, O, and Si only with a C:O:Si ratio of (1.7 ± 0.03):1:(1.1 ± 0.02). The C 1s narrow scans, shown in figure 4.4 (b) show very little chemical change (< 1% variation in component concentration across the spectra) in terms of oxidised components. Some traces of graphitic carbon are seen towards the ‘top’ edge. This sample shows the least variation in chemistry with position of all the channels scanned; however, it was also a sample with only a small channel exposed to the surface. As the line scan areas are smaller than the distance between scans it is possible that the line scan passed over the area of the channel with the bulk of any chemical changes lying between two scans, resulting in little apparent change.
4.2.3 14 kV channel

Survey spectra of a 14 kV breakdown channel revealed little (< 2 at %) variation in the C, O and Si content across the sample and no evidence of impurities. The average C:O:Si ratio is $(1.65 \pm 0.04):(1 \pm 0.03):1$, again showing a carbon deficiency compared to unaged PDMS. An overlay of the C 1s spectra is shown in figure 4.4 (c). As with the 10 kV channel only traces of oxidised carbon components are seen, accounting for < 2.5 % of the total C 1s signal at any position. Also seen are traces of graphitic carbon at the 2-3% level in four of the scanned positions, position 1 contains no evidence of graphitic carbon and position 2 contains the largest concentration at $6.7 \pm 1.1 \%$. As with the 10 kV channel the oxidised components are predominantly C=O/O-C=O and O-C=O, with C-O- only seen in one central position. In contrast to the 10 kV channel there is a visible increase in the level of oxidation in the central three scans, and this includes the scan with increased graphitic carbon content.

4.2.4 15 kV channel

The survey spectra from the line scan across a 15 kV breakdown channel show the presence of C, O and Si only as with the other channels. The average C:O:Si ratio is $(2.2 \pm 0.2):1:(1.2 \pm 0.1)$ showing a carbon rich and oxygen deficient surface compared to unaged PDMS. An overlay of the C 1s spectra is seen in figure 4.4 (d), although no clear pattern with position is seen, a large amount of graphitic carbon is present in a number of positions with concentration ranging from $2.5 \pm 1.4\%$ to $16.7 \pm 1.1\%$. There is no fit for oxidised carbon components in contrast to the channels at lower energies. This correlates with the relative increase in carbon content and decrease in oxygen content in comparison to the other channels.

4.2.5 Discussion

Across the four samples some trends are visible. There are greater amounts of graphitic carbon seen in the channels produced at higher voltages, namely the 14 and 15 kV samples. Oxidation is present in varying amounts at all energies except for the 15 kV channel, where no oxidised components have been fitted to the data. The only variable changed between these samples is the applied
voltage; all other parameters, such as the oxygen availability for oxidation, should be constant between samples. This may suggest a dependency of the final breakdown products on the discharge energy used to create the breakdown channel, with higher energies producing relatively more graphitic carbon content. Assuming any loss in concentration of PDMS over time is equal to the gain in graphitic carbon concentration (i.e. a first order rate equation) it is possible to test if graphitic carbon production is an activated process. The natural log of the total graphitic carbon concentration for each sample, calculated as the sum total area of graphitic carbon components divided by the total C 1s signal, is shown in figure 4.5 plotted against $1/V^2$. This plot represents a linearization of an Arrhenius rate equation,

$$C_G \propto e^{-\frac{E_a}{kT}},$$

where $C_G$ is the graphitic carbon concentration, $E_a$ is an activation energy required for the reaction to occur and $kT$ is the energy available. In this case the energy in the electric field applied to the sample is proportional to $V^2$.

![Figure 4.5. A plot of the total observed graphitic carbon concentration, $C_G$, for each PDMS breakdown channel against $1/V^2$.](image)

There are limited data points and the production and measurement of the graphitic carbon is dependant on a number of factors, such as the accurate positioning of XPS scans over the channels, the channel size and the tree growth rate for each sample. Despite this the plot suggests that the production
of graphite may be an activated process, with a rate exponentially dependant on the supplied energy and an energy barrier before production starts. An energy dependency of the oxidised components is unclear. It may be that there is a cut off in energy after which oxidation gives way to entirely graphitic carbon production. A possible explanation is that at higher energies complete oxidation to CO$_2$ occurs and as it is gaseous in nature it therefore escapes the sample surface, preventing its detection in XPS. CO$_2$ has been identified as a gaseous product formed from partial discharges and corona discharge in PE by Sekii [64] and Wolter [65]. Sekii found the CO$_2$ concentration increased with O$_2$ presence but energy dependence was not tested. There is a carbon deficiency relative to the nominal PDMS stoichiometry in all but the 15 kV spectra which may come about either by a reduction in the carbon present or an increase in both Si and O. CO$_2$ loss may account for a loss of carbon in these samples, with the lack of oxidation in the 15 kV channel explaining why carbon is not lost in this case. The energy dependency is further discussed in chapter 5.

In those samples with oxidised components, the components are in general present at all scanned positions. Graphitic carbon, when present, is also generally seen in most positions. The area of the exposed channel on the sample surface is expected to vary due to the stochastic nature of electrical breakdown and the dependency on the depth of the sectioning. However, the average width of the visible channels is similar in each case at ~ 400 µm. Due to the size and separation of the scans which comprised each line scan it is expected that the channel itself would be included in 1-2 scans depending on the alignment of the central scans with respect to the channel and the amount of surface-exposed channel. As the line scans cover a distance of 1.5 mm, for a ~400 µm channel this suggests the degradation is seen at least ~550 µm from the channel. While the Raman spectra (figure 4.3) do not extend further than 100 µm outside the channel there is evidence of degradation in the region scanned outside of the channel which agrees with these findings.

In comparison to the findings from the artificial voids in LDPE in chapter 3 there is a lesser level of degradation seen in these samples. This may be a result of differences in the oxygen availability between the two systems as a void may
be expected to contain a much larger amount of gas prior to electrical breakdown than the electrical tree channels which precede breakdown channels. Alternatively, the difference may be due to the different natures of the base polymers used. In particular, PDMS is known to display a self-healing mechanism on its surface which, over time, acts to bury aged surface components with low molecular weight oligomers (see chapter 1). PDMS also has higher bond energy for the Si-O backbone than LDPE increasing its resistance to degradation.

4.3 XPS imaging

XPS imaging, as explained in chapter 2, simultaneously scans an area while maintaining the spatial origin of detected electrons, producing a 2D image of the sample at a particular energy. By scanning in steps of energy, a 2D image of the surface may be formed where each pixel represents a full spectrum over the energy range selected. This allows images of elemental concentration and chemical state composition to be produced with a resolution of up to ~12 µm [104] for the 800 x 800 µm field of view used for the images presented here. Imaging scans were taken for three of the breakdown channel energies, 11, 14 and 15 kV. In each case, image scans were taken in 0.1 eV steps over the C 1s, O 1s and Si 2p energy ranges at a pass energy of 40 eV. The 14 kV sample is presented first as it provides a good overview of the features identified for comparison with the 11 and 15 kV data.

4.3.1 14 kV breakdown channel

Elemental concentration images for C, O and Si are shown in figure 4.6. Charge referencing the C 1s peak to 285.0 eV shifts the positions of the O 1s and Si 2p peaks to 532.1 and 102.1 eV respectively which are the expected peak positions for undamaged PDMS. A broad channel can be seen in the central region of each image, this channel appears intense in the C 1s image and weak in the O 1s and Si 2p images showing the presence of a carbonized channel in the image centre. The channel is approximately 400 µm across at its widest point. In the centre of the channel there is an area with no signal since the surface in this region is out of the focal plane of the spectrometer, i.e. a
relatively deep section of channel. A minimum count threshold for inclusion in the image has been used to filter out erroneous counts from this region. Two ‘islands’ can be seen inside the channel in the O 1s and Si 2p images, with no contribution from the carbon signal. These islands contain an approximately (2 ± 0.2):1 Si:O ratio. It is unclear what the origin of this signal is, the most stable product from the breakdown of the Si-O backbone in PDMS would be SiO₂ but this would require an Si:O ratio of 1:2 which is not seen here. Figure 4.7 shows an overlay of the three images seen in figure 4.6. This shows again the carbonized channel and also regions of relatively increased silicon content (in blue) on the upper channel edge, and increased oxygen seen (in green) on the lower channel edge. A line scan, shown in figure 4.7 (b), indicates the atomic concentration of C, O and Si along the line seen in figure 4.7 (a). This scan shows that the C 1s concentration approaches 100% in the central channel and outside the channel the C:O:Si ratio is approximately (2.9 ± 0.2):1:(1.2 ± 0.1). Both O 1s and Si 2p have a lower concentration than the expected 25% from the 2:1:1 C:O:Si theoretical stoichiometry of PDMS at ~19% and ~23% each in this region. When compared with the line scan of this sample in section 4.2.3 the elemental variation is significantly larger, the central channel area with 100% carbon content which is clear in the imaging was completely missed by the line scans. This demonstrates the relative advantages in using XPS imaging over line scans for detailed analysis of such features.

Figure 4.6. Elemental concentration images for (a) C 1s, (b) O 1s and (c) Si 2p for the 14 kV breakdown channel. Each image is 800 x 800 µm.
Figure 4.7. (a) An overlay of the elemental concentration images in figure 4.6. (b) A 500 µm line scan showing the elemental concentration along the line shown in (a). The zero of the distance scale represents the ‘top’ end of the line. C – Red, O – green, Si – blue. Figure from [105].

Analysis of the C 1s images revealed the presence of three components (labelled C 1, 2 and 3) and the spatial distribution of these components is shown in figure 4.8. The main C-H peak at 285.0 eV has been assigned to C 2, which positions C 1 at 284.8 eV and C 3 at 286.0 eV. C 1 then fits in the region of graphitic carbon and C 3 fits a C-O- assignment. The C 1 component in figure 4.8 (a) shows greatest concentration within the carbon-rich channel, this is where we would expect to see graphitic carbon produced and so this assignment fits well with findings from Raman and data on electrical trees [51, 100]. This component also shows a band outside the channel across the upper region of the sample which does not appear in the other components, suggesting the existence of graphitic carbon outside of the channel. This fits with the line scan of this sample which showed the presence of graphitic carbon across much of the 1.5 mm line. This region does not show the increase in carbon concentration seen over the channel although the carbon concentration is high over the whole image compared to unaged PDMS. There is also a difference in the C 1 component concentration at the top and bottom of the images which is not seen in the C 1s atomic concentration image. The C 2 component in figure 4.8 (b) also shows an increased concentration in the central channel though to a lesser extent, and overall has the most even
distribution of the three components. It is present in all regions apart from the central hole and the region of the upper band in the C 1 component. The C-H assignment to this component fits with its presence throughout the imaging area but the lack of presence in the upper region is unexpected. The C-H presence in the channel suggests that there is not complete coverage of graphitic carbon in the channel itself. This fits with the Raman findings and findings for ‘conducting’ electrical trees [51] which showed evidence of the original polymer signal in all scanned positions in channels containing graphitic carbon. The C 3 component shows the least concentration of the three over the image, with the majority of signal confined to a region within the upper left of the channel and some patches in the upper area outside the channel. This component has strong anti-correlation with the C 1 component. This shows that the oxidised and graphitic carbon exist separately with little mixing.

The O 1s analysis also resulted in three components, the images of which are shown in figure 4.9. The O 1, 2 and 3 components are found at binding energies of 532.9 eV, 533.6 eV and 532.2 eV respectively. The O 3 component at 532.2
eV is associated with Si-O bonds in PDMS and as would be expected figure 4.9 (c) shows that this component closely follows the elemental distribution seen in figure 4.9 (b). The O 1 (figure 4.9 (a)) component also shows a similar distribution to the elemental concentration. This peak is in the region for C-O- bonds and so would be expected to fit with the distribution of the corresponding C 1s component, C 3; however, this is not the case. Instead, a closer fit to the C 3 component (figure 4.9 (c)) is seen in the O 2 component in figure 4.9 (b) with the concentration greatest in the upper left region of the image, though the components do not overlap fully. The lack of signal from the two islands supports the idea that this component is related to carbon. The O 2 component is in the binding energy range for O-C=O species but no evidence of this species is seen in the C 1s analysis. It is possible that a component O-C=O is present in small quantities in the C 1s peak but is buried by noise in the data as the amount of oxidised carbon is seen to be low in the line scans in section 4.2 and the O 1s peak has a greater signal-to-noise ratio due to it’s higher sensitivity factor in XPS.

![Figure 4.9](image)

**Figure 4.9.** Three images showing the spatial distribution of the three O 1s components (a) O 1, (b) O 2 and (c) O 3 of the 14 kV breakdown channel. Each image is 800 x 800 µm.
The Si 2p analysis shows 2 components, Si 1 at 102.5 eV and Si 2 at 103.5 eV, the component images are shown in figure 4.10. The majority of the Si 2p concentration is seen in Si 1, which is attributed to Si-O bonds in PDMS. The higher binding energy Si 2 component is in the region for more oxidised SiO\textsubscript{x} bonding and an increased O:Si ratio is seen in the areas with a larger Si 2 component, suggesting this assignment is accurate. This suggests the energy of the discharges involved was enough to cause chain scission of the Si-O backbone in localised regions of the breakdown channel. This goes against the findings of Raman spectroscopy which revealed no evidence of damage to the Si-O backbone, however the high spatial resolution of Raman prevents a general overview of the breakdown region and these localised areas could easily be missed.

Figure 4.10. Images showing the spatial distribution of the two Si 2p components, (a) Si 1 and (b) Si 2 of the 14 kV breakdown channel. Each image is 800 x 800 \( \mu \)m.

### 4.3.2 15 kV breakdown channel

The atomic concentration images for C 1s, O 1s and Si 2p for the 15 kV breakdown channel are shown in figure 4.11. As in the 14 kV sample, the C 1s peak has been charge referenced to 285.0 eV binding energy, shifting the O 1s and Si 2p peaks to 532.7 and 102.9 eV respectively. These peaks are shifted to higher binding energy by \( \sim 0.7 \) eV with respect to the expected position for unaged PDMS. The centre of the scanned region contains an area from which no signal originates due to a deep channel. It is immediately clear that the elemental variation in the scanned region is significantly less than that seen in the 14 kV sample. There is no broad carbon-rich channel, only a small region of
increased carbon to the right hand side of the channel. Oxygen content is higher towards the bottom edge of the scanned region with no significant variation around the channel itself. There is a relative increase in silicon content seen on all the channel edges and a corresponding decrease in silicon content in the region where the oxygen content is higher. These features are shown clearly by the overlay image shown in figure 4.12, which also shows a line scan across the channel. The line scan shows the small amount of variation in carbon, oxygen and silicon across the channel. Along the line selected the C 1s, O 1s and Si 2p concentrations are 46.6 ± 4.0%, 22.1 ± 3.6% and 31.4 ± 3.8% at the end above the channel. Below the channel, the Si 2p content decreases by ~5% with a corresponding increase in O 1s content while the C 1s stays approximately constant. This results in an average C:O:Si ratio of (2.1 ± 0.1):1:(1.4 ± 0.05) above the channel and (1.8 ± 0.1):1:(1 ± 0.03) below it. The ratio for above the channel shows a high silicon content relative to unaged PDMS and is similar to that calculated from the XPS line scan in section 4.2.4, suggesting that this region is more typical of the channel in general. The area below the channel shows a slight carbon deficiency relative to unaged PDMS.

![Figure 4.11. Elemental concentration images for (a) C 1s, (b) O 1s and (c) Si 2p for the 15 kV breakdown channel. Each image is 800 x 800 µm.](image)
The C 1s image analysis shows the presence of three components, C 1, C 2 and C 3. The spatial distribution of each is shown in figure 4.13. The C 1 component has been assigned to C-H at 285.0 eV as it is relatively evenly distributed over most of the surface, with a dark area seen across the image top and in the bottom left. This assignment gives the C 2 and C 3 components binding energies of 284.8 eV and 285.7 eV respectively. From this the C 2 component is associated with graphitic carbon. This component shows a ~ 100 µm wide high concentration band across the region above the channel and some signal to the right of the image. There is no evidence of a band across the channel itself as was seen in the 14 kV sample. It is possible that this band represents a region of the breakdown channel that has been almost completely removed by the microtoming procedure, leaving a small band from the base of the channel. In this case the area with no signal does not represent the channel centre, but an area to the lower edge. There is, however, no corresponding increase in C 1s concentration as was seen in the 14 kV channel. The C 3 component is concentrated in the lower left corner of the image with a high concentration region to the top left of the channel. This component has a higher binding energy than the C-H peak but this binding energy is too low for it to be attributed to C-O- bonds. This energy may be associated with secondary shifts due to carbon atoms adjacent to oxidised species such as O-C=O but there is no evidence of these species and as there are no other elements in the sample this may either be an erroneous fit or a component shifted by sample charging. The shifts in the O and Si peak positions also suggest charging of the sample has occurred.

Figure 4.12. (a) An overlay of the elemental concentration images in figure 4.11. (b) A 650 µm line scan showing the elemental concentration along the line shown in (a). The zero of the distance scale represents the ‘top’ end of the line. C – Red, O – green, Si – blue.
Figure 4.13. Three images showing the spatial distribution of the three C 1s components (a) C 1, (b) C 2 and (c) C 3 of the 14 kV breakdown channel. Each image is 800 x 800 µm.

O 1s analysis again revealed three components, O 1 at 532.2 eV, O 2 at 532.7 eV and O 3 at 533.5 eV, shown in figure 4.14. The O 2 component has been assigned to Si-O as it shows the most even surface distribution and a strong correlation with the C-H component (C 1) in figure 4.11 (a). This component would be expected at 532.0 eV for PDMS but has been shifted 0.7 eV to higher binding energy. This shift was also seen in the overall O 1s peak used in the at % concentration images, suggesting there may be some differential charging present. It may be seen that the O 1 component is correlated with the C 2 component in figure 4.13 (b) attributed to graphitic carbon. The O 1 component is in the expected position for unaged PDMS and does not fit well with any assignments related to graphitic or graphite-like carbon suggested by this correlation. It is likely that this is a region of increased conductivity due to the presence of graphitic carbon, which causes the PDMS O 1s signal to be aligned closer to the expected binding energy. The O 3 component shows a strong correlation with the C 3 component in figure 4.13 (c). Both show a high concentration region in the lower left of the images and above the channel.
edge. As was the case in the 14 kV images, this component fits in the binding energy range for O-C=O species but there is no corresponding evidence for this species seen in the carbon images. Again, this may be the result of components not being identified due to noise in the data or a result of differential charging. There is, however, clear correlation between these components in both the 14 and 15 kV samples and it is not possible to confidently identify the O 3 components in either case.

![Figure 4.14](image)

The analysis of the Si 2p components reveals two components, Si 1 at 102.4 eV and Si 2 at 103.6 eV, shown in figure 4.15. The Si 1 component is assigned to Si-O bonds. It shows a distribution which appears to be a combination of the C 1/O 2 and C 2/O 1 images; a dark region is present in the bottom left of the image but the highest concentration region is a band across the top of the image. This is also the region of graphitic carbon content and therefore agrees with the suggestion that the presence of the graphitic carbon is causing differential charging of the sample surface for this sample. The Si 2 component is in the region for more oxidised SiOx species and shows small concentrated
regions close to the channel edge and a high concentration region to the lower left which correlate with the C 3 and O 3 components. There is a much greater concentration of this component compared to the 14 kV imaging data mostly due to the high concentration seen in the lower left region. This concentration region follows the same pattern in the C, O and Si images making it unclear if this region is a real feature or an artefact due to charging. To add to this, the Si:O ratio in this region is $(1 \pm 0.05):1$, suggesting such a large concentration of SiOx species assigned to Si 2 is dubious. A possible explanation for this is an effect of differential charging on the sample shifting intensity in this region away from the PDMS component.

Figure 4.15. Two images showing the spatial distribution of the two Si 2p components (a) Si 1 and (b) Si 2 of the 15 kV breakdown channel. Each image is 800 x 800 µm.

4.3.3 11 kV breakdown channel

The atomic concentration images for C 1s, O 1s and Si 2p for the 11 kV breakdown channel are shown in figure 4.16. As in the 14 kV and 15 kV samples, the C 1s peak has been charge referenced to 285.0 eV binding energy, shifting the O 1s and Si 2p peaks to 533.3 and 102.8 eV respectively. These peaks are shifted to higher binding energy by $\sim$1.3 eV for the O 1s and $\sim$0.7 eV for the Si 2p with respect to the expected positions for unaged PDMS. As with the 15 kV sample imaging this may suggest the presence of some differential charging. A series of three holes aligned from the top to the bottom of all of the images outline the channel. Some minor elemental variation is seen;
the C 1s concentration is increased on the lower left edge of the channel, higher O 1s content is seen in the lower left of the image and to the right edge of the channel and an increased Si 2p content is seen in the upper central region. An overlay of the three elements and a line scan across the central hole are shown in figure 4.17. The C:O:Si ratio at the left side of the line image is (2.6 ± 0.15):1:1 ± 0.1), this changes to (3.8 ± 0.2):1:(1.6 ± 0.1) on the left edge of the channel and (2.3 ± 0.1):(1.2 ± 0.1):1 on the right hand edge of the channel. In all three cases there is a relative abundance of carbon across the imaged area compared to unaged PDMS. A large drop in oxygen concentration is seen to the left side of the channel, where it accounts for only 15 ± 1.6 % of the total signal while the C:Si ratio is (2.3 ± 0.1):1 – similar to other regions of the image.

Figure 4.16. Elemental concentration images for (a) C 1s, (b) O 1s and (c) Si 2p for the 11 kV breakdown channel. Each image is 800 x 800 µm.

C 1s component images are shown in figure 4.18. The same three components seen in the 14 and 15 kV samples are identified, C 1 at 284.6 eV, C 2 at 285.0 eV and C 3 at 285.9 eV. They are assigned as previously. This results in C 1 assigned to graphitic carbon and C 3. The graphitic carbon (C 1 ) component is seen throughout the channel with a high concentration towards the upper left.
The C3 component binding energy is on the lower end of the borderline for an assignment to C-O- species and is anti-correlated with the C1 component, showing greatest concentration in the upper left region of the image, with some presence in the lower left and in the channel centre.

Figure 4.17. (a) An overlay of the elemental concentration images in figure 4.16. (b) A 300 µm line scan showing the elemental concentration along the line shown in (a). The 0 on the distance scale represents the ‘left’ end of the line. C – Red, O – green, Si – blue.

Figure 4.18. Images showing the spatial distribution of the three C 1s components (a) C 1, (b) C 2 and (c) C 3 of the 11 kV breakdown channel. Each image is 800 x 800 µm.
The O 1s image analysis reveals three components O 1, O 2 and O 3 at 532.7 eV, 532.4 eV and 533.5 eV respectively, as seen in figure 4.19. These have also been assigned as previously. The O 1 component displays a greater concentration along the axis of the channel in the image centre, with high intensities seen along the left edges of the holes in the signal and towards the bottom edge. The O 2 component shows a largely uniform distribution with some increased concentration at the left and right edges of the image. The O 3 component shows a very similar distribution to the O 2 component but with a lower overall concentration.

Si 2p analysis, shown in figure 4.20, shows two components, Si 1 and Si 2, at 102.6 eV and 103.4 eV respectively. These components are assigned to Si-O in PDMS for Si 1. The two components are anti-correlated with Si 1 having high concentration in along the central channel region and Si 2 being more concentrated along the left and right edges of the image. The distributions of these components are correlated with two of the O 1s components in figure 4.19, with Si 1 matching O 1 and Si 2 matching O 3. As was seen in the 15 kV imaging data the Si:O ratio in these regions does not exceed 1:1, suggesting that the Si 2 component is not due to the presence of SiOx components. The
same explanation given for the 15 kV images is applicable here, that the presence of these features is likely due to differential charging of the graphitic carbon containing channel region compared to the rest of the sample.

Figure 4.20. 2 images showing the spatial distribution of the two Si 2p components (a) Si 1 and (b) Si 2 of the 11 kV breakdown channel. Each image is 800 x 800 µm.

4.3.4 Discussion

There is a significant level of variation of the amount of chemical change seen between the three samples investigated using XPS imaging, particularly in the elemental concentrations. It is unclear why the variation in elemental concentrations across the channels is so low in the 11 kV and 15 kV samples as compared to the 14 kV sample. It is most likely due to differences in the channel morphology and the depth of the microtoming used in order to expose the channel at an optimal depth for XPS imaging to be effective. Nevertheless there are a number of common findings between the samples. Signal associated with unaged PDMS is seen in all samples; in the 14 kV sample the PDMS signal is completely attenuated in the O 1s and Si 2p images in the central breakdown channel leaving a channel which is completely carbonized whereas PDMS is present throughout the images for the 11 kV and 15 kV samples. Graphitic carbon is also seen in all three samples and is found to be concentrated in bands across the images which are considered to be the breakdown channel regions. In the 14 kV sample the graphitic carbon is found in the carbonized channel but also in a band in the upper region of the imaged area. In the 15 kV sample graphitic carbon is found in a band above where the
expected channel is, showing that the signal-depleted hole used to align over the centre of channel may in this case be at the channel edge instead. A limited amount of oxidation is seen in each sample. In all cases this is in the form of C-O- species seen in the C 1s and O 1s components and possible O=C=O species seen in the O 1s component only. It is thought that the lack of a corresponding component in the C 1s is due to it being lost in the noise present in the spectra used to generate the images. In all three samples the oxidation is seen to be concentrated along the channel edges with one edge having higher concentration in each case. Oxidation at the channel edges is expected from the artificial void study and these data support that although the oxidation is much more localised here. Inhomogeneity in the oxide concentration between channel sides is unexpected. While this may simply be due to the way the breakdown proceeded, the fact that this is present in three separate cases suggests there may be some process which causes oxidation to occur preferentially on one side of a channel wall.

In comparison to the line scans from section 4.2 a general increase in the relative carbon content is seen in all three samples. As the images are taken from a smaller area this shows an increase in the relative carbon content over the channel. This increased carbon content is seen up to the limits of the imaging area and so it is not possible to put a measurement to the size of this region but shows that it extends at least \( \sim 300 \, \mu m \) from the channel. These findings agree closely with the conclusions of chapter 3. In contrast to the line scans the oxide and graphitic carbon components are seen to be mostly localised to the channel and channel edges rather than showing a similar level of change even far from the channel. It is difficult to be certain if this is due to the species not being present in the imaged region or the noise in the imaging making it impossible to detect the low concentration oxidised products.

An energy dependence on the breakdown products produced, such as that suggested by the XPS line scans, cannot be seen in the imaging data. This does not mean there is no energy dependence, rather that the imaging data is inconclusive in this regard as there is too much local variation between the samples due to the differing morphology in the channel region. The XPS line
scans average data from a much larger area, allowing a broad overview of the sample surface which is better for establishing general trends in the relative concentration of components while the imaging data provides more specific data on their distribution close to the channel.

There is evidence for differential charging in both the 11 kV and 15 kV samples. This is most evident in the Si 2p images, as the Si:O ratio in the samples cannot account for a widespread presence of silica-like species suggested by the presence of a high binding energy component. There is, however, no such evidence seen in the 14 kV sample. It is suggested that this charging is a result of differing conductivity in the graphitic carbon regions causing relative shifts in the O and Si found in these regions. This may affect the 14 kV sample less as the main graphitic carbon region shows no O or Si signal.

4.4 XPEEM

XPEEM was used to investigate the surface of a 10 kV breakdown channel. Two regions of interest were investigated; the gold grid proved to be ineffective in countering the charging over the channels themselves and over most of the sample but it was possible to scan certain regions at the channel edges and just outside the channel with only limited charging. The charging over the channel is likely due to poor contact with the gold grid as the sample surface dips in the channel itself. XPEEM images were taken for the C 1s and Si 2p peaks using a 50 µm aperture. The XPEEM images for C 1s and Si 2p generated from the region outside the channel are shown in figure 4.21 along with an overlay image of the two elements and a secondary electron image which shows the sample topography. The sample surface is seen to be very rough in the secondary electron image (figure 4.21 (d)) with many pitted structures. This area of the sample should be outside the breakdown channel but is no more than 300 µm away due to the small region over which charge compensation was acceptable. As such, it is entirely possible that this is still within the damaged region due to the area of damage identified in the XPS imaging. The existence of micro pitting of polymer surfaces has been seen as a result of partial discharges and corona discharge processes [3, 102], potentially explaining this topography. It is also possible that this sample damage is due in part to the XPEEM technique as a
high electric field is applied to the sample during investigation and XPEEM has been shown to readily damage organic samples [106]. Sample damage in this case would likely be caused by both X-ray irradiation due to the high flux and discharges between the sample surface and either the HV electrode or the gold grid. The discharge process involved may be analogous to that occurring within voids and corona discharge in a limited oxygen environment.

The carbon and silicon content is seen to be anti-correlated, there are dark regions in the C 1s image which are more intense in the silicon image and vice versa. Greater signal to noise is seen in the Si 2p image. This is due to the higher photon flux available at the lower photon energies required to scan the Si 2p peak in comparison to C 1s. The features seen are approximately 5 µm across and suggest some lateral inhomogeneity of the carbon and silicon distribution in the PDMS polymer. In the circled regions in figure 4.21 part of the pitted structure can be seen, which shows corresponding signals in the C 1s and Si 2p images. This shows that the structure contains relatively high silicon and low carbon content. The maximum photon energy of the XPEEM beamline is unable to probe the O 1s peak and so it cannot be verified if this structure is SiO$_2$ from PDMS chain scission. However, it may be concluded that the degradation seen here causes a separation of the carbon and silicon in PDMS by removal of carbon from the features, likely by breaking the Si-C bond. Such separation was also seen in the XPS imaging of the 14 kV breakdown channel in section 4.3.1, where ‘islands’ of high silicon and oxygen content were seen on the channel edge though on a larger scale as these features are ~20-30 µm across, which suggests that the changes seen are not a result of sample damage from XPEEM but an actual feature of the PDMS breakdown channel.

There is limited research on polymers using XPEEM, the technique has a very high photon flux requirement for imaging at small scales making charge compensation very difficult for insulating samples. There have been no studies of this kind using XPEEM before but there are studies of mixed polymer brushes [107] and phase separation in polymer blends [108, 109]. However, these studies concentrate on sample morphology under differing conditions rather than chemical modification. Radiation damage due to XPEEM has been
studied but there is no observed separation of components as a result [110], again, this suggests that sample damage is not responsible for these results.

![XPEEM images for the region outside of the breakdown channel.](image)

Figure 4.21. XPEEM images for the region outside of the breakdown channel. (a) C 1s, (b) Si 2p, (c) an overlay of (a) and (b) with C in red and Si in blue highlighting anti-correlated C and Si regions, (d) secondary electron image showing surface topography. The circular aperture is 50 µm across. The circles highlight a structure in the secondary electron image which shows corresponding chemical information.

XPEEM images for C 1s and Si 2p and an overlay image for the region near the channel edge are shown in figure 4.22. Also shown in figure 4.22 (d) is a secondary electron image showing topography. As with figure 4.21 a greater signal to noise is seen in the Si 2p image due to the higher photon flux available. The edge of the hexagonal grid used for charge stabilization is clearly visible in these images and there is evidence of distortion towards the edges, likely to be a result of differential charging. This has a strong effect on the secondary electron image, where the inner edges are black from loss of signal and there is some smearing towards the edge. The centre of the image appears

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to be less affected by charging. This area shows a relatively smooth sample in contrast to the region away from the channel where there is extensive pitting. In comparison to the images away from the channel there is more detailed structure seen here in the C 1s and Si 2p images but much less in the topographic image. There are however common features between the topography and the Si 2p and C 1s images which suggest that much of the variation seen here is topographic. The carbon and silicon content here are correlated, with dark and intense regions matching up across the two images, further exemplified by the overlay image.

Photoelectron spectra taken from a 10 µm area from the centre of each image are shown in figure 4.23. The Si 2p peak consists of a single doublet with the 2p 3/2 component assigned to 103.2 eV based on C 1s at 285.0 eV and there is no evidence of differential charging of the peak despite the distortion seen at the grid edges. This binding energy suggests the silicon in this region is in a silica-like form implying chain scission of the PDMS backbone though it is not possible to check the oxygen content to confirm this as the photon energy required to probe the O 1s peak is not available on the XPEEM beamline. The C 1s spectrum shows the presence of C-O-, C=O/O-C=O and O-C=O species accounting for 14.4 ± 3.4%, 6.6 ± 1.1% and 13.6 ± 3.9% respectively of total C 1s intensity. There is no evidence of graphitic carbon in this region; this is in agreement with XPS line scan for this sample which also shows regions with no graphitic carbon near the channel edge. The oxide components account for a significant proportion of the total carbon and the ratios of the components are similar to those seen for long discharges in air corona [111] suggesting this represents an advanced stage of degradation in an abundance of oxygen.

There are two possible origins for the oxygen. Firstly, PDMS has one of the highest oxygen permeabilities of any polymer [112], approximately 60 times that of LDPE, allowing oxygen to diffuse into voids and tree channels. This is a result of the high flexibility of the Si-O bond creating a large amount of free volume inside the polymer. Secondly, chain scission of the PDMS backbone may provide additional oxygen to the system. The degree of oxidation is much larger than that seen in the XPS line scans and imaging. It is possible this is the
result of the smaller area scanned, causing a reduction in averaging with less oxidised areas. If oxidation is confined to small regions this may suggest the lower signal regions in the XPEEM images are areas with relatively higher oxygen content as this would cause a relative decrease in carbon and silicon signal. Alternatively, this may simply be a result of the chemical map following the topology of the secondary electron image.

Figure 4.22. XPEEM images for the region on the breakdown channel edge. (a) C 1s, (b) Si 2p, (c) an overlay of (a) and (b) with C in red and Si in blue. The magenta regions are areas with intensity from both C and Si. (d) Secondary electron image showing surface topography. The white circles highlight common features between the secondary electron image and the Si image. The circular aperture is 50 µm across.
Figure 4.23. Photoelectron spectroscopy spectra of (a) C 1s and (b) Si 2p taken from a 10 µm area in the centre of the corresponding images in figure 4.22.

4.5 SEM

Prior to XPS analysis, the 11 kV breakdown channel investigated in section 4.1.1 was analysed with a Philips XL-30 ESEM - as described in chapter 2. The resulting images are shown in figure 4.24. Two areas of figure 4.24 (a) have been magnified in figure 4.24 (b) and (c) with further magnifications of these shown in figure 4.24 (d) and (e) respectively. Figure 4.24 (b) and (d) show particulate debris on a disordered, rough channel wall. These features are similar to those identified in SEM images of breakdown channels and artificial voids seen by Freebody [102], who found a nodular structure with features ~ 1 µm in size. An SEM image of these features is shown in figure 4.25. Vaughan et al. [51] used SEM to study electrical trees in LDPE finding similar nodular structures. These structures survived etching of the polymer and as such were attributed to the formation of graphite-like carbon structures. The increase in surface roughness here also correlates well with that seen in the XPEEM images from a channel edge seen in figure 4.22.
Figure 4.24. SEM images of an 11 kV PDMS breakdown channel. An overview of the channel is seen in (a). Two regions of interest are highlighted showing loose disordered debris (b) and debris on an ordered background of grooves which follow the direction of the channel. Further magnified images from these regions are shown in (d) and (e).

Figure 4.24 (c) and (e) also show some evidence of the nodules seen in other research but additionally here the channel wall shows a grooved structure. These grooves are aligned with the axis of the breakdown channel and appear
to be 10-15 µm long and ~1-2 µm across. The origin of these grooves is unclear; they do not appear in literature on SEM of treeing or breakdown channels. The transition from the grooves to the rough walls is abrupt and is contained in one region of the channel. There is a possibility that the grooved region is dependant on distance from the point electrode and that the transition away from the grooved walls is due to the energy available for discharges reaching a threshold. The orientation of the channel with respect to the electrodes was not recorded during sample production, i.e. is it not known which end of the channel was closest to the point or plane electrodes and so this cannot be tested with the data available.

Figure 4.25. An SEM image of the 15 kV PDMS breakdown channel in figure 4.2 showing a nodular structure across the channel surface [102].

4.6 Conclusions

A series of electrical breakdown channels in PDMS produced at a range of voltages have been investigated using the surface sensitive techniques of XPS line scans, XPS imaging, XPEEM and SEM. XPS line scans show the presence of low levels of oxidised carbon components C-O, C=O/O-C-O and O-C=O throughout the channel regions. Graphitic carbon traces are seen at lower voltages with increased amounts seen at higher voltages suggesting there is an energy dependence on the production of graphitic carbon during the breakdown
process. There is some evidence for an exponential relationship between the total graphitic carbon content and the applied voltage. Oxidised and graphitic components are found to be present throughout the scanned regions in the XPS line scans showing that degradation is present at least ~ 650 µm distance from the channel itself given the 1.5 mm scan region and the 100-400 µm size of the channels seen in XPS imaging. There is no apparent pattern to the positional variation across the samples, though this is made unclear by the noise in the data due to the small concentrations detected.

C:O:Si ratios show an increase in carbon content in the XPS imaging as compared to the line scans. This increase is still present in regions outside of the channel. This shows that relative carbon content increases in the channel region as was seen in the artificial void study in chapter 3. In the XPS line scans and imaging the level of oxidation is small in comparison to the amount seen in other chapters of this thesis whereas the spectroscopy taken with XPEEM shows a level more in line with what is seen in chapters 3 and 5. From this we may infer that oxidation in PDMS breakdown channels is concentrated in localised regions due to the averaging effect of larger area scans. In the XPS imaging oxidised components are also seen in localised regions on the channel edges which agrees strongly with this assessment. The graphitic carbon content is in general seen in bands across the images which follow the channel. These findings are largely consistent with the findings of Raman spectroscopy which found uneven distributions of graphitic carbon in the channels with fluorescence present throughout and on the channel edges.

SEM imaging shows a rough surface with particulate debris which is in agreement with the apparent increase in structure seen in the XPEEM images from the channel edge and are consistent with previous research. Additionally, a region containing many grooved structures is seen in part of the channel, this feature has not been identified in previous research and further research would be required to ascertain under what conditions it occurs.
5. Corona and spark discharge ageing

This chapter presents studies of methods of producing electrical breakdown products in bulk to compare the chemistry seen with that from other methods presented in previous chapters. XPS analysis of samples produced from two methods is included. Firstly, corona discharge was applied to LDPE samples in air and in a controlled nitrogen atmosphere. Secondly, spark ageing in a number of liquid systems was investigated. The purpose of this method was to reproduce in bulk the chemistry seen in electrical treeing and breakdown using simpler chemical systems.

5.1 Corona discharge on LDPE

The process behind corona discharge is believed to be similar to that which gives rise to electrical treeing and breakdown within materials, as explained in Chapter 1. Corona discharge occurs in regions of high electric field density such as sharp edges of electrodes and insulation, and even water droplets on insulator surfaces. As such, it is a widespread issue in outdoor insulation, causing erosion and chemical modification of surfaces it comes into contact with. There have been a number of investigations of corona discharge with XPS as it is an established surface modification technique [29, 111, 113, 114] as well as a common issue in the ageing of outdoor polymer insulation [32, 33]. Here, an investigation into the effect of the presence/absence of oxygen in the atmosphere around a discharge was performed on samples of LDPE which had undergone corona discharge in air or a nitrogen atmosphere. Example images are shown in figure 5.1. Plaque samples of LDPE of dimension 30 x 30 x 1 mm were aged for 20 hours using a hypodermic needle electrode 1 mm above the sample surface with an applied voltage of 15-20 kV such that a stable corona was formed [115]. The centre of each sample can be seen to contain a roughly circular damaged region.

Despite the visible damage to the samples, investigation of the corona-aged LDPE using CRMS at the University of Southampton found no evidence of any chemical degradation or presence of the D and G bands attributed to disordered sp$^2$ carbon expected from the previous research on the artificial voids and tree
channels [102]. Some limited fluorescence was observed, taken to indicate degradation [116]. It was, however, noted that deposits began to accrue on the needle tips used to make the corona and further investigation showed that the D and G bands were present in these deposits [115, 116].

Figure 5.1. Two corona aged LDPE samples showing degraded regions in their centres. (a) LDPE aged in air. (b) LDPE aged in a nitrogen atmosphere. Scale bars are 1 mm.

The composition of the undamaged LDPE reference is shown in table 5.1, with the C 1s narrow scan shown in figure 5.2. Oxygen and nitrogen peaks are present as well as traces of silicon and sodium contamination. The majority of oxygen takes the form of C=O bonds (3.3 ± 0.2 % of the C 1s signal), C-O-bonds (1.5 ± 0.1 % of the C 1s signal). The nitrogen peak is a single component attributed to C-N bonds. LDPE is a purely hydrocarbon based polymer and as such the only expected XPS signal is a C 1s peak with a single component. The origins of the oxygen and nitrogen peaks are likely to be due to contamination or as a result of the sample preparation method.

XPS line scans across the degraded samples of LDPE from corona discharge in both air and nitrogen atmospheres were used to inspect changes over the surface. In both cases, a 110 µm spot size and 300 µm scan separation was used, with five scanned positions for the air-degraded LDPE and seven for nitrogen-degraded LDPE. The elemental composition for the central position spectrum of the degraded samples is also shown in table 5.1. In the air-degraded sample a large increase in oxygen content is seen, as well as a small
increase in nitrogen signal. It was found that the degradation is not significantly influenced by position across the surface, with variation of < 2.1 at % in all species at all positions probed.

Table 5.1. Elemental composition for an undamaged LDPE reference sample, air-aged and nitrogen-aged samples.

<table>
<thead>
<tr>
<th>At % by element</th>
<th>Undamaged LDPE</th>
<th>Air aged</th>
<th>N₂ aged</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>90.1 ± 0.30</td>
<td>67.9 ± 1.3</td>
<td>62.4 ± 1.3</td>
</tr>
<tr>
<td>O 1s</td>
<td>6.2 ± 0.10</td>
<td>24.8 ± 0.9</td>
<td>23.0 ± 1.0</td>
</tr>
<tr>
<td>Si 2p</td>
<td>1.3 ± 0.10</td>
<td>2.8 ± 0.7</td>
<td>11.5 ± 0.9</td>
</tr>
<tr>
<td>N 1s</td>
<td>2.4 ± 0.20</td>
<td>3.2 ± 1.2</td>
<td>3.2 ± 1.1</td>
</tr>
<tr>
<td>S 2p</td>
<td>-</td>
<td>1.4 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td>Na 1s</td>
<td>0.1 ± 0.02</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.2. C 1s narrow scan of the undamaged LDPE reference sample.

A C 1s narrow scan from a single position from the air-aged corona sample is shown in figure 5.3. As with the atomic concentrations, the components in the air-aged corona sample were not seen to change with scanned position and so figure 5.3 is representative of all positions. There is no graphitic carbon signal. As mentioned above, during CRMS investigations deposits were found on the needle electrode. It was in these deposits that signal associated with graphitic
carbon was found. This was explained by the corona discharge process producing volatile organic components from random chain scission of LDPE, which were then attracted to the electrode [102, 116]. It was speculated that PD activity in voids and tree channels containing an atmosphere rich in organic volatiles may be responsible for graphitic carbon formation [116].

![Figure 5.3. C 1s narrow scan from the central position of the LDPE exposed to corona discharge in air.](image)

It can be seen by comparison to the undamaged sample that a large amount of oxidation has been produced by the corona discharge. The intensities of the oxide components are much higher than those seen in the void samples discussed in chapter 3 and the breakdown channels in chapter 4. Approximately 1 in 3 carbon atoms on the surface are bonded to oxygen. The relative intensities of the oxide components also differ from those of the void samples where the general trend observed is of decreasing intensity with increasing oxidation state from C-O to C=O to O-C=O species. Here the O-C=O component has similar intensity to the C-O component and there is a lower C=O content. Iwata et al [111] studied the evolution of the C 1s peak during corona discharge on PE, as seen in figure 5.4. The oxide ratios seen in figure 5.2 are consistent with relatively long corona discharge exposure times whereas
oxide formation similar to that seen in voids is present after short corona discharge exposure times. It was suggested that over time in an oxygen rich atmosphere the C=O species are converted to O-C=O; this may in turn suggest that the void samples are being degraded in an atmosphere of limited oxygen content and so do not become oxidised to the same extent, or that over the timescales involved the corona discharge is much more damaging to the LDPE surface. This is consistent with the voids being encapsulated in the polymer, reducing oxygen availability. It seems reasonable that the degradation seen here is an advanced stage of the degradation seen in the void samples.

The N 1s spectrum of the air aged sample consists of two components at 400.5 and 402.2 eV BE. The 400.5 eV component is attributed to C-N bonds as an additional nitrogen oxide peak was not found in the O 1s spectrum. The C-N component is accounted for by a corresponding peak in the C 1s narrow scan in figure 5.2. The component at 402.2 eV is attributed to -NH$_3^+$ bonds. The concentration of nitrogen in the aged sample is accounted for by the undamaged sample but this species is only present in the corona discharge aged samples so it is likely that the corona discharge modifies the nitrogen already present on the surface.

Figure 5.4. C 1s narrow scans of PE exposed to corona discharge showing the evolution of oxide components over time [111].
The sample degraded in a nitrogen atmosphere was found to vary in composition as a function of position across the degraded part of the sample. The C 1s content increases in the centre of the scanned region relative to the edges as can be seen in figure 5.5. Somewhat surprisingly, there is again a large increase seen in the oxygen content in the damaged region. The reasons for this are not clear. The test cell in which the samples were produced was not airtight but was purged by a constant flow of nitrogen for 2 hours prior to the corona discharge. Zhang et al. [113] tested polyolefin films subjected to a number of inert gas corona discharges and also found evidence of oxidation in XPS data. Oxygen impurities and dissolved oxygen in the polymer and apparatus were suggested as the source. Other studies suggest the corona discharge forms large numbers of long-lived radicals on the surface which react strongly with oxygen upon removal from the nitrogen atmosphere [114, 117]. In this case the oxygen species would be formed after the corona discharge and not during it.

The C 1s narrow scans, shown in figure 5.6, also show large amounts of oxide formation. The relative ratios of these components do not match those seen in the air degraded sample; a more even distribution of components is seen instead, and this shows some similarity to the void 2 sample shown in chapter 3 with the exception of a graphitic carbon peak. There is some variation in component intensities across the sample, with a large C-O- component seen in position 7 and a large C=O component in position 1, but there is no clear pattern to the oxide formation with changing position such as that seen in the void 2 sample. The total concentration of oxidised carbon from the C 1s signal, shown in figure 5.5, is seen to be mostly flat over the damaged part of the sample surface, but the total C 1s concentration peaks towards the centre of the degraded region and drops off at the edges. This change is accompanied by a corresponding opposite change in oxygen, and to a lesser degree silicon, concentration. This variation is in agreement with that seen in the void 2 sample where oxide peaks decreased in the centre of the void, though the variation in the corona-aged sample is significantly smaller. The surfaces of the corona discharge samples are relatively flat in comparison to the void samples and the corona discharge appears to have produced a more uniform reaction across the
surface suggesting the sample morphology plays a significant role in degradation.

![Graph showing compositional variation with position of the LDPE sample aged in a nitrogen atmosphere](image)

Figure 5.5. (a) The compositional variation with position of the LDPE sample aged in a nitrogen atmosphere. Included is the total contribution from the oxidised carbon components (‘C 1s oxide’), which is seen to be stable with position, and the composition of the undamaged LDPE, at the position marked U. (b) An image of the sample with the positions of the XPS scans overlaid. The scans used a 110 µm x-ray spot size with a 300 µm separation between scans.

It is notable that the degradation seen in the XPS here is the highest in terms of oxidised components out of all the investigated ageing mechanisms while Raman spectroscopy shows no chemical changes from the original polymer. This is likely to be due to the higher surface sensitivity of XPS as CRMS spectra have been shown to contain significant contributions from above and below the focal point, reducing the depth resolution [99].
5.2 Breakdown product debris

The deposits formed on the needles from corona discharge were unfortunately too small to be analysed with XPS. A new method was devised at the University of Southampton to produce these deposits in bulk using a spark generator immersed in a liquid system. Samples were produced by Dr. Nicola Freebody and analysed as received. Three systems were investigated, dodecane (DD), dodecylbenzene (DDB) and PDMS oil. DD was chosen as it is a simple hydrocarbon and a short chain chemical analogue to LDPE; DDB was included to investigate the effects of additional complexity and a high carbon content compared to DD. PDMS oil was chosen to compare with PDMS elastomer used in chapter 4. For all samples 20 ml of liquid was degraded for 16 hours with the spark generator set to approximately 1 spark per second and a spark gap of 0.3 mm. The discharge energy and duration were controlled via a capacitor and resistor in the circuit used to power the spark generator. A voltage of 15 kV, resistance of 1.25 MΩ and a capacitance of 4 nF was used for all systems.
corresponding to an energy of approximately 450 mJ per discharge and a
duration of 25 ms. In the case of DD, two samples were investigated at two
different discharge energies to investigate whether this has an effect on the
products seen. For the second energy a 0.25 nF capacitance was used, giving
an approximately 28 mJ per discharge. These energies are larger than those
typically found for PD activity [118, 119], which are on the order of µJ, and this
may affect the chemistry involved but such energies were required to form
sufficient quantities of sample. This method produced a ‘sludge’ of degradation
products and the remaining liquid. This was then washed with acetone in a
centrifuge (in the case of DD, hexane was used due to its similar chemical
nature) to produce a dark sample of debris which was suitable for XPS analysis.
The amount of debris produced varied strongly between the liquid systems, with
liquid PDMS producing the largest amount. The PDMS debris was analysed
using the XPS spectrometer at Cardiff University and the remaining samples
were analysed using the XPS spectrometer at the University of Nottingham. In
all cases a 110 µm spot size was used for analysis.

5.2.1 PDMS

The elemental concentrations from a survey scan of the PDMS sample are
given in table 5.2. Along with the expected peaks from the PDMS base material
for carbon, oxygen and silicon, traces of iron, calcium and chromium are found,
with other trace metals potentially hidden by the noise in the data. These metals
are commonly used in the electrodes of commercial spark generators, such as
that which was used to produce the samples. The ratios of the PDMS
constituents have changed dramatically from the 2:1:1 C:O:Si of undamaged
PDMS; in particular the silicon content is significantly reduced in favour of a
high carbon concentration. This shows that Si-O does not make up the majority
of the oxygen content in the sample.
Table 5.2. Elemental concentrations of the PDMS breakdown sample taken from a survey scan.

<table>
<thead>
<tr>
<th>Element peak</th>
<th>BE position (eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>73.7 ± 0.3</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>21.0 ± 0.4</td>
</tr>
<tr>
<td>Si 2p</td>
<td>102.0</td>
<td>3.8 ± 0.3</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>348.0</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>Cr 2p</td>
<td>577.0</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Fe 2p 3/2</td>
<td>712.0</td>
<td>0.5 ± 0.1</td>
</tr>
</tbody>
</table>

C 1s and O 1s narrow scans are shown in figure 5.7. The C 1s peak contains components associated with oxides from 286.8 – 289 eV, a graphite component at 284.3 eV and two peaks not seen in previous data. One peak, at 282.8 eV fits in the range of metal carbides [92]. This is possibly a result of reactions between the oil and the spark electrode. Chromium carbides have been shown to form preferentially along grain boundaries in chromium-containing metal alloys [120], although there is not enough chromium present to account for this peak by itself. The Si 2p peak contains two doublets, one associated with PDMS and another in the position for silicon carbides [92]. It is therefore thought that the C 1s carbide peak is a result of multiple carbides of the elements identified in the survey spectrum and those potentially in smaller trace amounts. The final peak in the C 1s peak at 283.6 eV is unassigned. The binding energy is towards the edge of the energy range for silicon carbides; however, there is not enough silicon signal to account for it and that signal has already been attributed to the carbide peak at 282.8 eV.

Component peaks have been fitted in the O 1s narrow scan and constrained to account for the corresponding peaks in the carbon and silicon scans; a good fit is achieved with constraints to the peak areas allowed to vary by up to 10%. In addition to these components a peak at 530.4 eV has been assigned to metal oxides and peak at 531.7 eV is unassigned. The oxidised component intensities in the C 1s signal show similar ratios to the air aged corona discharge sample. This was explained by long discharges in an abundance of oxygen. It is not known how much oxygen is available at the point of discharge in the PDMS
liquid. The discharges occur submerged inside the liquid and so out of the air but there may be sufficient dissolved oxygen. The backbone of PDMS contains 50% oxygen and so chain scission occurring may provide extra oxygen over what is available in other systems.

Figure 5.7. C 1s (a) and O 1s (b) spectra from the PDMS breakdown sample. The ‘ on the O-C=O peaks in (b) designates which O atom from the species is responsible for the peak.
5.2.2 DD/DDB

For the data acquired from the DD and DDB samples a significant contribution is present from the double sided tape substrate used for mounting, due to a small amount of sample being available. In order to minimize the effect of this on the analysis three sets of scans were created for each sample in differing positions and a set of scans of the clean substrate has been used to create a peak model for the substrate. The substrate model contains a number of components in the 286.5 – 289.0 eV binding energy range which interfere with the fitting of oxide and π-π* components. This information has been used to determine the position with the smallest substrate contribution and the peak model has been subtracted from the data to produce difference spectra presented here for clarity.

DDB narrow scans for C 1s and O 1s are shown in figure 5.8. The survey scans show the presence of carbon, oxygen and silicon, with 71.2 ± 1.1, 24.8 ± 0.8 and 4.1 ± 0.7 at % respectively. Also present are traces of nickel, nitrogen, zinc and calcium in quantities of < 0.4 at %. DD contains only carbon and hydrogen and so the oxygen presence must come from either atmospheric contamination or dissolved oxygen. Contamination is unlikely to account for the degree of oxidation present. The solubility of air in liquid n-alkanes is known to be higher than that of water at standard temperature and pressure by a factor of ~ 10 [121], potentially accounting for the oxygen presence. The C 1s peak components show the presence of C-O-, C=O and graphitic carbon accounting for 27.4 ± 0.6, 4.0 ± 0.6 and 12.8 ± 0.5 % of the C 1s peak respectively. There is no component attributed to O-C=O, however, it should be noted that this component is present in the raw data but is assigned to the substrate. The inclusion of a second O-C=O peak due to the sample did not improve the fit and so was not added, but there is a possibility of a small O-C=O component from the sample which is below the limits of detection in the difference spectrum. Similarly the interference of the substrate and noise in the data prevented the fitting a π-π* component due to its small expected contribution (~5 % of the graphitic carbon peak). The O 1s peak has been fitted with components for C=O and C-O-corresponding with the C 1s components.
Figure 5.8. C 1s (a) and O 1s (b) spectra of the DDB breakdown sample. A contribution from the substrate has been subtracted from the data.

Also present is a component for Si-O bonds accounting for the silicon in the sample and, similarly to the PDMS sample, a component attributed to metal oxides is present. Unlike the PDMS sample, there is no contribution from carbides despite the trace metal content. The trace metals seen are also
different to those seen in the PDMS sample though these elements may be present but undetectable due to noise in the survey data.

As with the DDB sample, the 450 mJ DD breakdown sample contains carbon, oxygen and silicon only, with 47.2 ± 0.3, 32.2 ± 0.2 and 20.6 ± 0.2 at % respectively. This sample contains an unexpectedly large amount of silicon. The majority of this silicon is in the form of Si-O bonds (65.0 ± 0.2 %) with the remainder attributed to SiOx bonds. This suggests there is a contamination issue with this sample, as there should be no silicon presence from DDB. The C 1s narrow scan is shown in figure 5.9 (a). The level of oxidation seen is less than that from the PDMS sample, with components for C-O- and C=O accounting for 11.2 ± 0.4 and 1.4 ± 0.3 % of the C 1s peak respectively; there is no fitted component for O-C=O. A large graphitic component (28.8 ± 0.8 % of the C 1s peak) is present, with the associated π-π* transition component (1.0 ± 0.8 %); this is in agreement with the findings from the PDMS data and the Raman findings. The O 1s narrow scan, shown in figure 5.10 (a), has been fit with components attributed to C-O-, C=O, Si-O and a large component attributed to SiOx, with intensities consistent with those seen in the C 1s and Si 2p scans. There is a small shoulder to high binding energy which is not accounted for by the fit. This may suggest a discrepancy in the fit but alternative fits such as forcing the inclusion of an O-C=O component still result in this shoulder. Alternatively, this may suggest atmospheric contamination from H2O.

The 28 mJ DD sample survey scan shows carbon, oxygen and silicon contributions corresponding to 68.7 ± 0.8, 25.3 ± 0.7 and 6.1 ± 0.7 at % respectively. The C 1s and O 1s narrow scans are shown in figures 5.9 (b) and 5.10 (b) respectively. In this sample there is a large contribution from C-O-bonds, making up 29.4 ± 0.5 % of the total carbon concentration. C=O and O-C=O bonds are also present, accounting for 2.1 ± 0.1 % and 4.2 ± 0.1 % respectively. The ratio between these two components follows a similar pattern to that of corona discharge in air, with the C=O component being the smaller. In contrast to the PDMS and 450 mJ DD samples only a small graphitic carbon component is present, making up 2.4 ± 0.3 % of the carbon peak. The relative intensity of the components is significantly different from the 450 mJ DD
sample, suggesting that the discharge energy plays a role in the breakdown products produced. The Raman investigation into these samples concluded that discharge energy had no effect on the spark discharge samples and the data do not show changes in the discharge by-products; although the ratio of the graphitic D and G bands is seen to change with energy relative to the original polymer matrix, as shown in figure 5.11. There is no clear trend with discharge energy but the ratio of base polymer to graphite peaks is increased for the highest energy investigated. This is in contrast to the DD XPS data, where graphitic carbon is higher at higher energy. It is unclear why this is the case, but it may be an artefact of the high spatial resolution (~1 µm) of CRMS as it was noted during analysis that spectral composition was dependent on the sampling position chosen. While efforts were made to average data over multiple spectra, XPS is much more suited to give a relatively large area overview on these samples. There is variation in the peak intensities of the three scanned positions for this sample but in all cases the C-O- component is significantly larger than in any other sample and only a small graphitic component is seen. A potential factor in the increased oxidised content is that oxygen solubility decreases with increasing temperature [121] and the higher applied voltages increase the energy density in the discharge region raising the liquid temperature. It is possible that this has a measurable effect on the oxygen available for subsequent discharges. Directly measuring solubility change or oxygen content during discharges is unfeasible, however, it should be possible to make temperature measurements including a thermocouple in the experimental set up to get an idea of the solubility change.

Additionally, this data indicates that the production of graphitic carbon is energy dependant, increasing with higher applied voltage. This is consistent with the line scan data on PDMS breakdown channels in chapter 4 which shows evidence that graphitic carbon content increases exponentially over the four applied voltages investigated.
Figure 5.9. C 1s narrow scan spectra of the (a) 450 mJ and (b) 28 mJ DD breakdown samples. A magnification of the $\pi-\pi^*$ and C=O components is inset in (a). A contribution from the substrate has been subtracted from the data.
Figure 5.10. O 1s narrow scan spectra from (a) the 450 mJ and (b) the 28 mJ DD breakdown samples. A contribution from the substrate has been subtracted from the data.
In all three systems a high amount of oxidation is seen, in particular there is an intense C-O- component seen in DD and DDB, with the highest seen in the 28 mJ DD sample. In each case, the oxygen content of the C 1s peak is closer to the amount seen in air corona discharge than to voids and breakdown channels. This suggests that the discharges are occurring in the presence of greater local oxygen content than the voids and breakdown channels. Ratios of species are, however, not consistent across the systems; the PDMS sample has ratios similar to the air corona, whereas the DDB and DD samples are rich in C-O- bonds and there is no evident O-C=O component for the DDB and 450 mJ DD samples. The DDB sample shows a level of oxidation and graphitic content intermediate to the 450 mJ and 28 mJ DD samples, with a relatively high C-O- component and a smaller graphitic component than that seen in the 450 mJ DD and PDMS samples. Considering DDB contains a benzene ring in the base material it is unclear why it shows reduced graphitic content compared to systems without this.
By treating the interaction volume of the spark discharge as a sphere with diameter equal to the spark gap (0.3 mm) it is possible to give a rough estimate of the energy density involved. For the 450 mJ samples this gives $\sim 32 \times 10^9$ J m$^{-3}$ and for the 28 mJ sample $\sim 2 \times 10^9$ J m$^{-3}$. In the case of DD, which has a molar mass of $\sim 170$ g mol$^{-1}$ and a density of 750 kg m$^{-3}$, this results in an energy per discharge of $\sim 7200$ kJ mol$^{-1}$ for the 450 mJ sample and $\sim 450$ kJ mol$^{-1}$ for the 28 mJ sample. As expected from the comparison to typical PD energies at the beginning of section 5.2, the energy density of the 450 mJ sample energy is considerably higher than the C-C and C-H bond energies of $\sim 350$ kJ mol$^{-1}$ and $\sim 420$ kJ mol$^{-1}$ respectively. The energy density of the 28 mJ sample is also above the requirement to break these bonds. These energies will be underestimates as the interaction volume is likely smaller than the sphere used for these calculations. It is also important to note that the power is also high due to the short discharge lengths. As such, it is to be expected that there is strong evidence of degradation. The Si-O backbone of PDMS, with a bond energy of 443 kJ mol$^{-1}$ [70], would readily break from such discharges. This may explain why there is little evidence of the base PDMS in the PDMS breakdown products and why this is very different from the level of degradation seen breakdown channels in chapter 4.

The data suggest that there is complex chemistry occurring around the electrode involving the formation of oxides, graphitic carbon and potentially carbides. The presence of metal carbides has not been seen in other samples, nor in the voids or breakdown channels in previous chapters and it is not known whether this is purely a result of the production method or specific to the PDMS oil in contact with the electrode.

### 5.3 Conclusions

LDPE surfaces aged in oxygen and nitrogen atmospheres using corona discharge have been investigated with XPS. Following this, breakdown products formed from spark ageing of liquid PDMS elastomer, DD and DDB have been analysed.
Corona discharge is seen to produce a large amount of oxidised carbon species in both oxygen and nitrogen atmospheres. In the case of oxygen the degradation is highly uniform and forms a high proportion of C-O- and O-C=O species. For nitrogen corona there is some variation with position and the ratios of oxidised species are more even and closer to those seen in voids and breakdown channels. This shows that the atmosphere strongly affects the resulting chemical composition, in particular the oxygen content.

The corona produces no graphitic carbon on the sample surface. Investigations into corona discharge by researchers at the University of Southampton had similar findings but found this signal in electrode deposits. This in turn has resulted in a novel method of producing breakdown products via spark discharge ageing in sufficient amounts that they are available for XPS analysis. The systems investigated show evidence of graphitic carbon and a high degree of oxidation, particularly intense C-O- components, are seen. PDMS oil breakdown products have similar characteristics to the corona discharge of LDPE in chapter 3 with the addition of graphitic carbon and carbides. A potential energy dependence for the breakdown products formed is seen in DD, with a lower energy discharge producing high oxidation and low graphitic carbon content, while the reverse is true for the higher energies. A similar effect is seen the breakdown channels in chapter 4, with graphitic carbon content increasing with applied voltage and a lack of oxidation at the highest voltage used. This effect is not seen in the Raman work on this system but XPS is more suited to investigating broad changes in these samples due to the lack of interference from fluorescence and the larger area measured. The data on the effect of discharge energy is limited but the information gained shows potential for further investigation. Further study and lowering the discharge energy to levels in line with those seen in PD activity may reveal more information on the discharge process.
6. Conclusions

The results presented in this thesis show that with correct charge compensation and sample preparation XPS can be used as a valuable technique for the chemical characterisation of breakdown products from electrical discharge. Artificial voids are suitable for routine XPS analysis and have been shown to contain features analogous to those seen in electrical treeing. XPS imaging has been shown to be effective in revealing the distribution of elements and chemical species in electrical breakdown channels with ~ 10 µm resolution. Spark discharge ageing is capable of producing isolated breakdown products in sufficient amounts for routine XPS analysis allowing for detailed chemical analysis of chemistry produced in a controlled environment.

The degradation products from electrical discharge in artificial voids, electrical breakdown channels from electrical treeing, corona and spark discharge ageing have all been investigated using XPS. Across all the data presented in this thesis there is a tendency for significant surface oxidation, with C-O-, C=O/O-C=O and O=C-O bonds identified, even in the low oxygen environments in sealed voids and electrical tree channels. These oxidised species were not seen using Raman spectroscopy and thus XPS provides information on the chemistry of electrical degradation that Raman studies alone cannot.

The degree of oxidation seen in samples throughout this thesis shows that the presence of oxygen at the point of discharge makes a significant contribution to degradation in polymer insulation. The effect of oxygen concentration has been seen in studies of gaseous degradation products [64] and corona discharge measurements also show a strong effect on the surface chemistry. In addition, XPS demonstrates that the amount of oxygen available within the polymer is enough for oxidised products to form on channel walls. As tree channels do not exist at the beginning of degradation it is likely in this case that oxygen is present due to diffusion through the polymer. This is believed to be the first study of the spatial distribution of breakdown products across the inner surfaces of breakdown channels and voids using XPS and shows that the technique is a valuable tool for this field. While there have been some XPS studies on corona
discharge within artificial voids [67] and fractured surfaces of polyethylene cables [68, 69], they investigate only single spot analysis.

The level of oxidation was seen to be much stronger in artificial voids compared to electrical trees, both in terms of the intensity of oxidised components and the relative proportions of highly oxidised products, suggesting there is more oxygen present in this system. Even higher intensity oxidised species are seen in the corona and spark discharge aged samples. The relative ratios of the oxidised components in voids is consistent with relatively short corona discharges exposure times in air [111] whereas the spark discharge ageing samples show more similarity to high levels of corona damage from long exposure times such as that seen in the air-aged corona discharge in chapter 5. The fact that the breakdown products in both systems can be reproduced with corona discharge in air strengthens the idea that a similar process is involved in all cases.

XPS line scans and imaging reveal oxidation is concentrated on void/channel edges. Low levels of oxidised components are also seen across the full scanned area in XPS line scans of PDMS breakdown channels. These scans cover 1.5 mm of the surface and the channels as measured from the XPS imaging were between approximately 100 – 400 µm wide. This indicates that oxidation may occur at least ~ 650 µm from the channel in these cases.

In addition to oxidised products the presence of graphitic carbon was consistently found in all systems except for corona discharge. In the case of corona discharge graphitic carbon was found in electrode deposits by Raman spectroscopy. These findings are consistent with existing literature on the chemical by-products of electrical breakdown. Graphitic carbon was found to be concentrated along the centres or edges of channels and voids but may still be found in some concentration outside of these regions. While graphitic carbon was generally localised to the area around channels and channel edges, the XPS images of PDMS breakdown channels showed increased carbon content relative to nominal PDMS across the imaged area of 800 x 800 µm, suggesting this region may extend at least ~ 300 µm from the channels. Raman data have
indicated a high level of background fluorescence, attributed to breakdown products, up to ~ 100 µm from breakdown channels but such an extended degradation region has not been identified in previous research. Again, this shows XPS is capable of identifying breakdown products not seen with Raman spectroscopy.

A dependence on discharge energy is seen in the products formed in the line scans of the PDMS breakdown channels in chapter 4 and the spark discharge dodecane samples from chapter 5. This is seen in the form of a changing ratio between the oxidised and graphitic components of the C 1s signal with a trend for higher concentrations of oxidation components seen at lower energies and higher energies showing high graphitic content. Analysis of the PDMS breakdown channel line scans suggests an exponential relationship between the applied voltage and the total graphitic carbon content seen. This implies that the production of graphitic carbon is an activated process with an energy barrier which must be overcome before production starts. A similar analysis of the concentration of oxidised components is inconclusive and would require more data to establish if such a relationship is also followed for oxidation.

XPEEM and SEM imaging have been used to supplement XPS investigation of PDMS breakdown channels. This resulted in high resolution topographical maps of regions of a channel and some chemical analysis which were found to be largely consistent with XPS findings. XPEEM data showed areas approximately 5 µm in size where the carbon and silicon concentration was anti-correlated, roughly 130 µm away from the breakdown channel. This suggests that the damage is laterally inhomogeneous on the micron scale, and that it occurs at some distance from the channel, consistent with the findings of XPS. The topography in the XPEEM showed a highly pitted sample surface with the inhomogeneity suggesting structures based primarily on silicon. SEM images show the previously identified characteristics of electrical breakdown – a rough surface containing nodular structures ~ 1 µm in size [51, 102]. It is likely these structures are related to those seen in the XPEEM. Also observed in the SEM images is a region containing ordered grooves aligned with the channel axis,
which have not been seen before. So far nothing is known about what conditions may cause these features to arise.

The overall picture for the degradation route appears to be dependant on both oxygen availability and discharge energy. At low energy/oxygen availability, production of C-O- occurs, with higher oxidised species such as C=O and O-C=O appearing as the energy/oxygen availability increases. These species are initially seen with relative concentration decreasing going from C-O- to C=O to O-C=O but as the oxygen availability and energy increase further the proportion of the O-C=O component increases relative to the other components suggesting that C-O- and C=O are converted to O-C=O. Such relative ratios are seen in the air corona of LDPE in chapter 4 and spark discharge by-products from PDMS. Detection of CO$_2$ as a gaseous breakdown product [63-65] suggests that the oxidation may proceed further to CO$_2$ production, causing a loss of carbon and oxygen from the surface. When the energy available exceeds a certain threshold graphitic carbon production seems to become the dominant process. As the enthalpy of formation of graphite is 0 kJ mol$^{-1}$ and -393 kJ mol$^{-1}$ for CO$_2$, oxidation is clearly energetically favourable. Indeed combustion of hydrocarbons will preferentially form CO$_2$, forming graphite in the absence of oxygen. This suggests that the applied voltage plays a role in the oxygen availability of the system. It was suggested in chapter 5 that this may be due to local temperature increases reducing the oxygen solubility in liquid systems. Permeability studies of thermooxidative degradation in rubbers show permeability to be highly temperature dependant and that the oxygen permeability may decrease with ageing time [122]. This may suggest that oxidation continues until the oxygen availability is reduced such that graphitic carbon becomes the primary degradation path. In this case the role of energy is to affect the speed at which this change occurs.

There is evidence for discharges producing lateral imhomogeneity in the C:Si ratio of PDMS. This may suggest the creation of an incomplete carbon overlayer. This is consistent with the XPS of breakdown channels and voids and the findings of Raman spectroscopy on electrical trees, as the polymer matrix is still visible in many graphitic carbon containing regions. Alternatively, this may
be the result of the loss of carbon from the surface, which may occur via eventual conversion of methyl groups to CO$_2$, which subsequently escapes from the surface. The XPEEM data was produced from a 10 kV breakdown channel, from the XPS data on an 11 kV breakdown channel (the closest energy available) the regions within 130 µm of the channel show a relative abundance of carbon compared to PDMS. As such it is likely that the creation of a carbon overlayer is the dominant process in the XPEEM.

This work can be extended to investigation of other polymers of importance to the field such as epoxy resins in both voids and treeing experiments. The use of spark discharge ageing and the grooved structures identified by SEM merit further investigation, as does the inhomogeneity seen in the XPEEM data. Improvements to the spatial resolution and signal to noise ratio of XPS imaging continue and in future it should be possible to directly image electrical tree channels without having to induce breakdown. This would allow chemical mapping across a large section of tree channel at a point during growth.
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