

# **Tracking the Effect of Accelerated Aging on Cross-Linked Polyethylene Pipe using Fourier Transform Infrared Microscopy**

by  
Joseph D'Amico

A Thesis  
presented to  
The University of Guelph

In partial fulfilment of requirements  
for the degree of  
Master of Science  
in  
Physics

Guelph, Ontario, Canada

© Joseph D'Amico, January, 2022

## **ABSTRACT**

### **TRACKING THE EFFECT OF ACCELERATED AGING ON CROSS-LINKED POLYETHYLENE PIPE USING FOURIER TRANSFORM MICROSCOPY**

Joseph D'Amico

University of Guelph, 2022

Advisor:

John Dutcher

Cross-linked polyethylene (PEX-a) pipes have been quickly replacing metal piping in home and industrial applications due their cost-effective manufacturing process, ease of installation, and long projected lifetimes. However, PEX-a pipes are not immune to oxidative degradation from their environment while in-use, creating the opportunity for premature failure. Therefore, understanding the degradation process is critical to helping extend lifetimes and prevent expensive failures. We have developed several experimental protocols to accelerate the ageing process in-house in our efforts towards this goal, isolating the effects from various environmental stresses present during in-service conditions. By conducting FTIR microscopy measurements on unused/virgin pipes, as well as both in-service and in-house aged pipes, we have found several key indicators of an aged pipe that play a role in pipe failure. Principal component analysis (PCA) was conducted to identify characteristics of PEX-a pipes subjected to these various ageing environments.

## ACKNOWLEDGEMENTS

I would like to extend my sincerest gratitude, first and foremost, to my supervisor John Dutcher. The insight and guidance he provided leading up to and throughout my graduate degree was paramount to my success. Dr. Dutcher has been an exceptional role model, not only as an exemplary scientist but also as a sincere and caring human. I have learned so much during my time in his research group on how to conduct good science and communicate it in an effective manner. I'll always feel lucky to have been given the wonderful opportunity to be apart of his group and experience all the great things associated with that privilege.

Thank you also to Dr. Stefan Kycia and Dr. Michael Massa for offering their thoughts and advice during my committee meetings. The insight they provided proved to be invaluable towards our research goals.

I would be remiss to forget all my spectacular lab mates, who always took the time to stop and discuss various aspects of our work. The amazing atmosphere they helped to cultivate within the group kept me excited to come to work everyday. Specifically, I would like to thank my numerous data collection partners, Scott, Ben, Fatemeh and Jonathan for their company during the long days on the FTIR microscope. I would like to thank Melanie for her never-ending patience with me as I consistently asked for her help in understanding the machine learning aspects of our analysis. I am deeply grateful towards Callum, for taking on the daunting project of organizing our immense dataset. I also must extend appreciation to Mike for his insight and advice throughout my learning process on the project, without him challenging my understanding, I would not be where I am today.

I must also thank my large extended family for their words of amazement and encouragement towards my endeavors as a research scientist. Above the rest, my parents, Tony and Lina, provided me with the resources and tools to tackle this project to the best of my ability.

Finally, to our industrial partners at PEXCor, I am deeply appreciative for the many samples they provided to fuel our curiosity and research efforts and the many meetings which provided encouragement and inspiration for new avenues of research.

## TABLE OF CONTENTS

Abstract.....	ii
Acknowledgments.....	iii
Table of Contents.....	v
List of Tables.....	vii
List of Figures.....	viii
1 Introduction.....	1
1.1 High Density Polyethylene.....	1
1.1.1 Chemical Structure & Physical Properties.....	1
1.1.2 Crosslinking Mechanisms.....	1
1.1.3 Extrusion to form Pipes.....	3
1.2 Degradation of Cross-Linked Polyethylene (PEX-a) pipe.....	3
1.2.1 Chemical Changes.....	3
1.2.2 Physical Changes.....	5
1.3 Stabilization of PEX-a Pipes.....	6
1.3.1 Hindered Amine Light Stabilizers.....	6
1.3.2 Phenolic Antioxidants.....	7
1.3.3 Undesired Reactions with Antioxidants.....	8
1.4 Research Goals and Scope of Thesis.....	10
2 Background.....	12
2.1 Fourier Transform Infrared (FTIR) Spectroscopy.....	12
2.1.1 Transmission FTIR.....	12
2.1.1.1 IR Spectral Bands of PEX-a pipe.....	13
2.1.1.2 Determination of Characteristic IR Index Values.....	17
2.1.2 FTIR Microscopy.....	23
2.2 Principal Component Analysis (PCA).....	25
2.3 American Standard Test Method (ASTM) for Ageing PEX-a Pipes.....	26
2.4 Previous Studies of Accelerated Ageing of PEX-a Pipes.....	28

3 Materials and Methods.....	31
3.1 PEX-a Pipe Samples.....	31
3.2 Accelerated Ageing of PEX-a Pipe.....	32
3.2.1 Exposure to UV/Ozone.....	33
3.2.2. Exposure to Elevated Temperature.....	34
3.2.2.1 Immersion in Hot Air.....	34
3.2.2.2 Immersion in Hot Water.....	35
3.2.2.3 Recirculating Hot Water at High Pressure.....	36
3.3 Preparation of Axial Pipe Slices for Transmission FTIR Microscopy.....	39
3.4 Transmission Infrared (IR) Measurements of Axial Slices of PEX-a Pipe.....	40
3.5 Analysis of FTIR Microscopy Data.....	42
3.5.1 Mapping of the IR Indices Across Pipe Wall.....	42
3.5.2 PCA of FTIR Spectra.....	42
4. Results and Discussion.....	44
4.1 FTIR Microscopy Measurements of PEX-a Pipe Subjected to Accelerated Ageing.....	44
4.1.1 Exposure to Elevated Temperature.....	45
4.1.1.1 PEX-a Pipe Ageing in Hot Air Immersion Environment.....	45
4.1.1.2 PEX-a Pipe Ageing in Hot Water Immersion Environment...	53
4.1.1.3 PW PEX-a Pipe Ageing in Recirculating Hot Water at Elevated Pressure.....	60
4.1.2 PW PEX-a Pipe Ageing in UV/Ozone Environment.....	70
4.2 FTIR Microscopy Measurements of In-Service PW PEX-a Pipes.....	73
4.3 PCA of FTIR Measurements of PW PEX-a Pipe Subjected to Accelerated Ageing at Elevated Temperature.....	77
4.3.1 Tracking Accelerated Ageing Pathways in PC Space.....	77
5 Summary and Future Work.....	81
References.....	84

## LIST OF TABLES

<b>Table 2.1:</b> Tabulated list of relevant functional groups present in the PEX-a pipe spectrum, along with their wavenumber range, bond vibration and chemical origin.....	23
<b>Table 3.1:</b> Tabulated accelerated ageing conditions including the specified temperature range, ageing medium and length of PEX-a pipe sample used.....	31
<b>Figure 4.1:</b> Tabulated shift factors for each temperature tested.....	70

## LIST OF FIGURES

**Figure 1.1:** Chemical mechanism of peroxide-induced cross-linking of polyethylene. In reaction 1, a peroxide is cleaved under high energy; in the case of PEX-a pipes, NIR light is used to form two oxygen radicals. These oxygen radicals then cause hydrogen abstraction in reaction 2, leaving carbon radicals behind. In reaction 3, two neighboring polyethylene chains with carbon radicals form a cross-linked chemical bond..... 2

**Figure 1.2:** Polyethylene oxidation reaction pathway outlining the mechanism of oxidative damage propagation. The carbon radical present on the reactant in the first line is initiated via environmental stress such as exposure to UV light or heat. It then can react with oxygen to form an oxygen radical, which can then transfer the radical onto a carbon chain, beginning the process again. Thus, polyethylene oxidation can propagate throughout the material if it is not otherwise stopped.....4

**Figure 1.3:** a) Photograph of virgin/unused PEX-a pipes of various sizes. b) Photograph of 1/2” PEX-a pipe aged for 4 weeks at 80° C and 80 psi.....5

**Figure 1.4:** Chemical mechanism of stabilization for a general hindered amine light stabilizer (HALS) additive. The nitrogen bond is readily available for reaction with oxygen, forming a nitroxide radical. This form can then scavenge radicals from the polyethylene chains and cyclically transform both carbon radicals and oxygen radicals into non-radical products, continuously reforming the nitroxide radical form.....7

**Figure 1.5:** Chemical mechanism of stabilization for a general phenolic antioxidant additive. The active site for these additives is the hydroxyl group bonded to the phenyl ring. This site can scavenge oxygen radicals present in the environment to form non-radical products twice. This reaction shifts the electron sharing within the phenyl ring, allowing for a third oxygen radical to be scavenged by the other end of the phenyl ring..... 8

**Figure 1.6:** Chemical structure of the stabilizing additives used in the PEX-a pipes studied in this thesis: Tinuvin 622 (left) and Irganox 1010 (right). Tinuvin 622 is the HALS additive, which is a long chain polymer with one active site per monomer (highlighted in red). Irganox 1010 is



the phenolic antioxidant, which is a large molecule with 4 active sites per molecule (highlighted in red)..... 9

**Figure 2.1:** The carbonyl region of a PW PEX-a sample subjected to Milli-Q water immersion accelerated ageing and UV/ozone experiments. The IR spectrum for a virgin PEX-a sample (black) had a large intensity at  $1740\text{ cm}^{-1}$ . After 4 weeks of hot water immersion ageing at  $80^{\circ}\text{C}$  (red), the intensity at  $1740\text{ cm}^{-1}$  was significantly reduced. The sample was then exposed to UV/ozone for 60 min (blue), which caused significant oxidation, increasing the intensity within the wavenumber range  $1730\text{ cm}^{-1}$  to  $1680\text{ cm}^{-1}$ ..... 15

**Figure 2.2:** Representative ester peak exhibited by a PW PEX-a pipe. The sharper feature present on the shoulder around  $1182\text{ cm}^{-1}$  arises from crystalline polyethylene, while the broader peak centred on  $1162\text{ cm}^{-1}$  arises from the ester groups present in both Tinuvin 622 and Irganox 1010 additives..... 16

**Figure 2.3:** Labelled diagram of the naming scheme for the atoms involved in an ester linkage. .... 16

**Figure 2.4:** Representative phenolic hydroxyl double peak exhibited by a PW PEX-a pipe. The two peaks correspond to the O-H stretch in the two polymorphs of the phenolic antioxidant Irganox 1010..... 17

**Figure 2.5:** Visualization of characteristic index values as calculated from their respective peaks. (a) A typical carbonyl peak from the centre of a virgin 1/2" PW PEX-a pipe wall. The peak area was calculated using a trapezoid rule for integration of the peak. The small shoulder on the lower wavenumber side of the peak shifts the peak centroid ( $1736\text{ cm}^{-1}$ ) away from the peak max wavenumber value of  $1740\text{ cm}^{-1}$ . (b) A typical ester peak from the centre of a virgin PW PEX-a pipe wall. The peak area was calculated using a trapezoid rule for integration of the peak. The sharp shoulder on the higher wavenumber side of the peak shifts the peak centroid ( $1161.3\text{ cm}^{-1}$ ) away from the peak max wavenumber value  $1160\text{ cm}^{-1}$ . The peak max index was calculated as the normalized value of the maximum absorbance..... 19

**Figure 2.6** Schematic diagram of an FTIR spectrometer + optical microscope. A schematic diagram of the Michelson interferometer inside the FTIR instrument is shown on the the left and

a general optical microscopy image is shown on the right. In addition to an optical lens for viewing of the sample, the microscope is generally outfitted with a camera (above the eye-piece lenses) for digital viewing..... 24

**Figure 2.7:** The logarithm of the hoop stress versus the logarithm of time in which the three stages of PEX-a pipe failure are indicated. The shaded region represents conditions to which PEX-a pipe can be subjected without failing. Conditions that lie outside the shaded area results in pipe failure, with different stages of failure indicated for the different directions shown in the figure. Image adapted from [24]..... 27

**Figure 3.1:** Schematic diagram of PEX-a pipe showing the extrusion direction of the pipe and the slicing of the pipe to create thin axial slices ( $\sim 100\ \mu\text{m}$  in thickness)..... 32

**Figure 3.2:** Images of the Jelight Company model 342 UVO-Cleaner used for the UV/ozone ageing of PEX-a pipe slices. The handle opens a drawer into which the samples are placed; the drawer is then closed to form a full seal. A timer is provided on the front with automatic shut-off capabilities..... 34

**Figure 3.3:** Lab ovens used to age PEX-a pipe samples immersed in high temperature air and Milli-Q water. The oven temperature was adjusted with a knob on the outside of the oven and monitored using a glass mercury thermometer..... 47

**Figure 3.4:** (a) Schematic diagram of the recirculating system shown in (b). This system was used to subject PEX-a pipe segments ( $\sim 60\ \text{cm}$  long) to high temperature distilled water at high pressure..... 38

**Figure 3.5:** Schematic diagram of the production of axial slices from UV/ozone and immersion aged PEX-a pipe segments. Since these ageing environments expose all surfaces of the pipe segments, including the pipe ends,  $\sim 3\ \text{mm}$  of the pipe end was removed before producing an axial slice using the microtome for use in the FTIR microscopy experiments..... 40

**Figure 3.6:** Schematic diagram of an axial slice of a PEX-a pipe showing the direction of a measured line profile. Spectra were collected across the pipe wall thickness with a spacing

between spectra of 100  $\mu\text{m}$ . The numbers indicate the locations “around the clock”, with the measurement corresponding to 9 o’clock.....41

**Figure 4.1:** (a) Representative radial distance profile of a characteristic IR index (carbonyl area) determined from FTIR measurements of a ½” PW PEX-a pipe aged with recirculating 80°C hot water for 21 days, shown as a function of the percentage of the radial distance across the pipe wall thickness. The inner surface of the pipe wall corresponds to 0% and the radial distance increases radially outward, as indicated schematically in (b).....45

**Figure 4.2:** (a) and (b): Radial distance line profiles for virgin ½” RFH PEX-a pipes (black) and RFH pipes exposed to the 80°C hot air immersion ageing environment for different ageing times: 1 week (red), 2 weeks (green) and 3 weeks (blue). Index values are average values of data points measured within 3% of the radial distance values over four line profiles. (c) and (d): Representative IR spectra, from points highlighted in orange on a) and b), of virgin RFH PEX-a pipes (black) and RFH pipes exposed to the 80°C hot air immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region..... 47

**Figure 4.3:** (a) and (b): Radial distance line profiles for virgin ½” T301 PEX-a pipes (black) and T301 pipes exposed to the 80°C hot air immersion ageing environment for different ageing times: 1 week (red), 2 weeks (green) and 3 weeks (blue). Index values are average values of data points measured within 3% of the radial distance values over four line profiles. (c) and (d): Representative IR spectra, from points highlighted in orange on a) and b), of virgin T301 PEX-a pipes (black) and T301 pipes exposed to the 80°C hot air immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region..... 49

**Figure 4.4:** (a) and (b): Radial distance line profiles for virgin 1” PW PEX-a pipes (black) and PW pipes exposed to the 85°C hot air immersion ageing environment for different ageing times: 3 days (pink), 6 days (orange), 8 days (green), 10 days (red) and 14 days (blue). (c) and (d): Index values are average values of data points measured within 3% of the radial distance values over three line profiles. Representative IR spectra, from points highlighted in orange on a) and b), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 85°C hot air immersion

ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region..... 51

**Figure 4.5:** Representative radial distance profiles of characteristic IR indices for virgin 1” PW PEX-a pipe (black) and PW pipe exposed to 85° C air for 3 weeks (red): (a) vinyl max index and (b) Irganox area index.....52

**Figure 4.6:** (a) and (b): Radial distance line profiles for virgin 1” PW PEX-a pipes (black) and PW pipes exposed to the 85°C Milli-Q water immersion ageing environment for different ageing times: 3 days (pink), 6 days (orange), 8 days (green), 10 days (red) and 14 days (blue). (c) and (d): Index values shown are average values of data points measured within 3% of the radial distance values over three line profiles. Representative IR spectra, from points highlighted in orange on a) and b), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 85°C Milli-Q water immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region.....54

**Figure 4.7:** Representative radial distance profiles of characteristic IR indices for virgin 1” PW PEX-a pipe (black) and PW pipe exposed to 85° C Milli-Q water for 3 weeks (red): (a) vinyl max, (b) Irganox index..... 56

**Figure 4.8:** (a) Carbonyl area versus carbonyl centroid graph of virgin ½” PW PEX-a pipe (orange) and PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red). (b) Average spectra calculated from the inner 80% of three line profiles of virgin PW PEX-a pipe (orange) and PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red). (c) Carbonyl area versus carbonyl centroid graph of virgin RFH PEX-a pipe (light green) and RFH PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (dark green). (d) Average spectra calculated from the inner 80% of three line profiles of virgin RFH PEX-a pipe (light green) and RFH PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (dark green). (e) Carbonyl area versus carbonyl centroid graph of virgin T301 PEX-a pipe (blue) and T301 PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (navy). (f) Average spectra calculated from the inner 80% of three line profiles of virgin T301 PEX-a pipe (blue) and T301 PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (navy). g) Average carbonyl area versus carbonyl centroid graph of virgin PW (orange), RFH (light green) and T301 (blue) PEX-a pipe and PW (red), RFH (dark green) and T301 (navy) PEX-a pipe aged 80° C

Milli-Q water for 4 weeks. Dashed arrows indicate the trajectories for each formulation within the plot over the 4 weeks of ageing.....59

**Figure 4.9:** (a) and (b): Average radial distance profiles for virgin ½” PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 60°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. (c) and (d): Average radial distance profiles for virgin PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 70°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. For each figure, we show the average values of data points measured within 3% of the radial distance values for three line profiles collected at each ageing time. (e): Representative IR spectra, from points highlighted by the orange rectangles in a), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 60°C recirculating water ageing environment at 80 psi for 28 days (blue) and 42 days (red). (f): Representative IR spectra, from points highlighted by the orange rectangles in c), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 70°C recirculating water ageing environment at 80 psi for 21 days (orange) and 42 days (red)..... 62

**Figure 4.10:** (a) and (b): Average radial distance profiles for virgin ½” PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 80°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. (c) and (d): Average radial distance profiles for virgin PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 90°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. For each figure, we show the average values of data points measured within 3% of the radial distance values for three line profiles collected at each ageing time. (e): Representative IR spectra, from points highlighted by the orange rectangles in a), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 80°C recirculating water ageing environment at 80 psi for 21 days (orange) and 42 days (red). (f): Representative IR spectra, from points highlighted by the orange rectangles in c), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 90°C recirculating water ageing environment at 80 psi for 10 days (green) and 42 days (red)..... 64

**Figure 4.11:** (a): Average radial distance profiles for ½” PW PEX-a pipes exposed to the 60° C (blue) 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for

42 (blue) 21 (green), 10 (red) and 5 (black) days. b): Representative IR spectra, from points highlighted in orange on a), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 60° C for 42 days (blue), 70° C for 21 days (green), 80° C for 10 days (red) and 90° C for 5 days (black). (c): Average radial distance profiles for PW PEX-a pipes exposed to the 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for 28 (green), 14 (red) and 7 (black) days. (d): Representative IR spectra, from points highlighted in orange on c), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 70° C for 28 days (green), 80° C for 14 days (red) and 90° C for 7 days (black). (e): Average radial distance profiles for PW PEX-a pipes exposed to the 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for 42 (green), 21 (red) and 10 (black) days. f): Representative IR spectra, from points highlighted in orange on e), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 70° C for 42 days (green), 80° C for 28 days (red) and 90° C for 14 days (black). For a), c) and e), the average value was calculated from points within 3% radial distance of one another, from three line profiles collected at each ageing time..... 67

**Figure 4.12:** a) Log-log plot of penetration depth  $\delta$  in microns against ageing time in days for ½” PW PEX-a pipe samples aged at 80 psi and the temperatures outlined in the legend. The solid lines correspond to best fits of each data set to a straight line. Since the 90 °C data set reaches a plateau of penetration effect, the last two data points were not included in the fit. The best-fit power law equations were;  $\delta = 182.80t^{0.6568}$ ,  $\delta = 114.78t^{0.6766}$ ,  $\delta = 73.7116t^{0.6714}$  and  $\delta = 40.2684t^{0.7045}$  for the 90 °C, 80 °C, 70 °C and 60 °C respectively, with  $R^2$  values of 0.9818, 0.9761, 0.9858 and 0.9181. b) Master plot of the time-temperature superposition of all the data sets measured at the four different temperatures, shifted to coincide with the 80 °C set.....69

**Figure 4.13:** a) Carbonyl area index versus carbonyl centroid index of virgin ½” PW PEX-a (black), PW PEX-a pipe after 2 hours of UV/ozone exposure (green), PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red) and PW PEX-a pipe after 4 weeks of 80° C Milli-Q water followed by 2 hours of UV/ozone exposure (blue). The dashed lines indicate the trajectories of the data with UV/ozone exposure. (b) and (c): Representative spectra of the carbonyl region of (b) virgin PW PEX-a pipe and (c) PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks. The

black and red curves were measured before exposure to UV/ozone, and the green and blue curves were measured after 2 hours of exposure to UV/ozone. The spectra were collected midway through the pipe wall thickness (~50% radial distance)..... 71

**Figure 4.14:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for a virgin 1" PW PEX-a pipe (black) and a PW pipe exposed to in-service conditions for more than 4 years, which experienced pipe failure (red). Index values shown are average values of data points measured within 3% of the radial distance values for three line profiles..... 73

**Figure 4.15:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for 1" PW PEX-a pipes that were subjected to the same in-service conditions for 1 year (blue), which did not experience pipe failure, and 3 years (red), which did experience pipe failure. Index values are average values of data points measured within 3% of the radial distance values for six line profiles..... 75

**Figure 4.16:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for a virgin 1" PW PEX-a pipe (black), a PW PEX-a pipe exposed to in-service conditions for more than 4 years, inducing pipe failure (red), and a PW PEX-a pipe aged in a hot water immersion environment at 80° C (blue). Index values are average values of data points measured within 3% of the radial distance values for three line profiles..... 76

**Figure 4.17:** a) PC1 versus PC2 plot for PW pipes aged in the various 80 °C ageing environments. The colours correspond to different data sets as listed in the legend. The PC space was calculated using 1000+ IR spectra of 11 absorbance peaks, from the middle 50% of the pipe wall thickness. The first two principal components explain 89% of the variance in the dataset, with PC1 and PC2 explaining 76% and 13%, respectively. Each point in the plot corresponds to one spectrum. b) Fingerprint region loading spectrum for PC1 and PC2. c) Carbonyl region loading spectrum for PC1 and PC2..... 79

# **1 Introduction**

## **1.1 High Density Polyethylene**

### **1.1.1 Chemical Structure & Physical Properties**

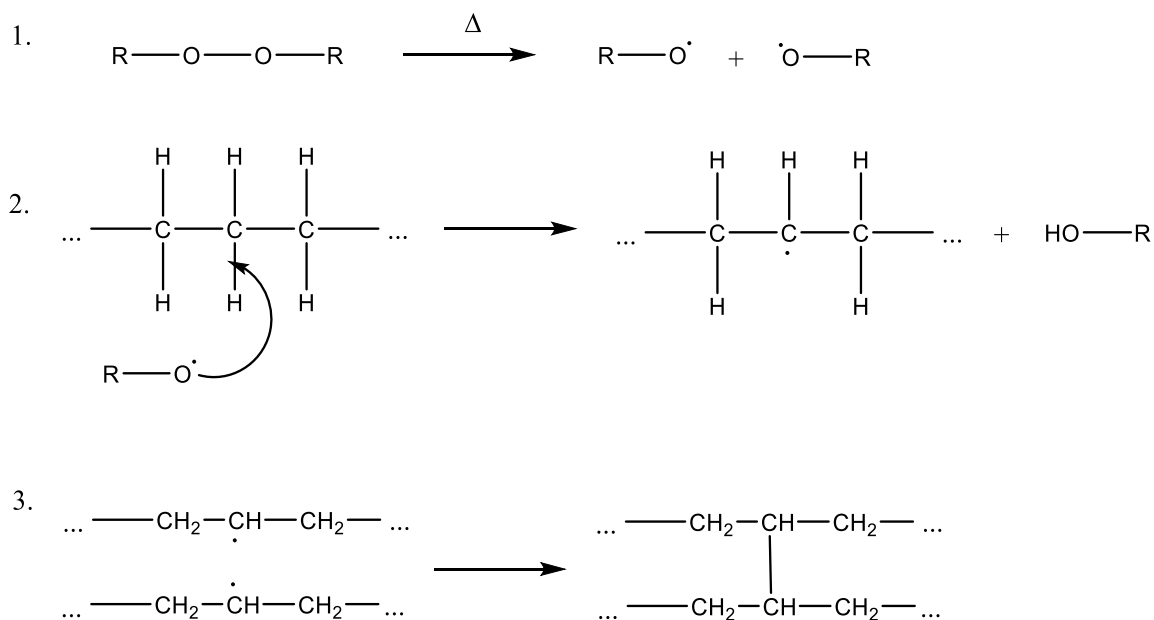
High density polyethylene (HDPE) is comprised of long, highly ordered chains of saturated carbon – carbon bonds. These chains typically order into highly crystalline lattices, consisting of tightly packed, uniformly separated chains with very little branching<sup>1-3</sup>. The degree of crystallinity for HDPE is typically about 60%, with the rest of the material corresponding to amorphous polyethylene, in which the chains are randomly arranged<sup>1-3</sup>. This combination of crystalline and amorphous regions, at a scale on the order of 10 nm – 1  $\mu$ m, creates a strong material with a high strength to density ratio, in which the crystalline regions provide structural integrity, and the amorphous regions allow some level of flexibility<sup>3</sup>. Because of its structure, HDPE has a Young's modulus and tensile strength that are comparable to that of steel<sup>4</sup>. These properties, combined with its low density of 940 Kg/m<sup>3</sup>, provide a very strong, lightweight material that can be used in many fields of research and applications in technology<sup>4</sup>.

### **1.1.2 Crosslinking Mechanisms**

Although HDPE has impressive mechanical properties, it is possible to improve them by crosslinking the polymer chains. Crosslinking is widely used to increase the thermal resistance of polymers, and to improve their mechanical properties such as impact strength, tensile strength, scratch resistance and resistance to brittle fracture<sup>1-3,5,6</sup>. In the case of polyethylene, there are three main mechanisms to produce cross-linkages: peroxide crosslinking (PEX-a), silane crosslinking (PEX-b) and irradiation crosslinking (PEX-c)<sup>1,5</sup>. In the present study, we focus on



peroxide cross-linked polyethylene (PEX-a). This process involves incorporating a peroxide into the PE matrix at high temperatures, then cooling the material before irradiating it with near-infrared (NIR) light <sup>1,3,5,6</sup>.



**Figure 1.1:** Chemical mechanism of peroxide-induced cross-linking of polyethylene. In reaction 1, a peroxide is cleaved under high energy; in the case of PEX-a pipes, NIR light is used to form two oxygen radicals. These oxygen radicals then cause hydrogen abstraction in reaction 2, leaving carbon radicals behind. In reaction 3, two neighboring polyethylene chains with carbon radicals form a cross-linked chemical bond.

The peroxide reacts with the NIR light and is converted into free oxygen radicals. The free radicals strip protons from the polyethylene chains leaving active carbon reaction sites, which form a bond with each other, i.e., a crosslink between polyethylene chains. The formation of crosslinks reduces the degree of crystallinity of the material while improving its thermal resistance, as well as its resistance to environmental weathering and cracking<sup>2</sup>, making this material ideal for hot water pipe applications.

### **1.1.3 Extrusion to Form Pipes**

Cross-linked polyethylene (PEX-a) pipes have increasingly been used to replace metal piping in household and industrial applications due to their cost-effective manufacturing process, ease of installation, and long projected lifetimes<sup>2,5,7</sup>. During the manufacturing process, HDPE is heated and crosslinked before being extruded into the form of a pipe. These products capitalize on the material's high structural integrity and the ability to hold its shape when subjected to various physical stresses, making them highly desirable in modern manufacturing.

PEX-a pipes are widely used in homes to transport potable water. Installation of pipe within the walls of a building introduces several challenges such as cutting pieces to the right size and utilizing the necessary joint pieces. A lightweight, soft, and flexible material such as PEX-a greatly simplifies this process, as cutting pieces on site is easily done with a sharp edge cutter, and the pieces themselves can flex and bend into place without the need for joints. As well, early testing of predicted lifetimes for these products projected a useful in-service lifetime as long as 50 years, further increasing the perceived value of these products<sup>5,7</sup>.

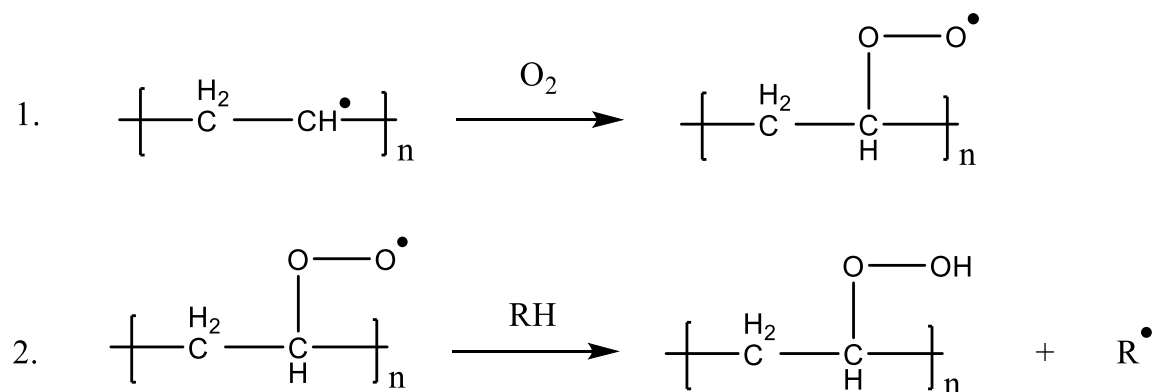
## **1.2 Degradation of Cross-Linked Polyethylene (PEX-a) Pipe**

### **1.2.1 Chemical Changes**

Although PEX-a material has many desirable properties for use in a variety of industries, it has some drawbacks. In particular, it is susceptible to a variety of undesirable chemical reactions, the most notable of which is oxidation<sup>7-10</sup>. Reactions with oxygen occur commonly in

most environments in which we live, and oxidative damage can break down the chemical integrity of most materials.

The mechanism of polyethylene oxidation is well understood and it is outlined in Figure 1.2. Heat such as that produced by absorption of high energy light can induce hydrogen abstraction on the polyethylene chains, allowing oxygen in the environment to bind to the chains. This reaction is highly detrimental since it results in the production of free radicals, effectively propagating hydrogen abstraction throughout the bulk material. Chain scission is another example of an undesirable chemical reaction in polyethylene. This reaction is also initiated by heat, and it cleaves the long polyethylene chains to shorter fragments, compromising the integrity of the material. Most of these reactions will occur in the amorphous regions of PEX-a as they are much more accessible than the highly ordered, dense crystalline regions.



**Figure 1.2:** Polyethylene oxidation reaction pathway outlining the mechanism of oxidative damage propagation. The carbon radical present on the reactant in the first line is initiated via environmental stress such as exposure to UV light or heat. It then can react with oxygen to form an oxygen radical, which can then transfer the radical onto a carbon chain, beginning the process again. Thus, polyethylene oxidation can propagate throughout the material if it is not otherwise stopped.

### 1.2.2 Physical Changes

Chemical degradation such as oxidation causes physical changes to PEX-a pipe. Whereas oxidation in metals leads to the formation of oxides in a surface layer of rust, oxidation of PEX-a causes discolouration and brittleness. Undyed PEX-a pipes are a translucent off-white colour following the manufacturing process, but they become yellow and eventually brown over time as oxidation occurs (Figure 1.3).

The change in colour with oxidation is a visual indication that the flexible polymer has started to become brittle. A consequence of this degradation of the mechanical properties of the PEX-a pipe is that in the presence of a continuous applied stress such as the water (hydrodynamic) pressure within the pipe, cracks can form on the inner surface of the oxidized PEX-a pipe. In extreme cases, cracks can penetrate through the pipe wall, causing catastrophic pipe failure. Although cracks tend to form at defects on the inner surface of the pipe, the mechanism of crack propagation is not well understood<sup>8</sup>.

a)



b)



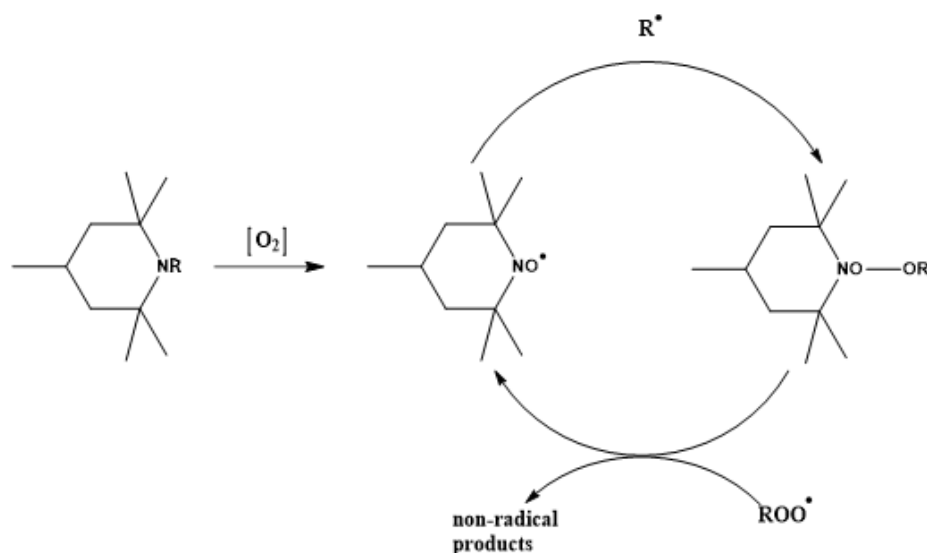
**Figure 1.3:** a) Photograph of virgin/unused PEX-a pipes of various sizes. b) Photograph of 1/2” PEX-a pipe aged for 4 weeks at 80° C and 80 psi.

### 1.3 Stabilization of PEX-a Pipes

To reduce the chemical and physical changes produced by the various degradation mechanisms, stabilizing compounds are typically added to the PEX-a pipe formulation. These additive compounds are classified according to their function into two categories: hindered amine light stabilizers (HALS) and phenolic antioxidants<sup>12-22</sup>.

#### 1.3.1 Hindered Amine Light Stabilizers

Hindered amine light stabilizers (HALS) contain a six-pointed ring consisting of five carbon atoms and one nitrogen atom, with a methyl group bonded to each of the two carbon atoms adjacent to the nitrogen atom. The hindered amine group continually converts oxygen radicals into non-radical products, effectively disabling their oxidative capability while regenerating a nitroxide radical instead of consuming the HALS. This process is referred to as the Denisov cycle and is shown schematically in Figure 1.4. HALS have been shown to be very long-lasting due to the cyclic mechanism effectively regenerating the active site, and the compounds remain active for long periods of time<sup>13-15</sup>.

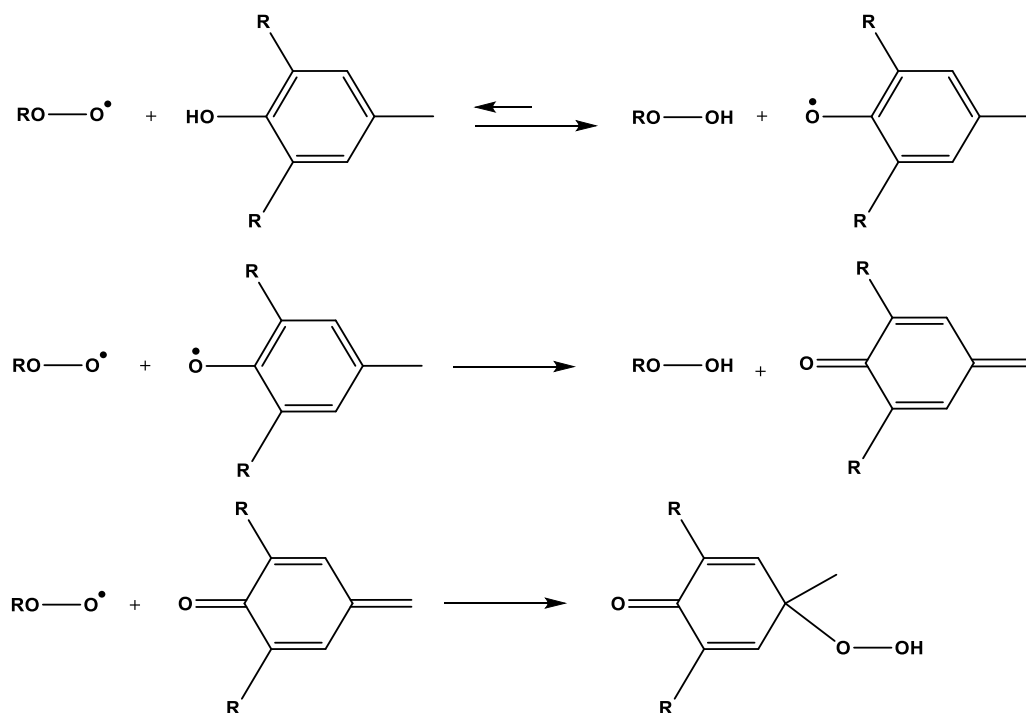


**Figure 1.4:** Chemical mechanism of stabilization for a general hindered amine light stabilizer (HALS) additive. The nitrogen bond is readily available for reaction with oxygen, forming a nitroxide radical. This form can then scavenge radicals from the polyethylene chains and cyclically transform both carbon radicals and oxygen radicals into non-radical products, continuously reforming the nitroxide radical form.

### 1.3.2 Phenolic Antioxidants

Phenolic antioxidants are compounds containing a phenyl group, commonly referred to as a benzene ring (a 6 membered carbon ring with alternating double bonds), with an alcohol group bonded to one of the phenolic carbons, and a methyl group bound to each of the two adjacent carbons. As for HALS, the phenolic antioxidant additives scavenge oxygen radicals from the PEX-a matrix as they are more reactive than the polyethylene chains. The stabilizing mechanism

is shown in Figure 1.5. Unlike HALS, the phenolic antioxidant compounds are not regenerated and can only stabilize up to three oxygen radicals each<sup>14,15,19,21</sup>.



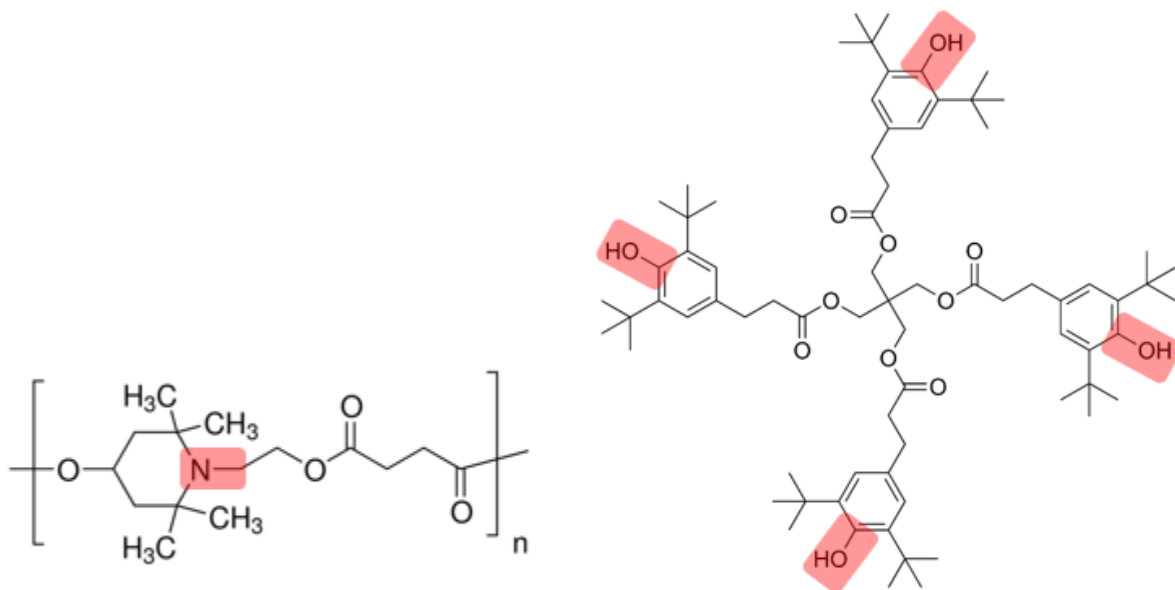
**Figure 1.5:** Chemical mechanism of stabilization for a general phenolic antioxidant additive.

The active site for these additives is the hydroxyl group bonded to the phenyl ring. This site can scavenge oxygen radicals present in the environment to form non-radical products twice. This reaction shifts the electron sharing within the phenyl ring, allowing for a third oxygen radical to be scavenged by the other end of the phenyl ring.

### 1.3.3 Undesired Reactions with Additives

The PEX-a pipes that we investigated used one phenolic antioxidant (Irganox 1010) and one HALS additive (Tinuvin 622); their chemical structures are shown in Figure 1.6. Tinuvin 622 is synthesized as a long chain polymer so that the additive molecules will remain within the PEX-a matrix, as a single monomer would be small enough to diffuse out of the polymer matrix.

An Irganox 1010 molecule contains four hindered amine groups, each with the capacity to continually scavenge oxygen radicals.



**Figure 1.6:** Chemical structure of the stabilizing additives used in the PEX-a pipes studied in this thesis: Tinuvin 622 (left) and Irganox 1010 (right). Tinuvin 622 is the HALS additive, which is a long chain polymer with one active site per monomer (highlighted in red). Irganox 1010 is the phenolic antioxidant, which is a large molecule with 4 active sites per molecule (highlighted in red).

Unfortunately, the additive compounds do not exclusively react in the desired way, and it is possible for other reactions to occur between the additive compounds and compounds in the environment<sup>14,16,17,18,20-23</sup>. A particularly reactive site within the additives is the ester linkage, the single carbon-oxygen bond, which is sensitive to hydrolysis from water present in its environment. Each Tinuvin 622 monomer has two ester linkages that can both be cleaved during a hydrolysis reaction, leaving behind molecular fragments that could diffuse out of the PEX-a matrix. The ester linkages within Irganox 1010 are at the center of the molecule so that, with



such large functional groups surrounding them, they are not as available to react as the ester linkages in Tinuvin 622.

## **1.4 Research Goals and Scope of Thesis**

In the Dutcher Lab, we are using sophisticated experiments and data analysis to investigate degradation processes in PEX-a pipes so that the mechanism of pipe failure can be better understood. By using various accelerated ageing environments, our intent is to provide new information that can be used to improve the properties of these pipes so that in-service pipes will last longer. This work is performed in collaboration with our industry partner PexCor Manufacturing Company in Calgary, AB, with the hope of providing PexCor with a competitive advantage in the marketplace.

In this thesis, I present the results and analysis of Fourier Transform Infrared (FTIR) microscopy measurements of the chemical properties of PEX-a pipes subjected to different, exaggerated ageing environments – immersion in hot air, immersion in hot water, exposure to recirculating hot water at elevated pressure, as well as exposure to UV/ozone. As part of this work, I designed and implemented the recirculating water system that provides our most realistic and in-depth study of PEX-a pipe ageing.

Our primary goals with accelerated ageing, are to induce the same form of degradation as seen in the field, only at a faster rate. In order to do this, we subject pipes to environments that are elevated but not extreme. For example, our high temperature experiments reach temperatures of 90° C, up from the 50° C - 60° C temperatures seen in home applications and the 80° C

temperatures seen in industrial applications. While we do not wish to wait years for the ageing to occur, we also want to expose pipes to a realistic environment.

In Chapter 2, I provide background information on the experimental techniques and a description of the principal component analysis (PCA) of the data. In Chapter 3, I present a description of the materials and methods used in the present study. In Chapter 4, I present the results and discussion of our experiments. In Chapter 5, I provide a summary of the main results and suggestions for future work.

## 2 Background

### 2.1 Fourier Transform Infrared (FTIR) Spectroscopy

#### 2.1.1 Transmission FTIR

Infrared (IR) spectroscopy can probe the chemical composition of a material by probing the vibrational energy states of chemical bonds within the material. Atoms bonded together within a molecule vibrate at quantized energy levels which can be determined by experiment and interpreted in terms of quantum theory. The energy of infrared photons is of the same order as the energy gaps between these vibrational states, so that the chemical bonds can absorb infrared photons. By measuring the energies of absorbed photons, one can study the chemical bonds within the material. Further, by detecting a relative number of absorbed photons, one can determine the amount of said chemical present in the material. The technique of infrared spectroscopy has been refined through the use of a Michelson interferometer and by analyzing the data using Fourier transforms, referred to as Fourier Transform Infrared (FTIR) spectroscopy. This approach allows all wavelengths within the mid IR range ( $3650\text{ cm}^{-1}$  to  $650\text{ cm}^{-1}$ ) to be measured at once with a typical resolution of  $2\text{ cm}^{-1}$ , which improves the signal to noise and reduces the scan time relative to IR spectrometers based on dispersive elements.

FTIR spectroscopy has been used extensively to characterize the chemical properties of polymers<sup>12,22,25,26</sup>. In practice, peaks in the absorbance are measured and related to characteristic vibrational frequencies of chemical species within the sample. The centre frequency, width and intensity of the peaks are sensitive to the local environment of the chemical bonds, and thus can provide information on the conformation, orientation, and phase state of the molecules. As such,

information on physical properties can be obtained from FTIR spectra through the chemical fingerprints.

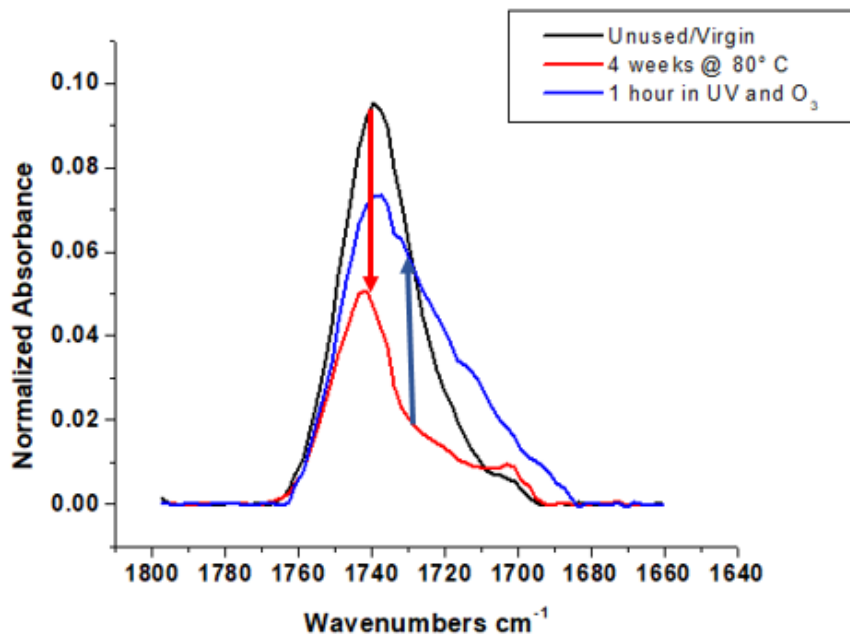
#### **2.1.1.1 IR Spectral Bands of PEX-a Pipe**

IR spectra of PEX-a pipe consist of bands that are characteristic of both the polyethylene and the additive compounds. One of the most notable bands within the IR spectra is centred at  $2019\text{ cm}^{-1}$ , which arises from both amorphous and crystalline polyethylene<sup>2</sup>. This band provides a useful reference peak within each spectrum; by normalizing the intensity values in each spectrum to the area under this peak, we can directly compare spectra collected on different axial slices that differ slightly in thickness. The carbonyl peak at  $\sim 1740\text{ cm}^{-1}$ , which corresponds to the stretching vibration of carbon – oxygen double bonds, is particularly useful in characterizing the ageing of PEX-a pipes. Since carbonyl groups are typically present in the additive compounds, the carbonyl peak can provide a measure of the additive content of the PEX-a pipe. The contribution to the carbonyl peak from the additives will in general decrease with ageing time as the additives are consumed. In addition, carbonyl groups are produced in the oxidation of polyethylene, and this contribution to the carbonyl peak will in general increase with ageing time. The carbonyl groups from oxidation products vibrate at slightly lower wavenumbers than those from the additive compounds, as the carbonyl groups in the oxidation products generally occur in the form of carboxylic acids, ketones or aldehydes, allowing the identification of these two contributions to the carbonyl peak (Figure 2.1)<sup>7-10</sup>. To confirm this interpretation, we can use the intensity of the ester peak centred at  $1160\text{ cm}^{-1}$  (Figure 2.2) that arises from the stretching of carbonyl carbon – ester oxygen single bonds (Figure 2.3). The carboxylic acids, ketones and aldehydes that arise from oxidation of polyethylene will not absorb in this fingerprint region, allowing for a cleaner determination of additive loss. However, degradation products of the

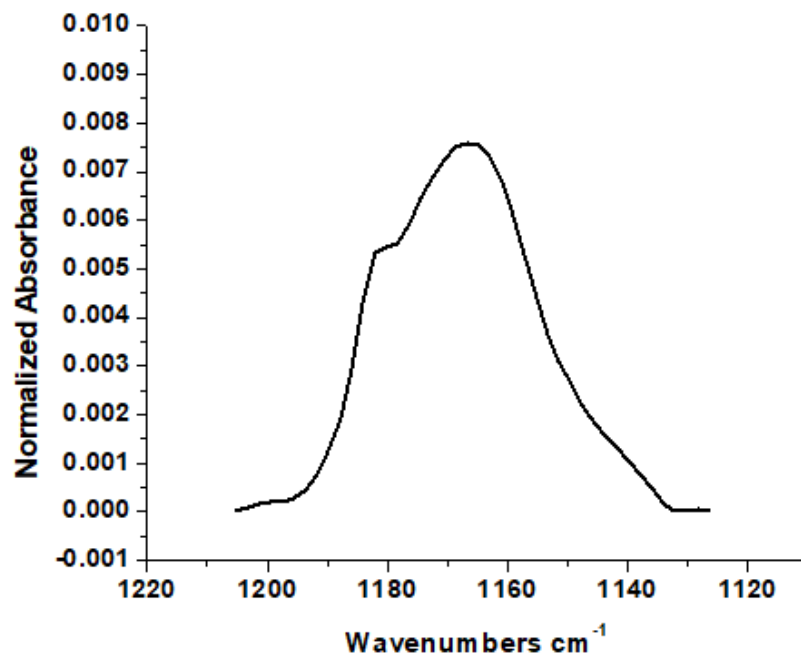
additives themselves may still contain ester linkages which would absorb in this region, further complicating the distinction between additive loss and pipe degradation<sup>7-10</sup>. Alternatively, a double peak centred at  $3600\text{ cm}^{-1}$  (Figure 2.4) arises exclusively from the O-H stretch of the phenolic hydroxyl groups present in the two polymorphs of the antioxidant additives and the intensity and/or area of this feature can be used to track changes to the additive content in the samples.

As discussed in Chapter 1, there are many absorbance bands arising from polyethylene, and although the major vibrations dominate and saturate the spectrum, smaller intensity overtones and combination bands (multiple functional groups vibrating at the same frequency) can be used to gain information on the structural integrity of the polyethylene matrix. Crystalline polyethylene exhibits a different signal than that of amorphous polyethylene, i.e., some peaks arise exclusively from crystalline polyethylene and some peaks arise exclusively from amorphous polyethylene. By dividing the area under the crystalline peak in the wavenumber range from  $1870\text{ cm}^{-1}$  and  $1960\text{ cm}^{-1}$  by the area under the amorphous peak in the wavenumber range from  $1273\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$ , a measure of crystallinity ratio of the polyethylene can be determined. Another useful band is the carbon – hydrogen out-of-plane bending vibration centred at  $910\text{ cm}^{-1}$ . This vibration only occurs when the carbon atom in question is double bonded to another carbon atom, this is commonly referred to as a terminal vinyl group. The polyethylene consists of long chains, and carbon – carbon double bonds only exist at the ends of chains. These groups will be present at varying levels throughout a PEX-a pipe based on the process of cross-linking and polymerization in the manufacturing process. However, as the polymer matrix oxidises and degrades, more terminal vinyl groups will be created via chain

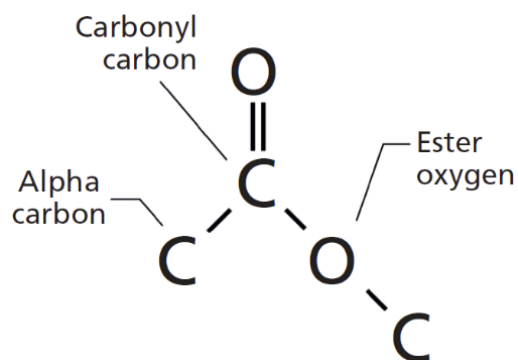
scission. Therefore, changes in the  $910\text{ cm}^{-1}$  peak with ageing time, compared to an unused/virgin sample, provide a measure of the degree of chain scission.



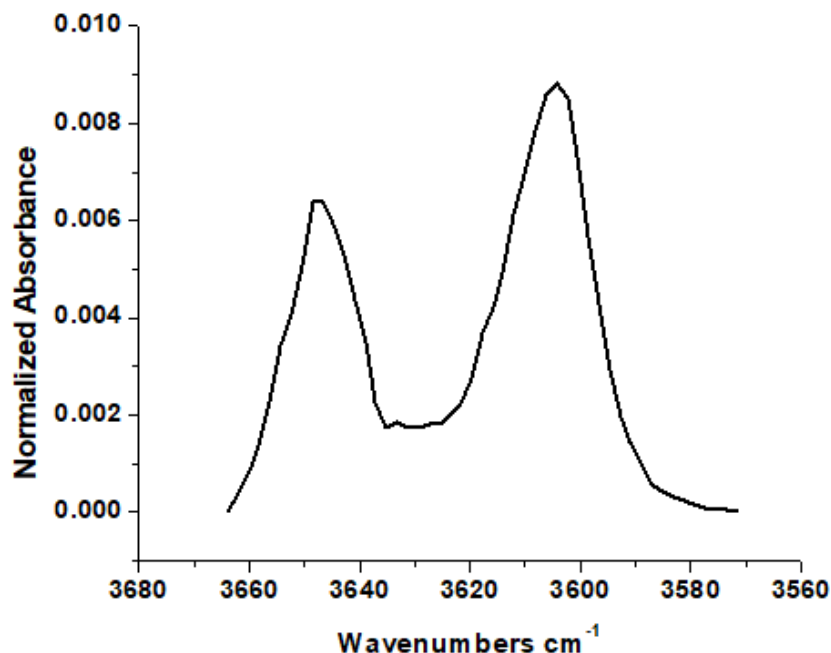
**Figure 2.1:** The carbonyl region of a PW PEX-a sample subjected to Milli-Q water immersion accelerated ageing and UV/ozone experiments. The IR spectrum for a virgin PEX-a sample (black) had a large intensity at  $1740\text{ cm}^{-1}$ . After 4 weeks of hot water immersion ageing at  $80^{\circ}\text{C}$  (red), the intensity at  $1740\text{ cm}^{-1}$  was significantly reduced. The sample was then exposed to UV/ozone for 60 min (blue), which caused significant oxidation, increasing the intensity within the wavenumber range  $1730\text{ cm}^{-1}$  to  $1680\text{ cm}^{-1}$ .



**Figure 2.2:** Representative ester peak exhibited by a PW PEX-a pipe. The sharper feature present on the shoulder around 1182 cm<sup>-1</sup> arises from crystalline polyethylene, while the broader peak centred on 1162 cm<sup>-1</sup> arises from the ester groups present in both Tinuvin 622 and Irganox 1010 additives.



**Figure 2.3:** Labelled diagram of the naming scheme for the atoms involved in an ester linkage.



**Figure 2.4:** Representative phenolic hydroxyl double peak exhibited by a PW PEX-a pipe. The two peaks correspond to the O-H stretch in the two polymorphs of the phenolic antioxidant Irganox 1010.

#### 2.1.1.2 Determination of Characteristic IR Index Values

To quantify the changes that occurred in key IR absorbance peaks during the ageing process, we defined several characteristic index values to characterize various characteristics of the peaks: the maximum absorbance value (peak max), the area under the absorbance peak, and the wavenumber corresponding to the centre of area of the absorbance peak (peak centroid). The peak max and area under the peak both provide a measure of the amount of the corresponding chemical group within the sample, whereas the peak centroid can provide information on changes to chemical groups, e.g., the centroid of the carbonyl peak shifting to lower wavenumbers indicates the formation of oxidation products. When the IR spectra are properly

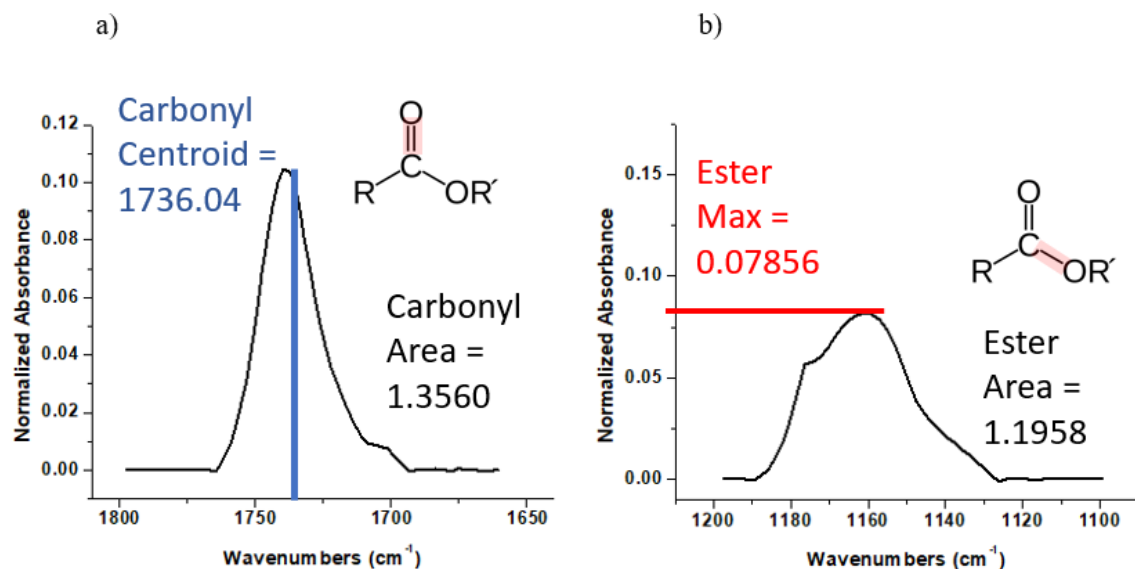


normalized, the index values allow the comparison of the amount of the corresponding chemical groups in different IR spectra, providing metrics that can be used to track the effects of accelerated ageing.

The index values were calculated using a Python script in which the peak region of interest was baselined, the absorbance peak intensities were normalized relative to that of the 2019 cm<sup>-1</sup> peak, and the peak max intensity was determined. In addition, the peak areas were calculated using a trapezoid rule for integration of the peak, which allowed the determination of the peak centroid. Peak centroids are calculated as a weighted average of the absorbances at each wavenumber in a particular band:

$$\text{Centroid} = \frac{\sum_{\nu} \nu \times A(\nu)}{\sum_{\nu} A(\nu)} \quad (1)$$

where the sum over  $\nu$  is bounded by the specified wavenumber range,  $A(\nu)$  is the absorbance at wavenumber  $\nu$ . In Figures 2.5 (a) and (b), we show examples of index values calculated from their IR absorbance peaks.



**Figure 2.5:** Visualization of characteristic index values as calculated from their respective peaks. (a) A typical carbonyl peak from the centre of a virgin PW PEX-a pipe wall. The peak area was calculated using a trapezoid rule for integration of the peak. The small shoulder on the lower wavenumber side of the peak shifts the peak centroid (1736 cm<sup>-1</sup>) from the peak max wavenumber value of 1740 cm<sup>-1</sup>. (b) A typical ester peak from the centre of a virgin PW PEX-a pipe wall. The peak area was calculated using a trapezoid rule for integration of the peak. The sharp shoulder on the higher wavenumber side of the peak shifts the peak centroid (1161.3 cm<sup>-1</sup>) from the peak max wavenumber value 1160 cm<sup>-1</sup>. The peak max index was calculated as the normalized value of the maximum absorbance.

IR peaks of interest in a spectrum of a PEX-a pipe sample can have a variety of contributions, leading us to use different metrics to visualize their properties. As mentioned in section 2.1.1.1, the carbonyl peak contains contributions from additive compounds as well as oxidation products in the form of carboxylic acids, ketones and aldehydes. Since these oxidation products absorb at distinctly lower wavenumbers (1720 cm<sup>-1</sup> – 1700 cm<sup>-1</sup>) than the additive carbonyls (1740 cm<sup>-1</sup>),

the carbonyl centroid, calculated using the wavenumber range of  $1680\text{ cm}^{-1}$  to  $1785\text{ cm}^{-1}$ , provides valuable information on the degree of oxidation present in the sample<sup>7-10</sup>. We use the carbonyl area index to monitor the degree of additive loss and compare these changes with those for the carbonyl centroid index to obtain a measure of the degree of oxidation. For example, if the carbonyl area decreases but the shift in the carbonyl centroid is small, then we infer that there was a loss of additives with little oxidative degradation during the ageing process. During in-service use of PEX-a pipe, additive loss is generally more significant than oxidation.

The ester peak at  $1160\text{ cm}^{-1}$  is similarly complex, containing contributions from additives and degradation products, including a distinct shoulder centered at  $1181\text{ cm}^{-1}$ , which we attribute to crystalline polyethylene<sup>7-10</sup>. In contrast to the carbonyl peak, the contributions to this peak from different species have significant overlap, limiting the usefulness of the ester centroid index. Theoretically, an IR absorbance peak area and peak max are exactly correlated, however, the complexity of this peak causes deviation between the two. Furthermore, different formulations of PEX-a pipe exhibit ester peaks of slightly different intensity and shape. Because of this complexity, we choose the ester peak max, centred at  $\sim 1161\text{ cm}^{-1}$ , to characterise changes to this peak with ageing. In general, changes to the ester peak max index and the carbonyl peak index due to ageing are highly correlated, since they both track the loss of additives. However, a detailed interpretation of the ester peak max index is more challenging.

Other IR peaks present in PEX-a pipe spectra are more straightforward to interpret, including the terminal vinyl peak at  $910\text{ cm}^{-1}$  and the phenolic hydroxyl doublet at  $3600\text{ cm}^{-1}$ . The terminal vinyl peak is very sharp and has contributions only from terminal vinyl groups on the polyethylene chains. For this peak, the peak area is a sufficient metric to monitor changes to this peak and it is calculated using a trapezoid rule for integration of the peak with a

wavenumber range of  $894\text{ cm}^{-1}$  and  $924\text{ cm}^{-1}$ . PEX-a pipes have an initial concentration of terminal vinyl groups, and this concentration increases with ageing because of chain scission that occurs during oxidation. The phenolic hydroxyl doublet, arising from the two polymorphs of this functional group is also a sharp feature in the IR spectra due to the lack of hydrogen bonding in the polyethylene matrix. Hydrogen bonding causes the bond to vibrate at a range of frequencies due to the varying strength of the intermolecular forces, however, no hydrogen bonding occurs when the solvent is polyethylene. Decreases in the area of this doublet feature, calculated within the wavenumber range of  $3550\text{ cm}^{-1}$  and  $3725\text{ cm}^{-1}$ , provides a measure of the decrease in the amount of Irganox 1010 additive present in the PEX-a pipe samples, which is consumed as it scavenges oxygen radicals. Other notable IR peaks include the amorphous and crystalline polyethylene peaks, with peak frequencies of  $1304\text{ cm}^{-1}$  and  $1915\text{ cm}^{-1}$  respectively; however these peaks are not significantly affected by the ageing process, and I will not discuss changes to these peaks with ageing in this thesis.

For completeness, I provide a list of the IR indices used in this thesis, together with Table 2.1 that highlights the important features of the functional groups that are used to calculate the indices.

(1) The *carbonyl area index* is calculated as

$$\text{Carbonyl Area} = \int_{1680}^{1785} \frac{A(\nu)}{a_{2019}} d\nu \quad (2),$$

where  $A(\nu)$  is the absorbance at each wavenumber  $\nu$  in  $\text{cm}^{-1}$ , and  $a_{2019}$  is the area under the  $2019\text{ cm}^{-1}$  normalization peak.

(2) The *carbonyl centroid index* is calculated as

$$\text{Carbonyl Centroid} = \frac{\sum_{\nu=1680}^{1785} \nu \times \frac{A(\nu)}{a_{2019}}}{\sum_{\nu=1680}^{1785} \frac{A(\nu)}{a_{2019}}} \quad (3)$$

where  $A(\nu)$  is the absorbance at each wavenumber  $\nu$  in  $\text{cm}^{-1}$ ,  $a_{2019}$  is the area under the 2019  $\text{cm}^{-1}$  normalization peak, and  $N$  is the total number of wavenumbers in the sum.

(3) The *ester area index* is defined as

$$\text{Ester Area} = \int_{1124}^{1196} \frac{A(\nu)}{a_{2019}} d\nu \quad (4),$$

where  $A(\nu)$  is the absorbance at each wavenumber  $\nu$  in  $\text{cm}^{-1}$ , and  $a_{2019}$  is the area under the 2019  $\text{cm}^{-1}$  normalization peak.

(4) The *vinyl area index* is calculated as


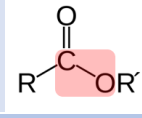
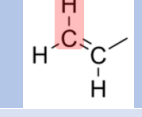
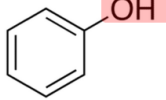
$$\text{Vinyl Area} = \int_{894}^{924} \frac{A(\nu)}{a_{2019}} d\nu \quad (5),$$

where  $A(\nu)$  is the absorbance at each wavenumber  $\nu$  in  $\text{cm}^{-1}$ , and  $a_{2019}$  is the area under the 2019  $\text{cm}^{-1}$  normalization peak.

(5) The *Irganox area index* is calculated as

$$\text{Irganox Area} = \int_{3550}^{3725} \frac{A(\nu)}{a_{2019}} d\nu \quad (6),$$

where  $A(\nu)$  is the absorbance at each wavenumber  $\nu$  in  $\text{cm}^{-1}$ , and  $a_{2019}$  is the area under the 2019  $\text{cm}^{-1}$  normalization peak.

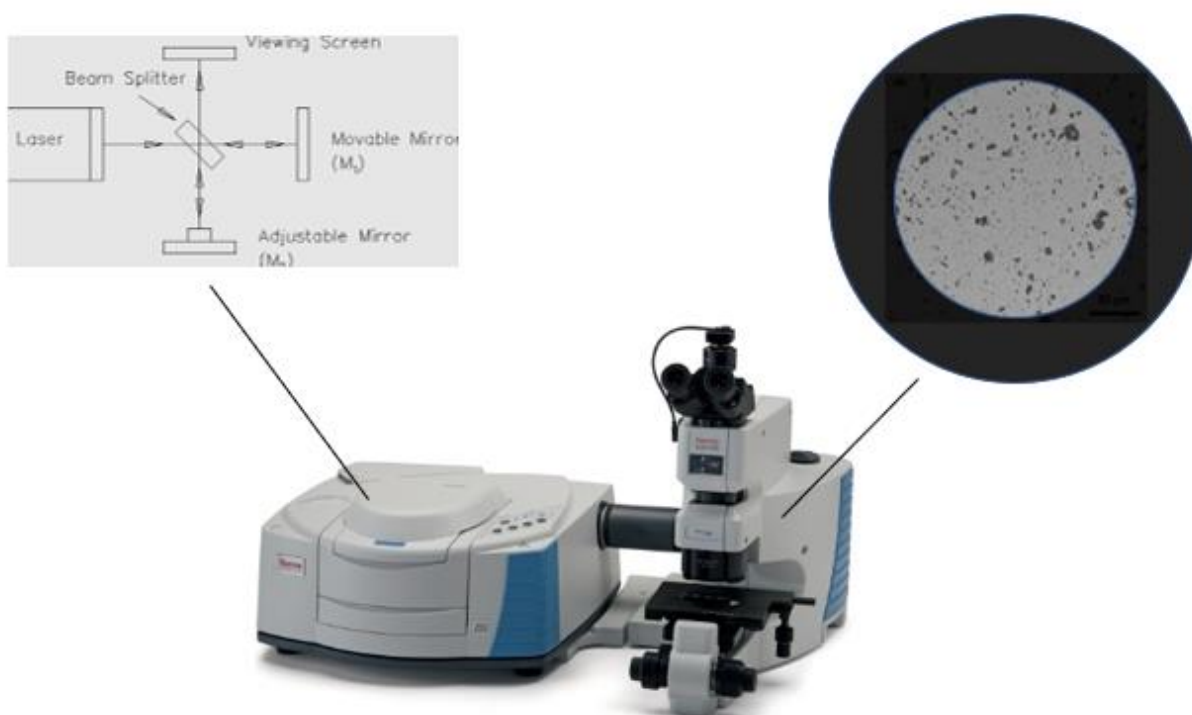
Functional Group	Wavenumber Range	Bond Vibration	Chemical Origin
Carbonyl	1680 cm <sup>-1</sup> – 1785 cm <sup>-1</sup>		Additive + Oxidation
Ester	1124 cm <sup>-1</sup> – 1196 cm <sup>-1</sup>		Additive + Degradation
Terminal Vinyl	894 cm <sup>-1</sup> – 924 cm <sup>-1</sup>		End of PE Chains
Phenolic Hydroxyl	3550 cm <sup>-1</sup> – 3725 cm <sup>-1</sup>		Additive

**Table 2.1:** Tabulated list of the functional groups used to calculate the characteristic IR indices used in this work, together with their wavenumber range, bond vibration and chemical origin.

### 2.1.2 FTIR Microscopy

By combining the chemical specificity of FTIR spectroscopy with the high spatial resolution of optical microscopy, we obtain the technique of FTIR microscopy in which we can map chemical fingerprints within a sample with a spatial resolution of tens of micrometers. FTIR microscopes typically combine an FTIR spectrometer, an optical microscope and a photoelectric IR detector with several beam splitters such that both visible and IR light can pass through a microscope lens to the sample. This allows the user to choose a location on the sample, using the optical microscope, and measure FTIR spectra at that location, using the FTIR spectrometer. In

the present study, we use FTIR microscopy to measure high spatial resolution spectra across the wall thickness of PEX-a pipe to track the various chemical species that play a role in the chemical and physical integrity of the pipe.



**Figure 2.6** Schematic diagram of an FTIR spectrometer + optical microscope. A schematic diagram of the Michelson interferometer inside the FTIR instrument is shown on the the left and a general optical microscopy image is shown on the right. In addition to an optical lens for viewing of the sample, the microscope is generally outfitted with a camera (above the eye-piece lenses) for digital viewing.

## 2.2 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is an unsupervised, statistical multivariate data analysis technique used for dimensionality reduction and trend visualization<sup>27</sup>. This is performed by reducing a multivariate data set of correlated variables down to fewer, uncorrelated variables that describe the most important features of the data set, allowing trends to be more easily visualized. The new variables, known as principal components (PCs), are linear combinations of the original variables and are defined orthogonally to each other, in the direction of maximum variance in the data. This is done through a series of linear operations on a  $n \times m$  matrix composed of  $m$  variables (wavenumbers in this study) and  $n$  observations (IR spectra in this study). Typically, either a singular value decomposition (SVU) or an eigenvalue decomposition (EVD) is employed to extract the eigenvectors that define the new  $m$ -dimensional PC-space<sup>27</sup>. The original data set is then projected into this PC-space with a one-to-one correspondence, i.e., each observation in the original data set corresponds to one observation in PC-space.

The principal component-space (PC-space) is mapped by the calculated eigenvectors or principal components (PCs) and is the same size as the space mapped by the original variables (wavenumbers in our case). Mathematically, these eigenvectors each have associated eigenvalues, and, in this context, the eigenvalues represent the total amount of variance explained by each PC. The PCs are generally ordered in descending order of explained variance, with the first few PCs selected to visualize a large amount of variance with a small number of variables. The visualization of the eigenvalues versus the eigenvectors is known as a scree plot and is used to determine the number of leading PCs that should be considered for the dataset. This introduces some subjectivity into the analysis as one needs to decide the minimum number of PCs that is appropriate to capture most of the variance. For the PCA performed in this study,



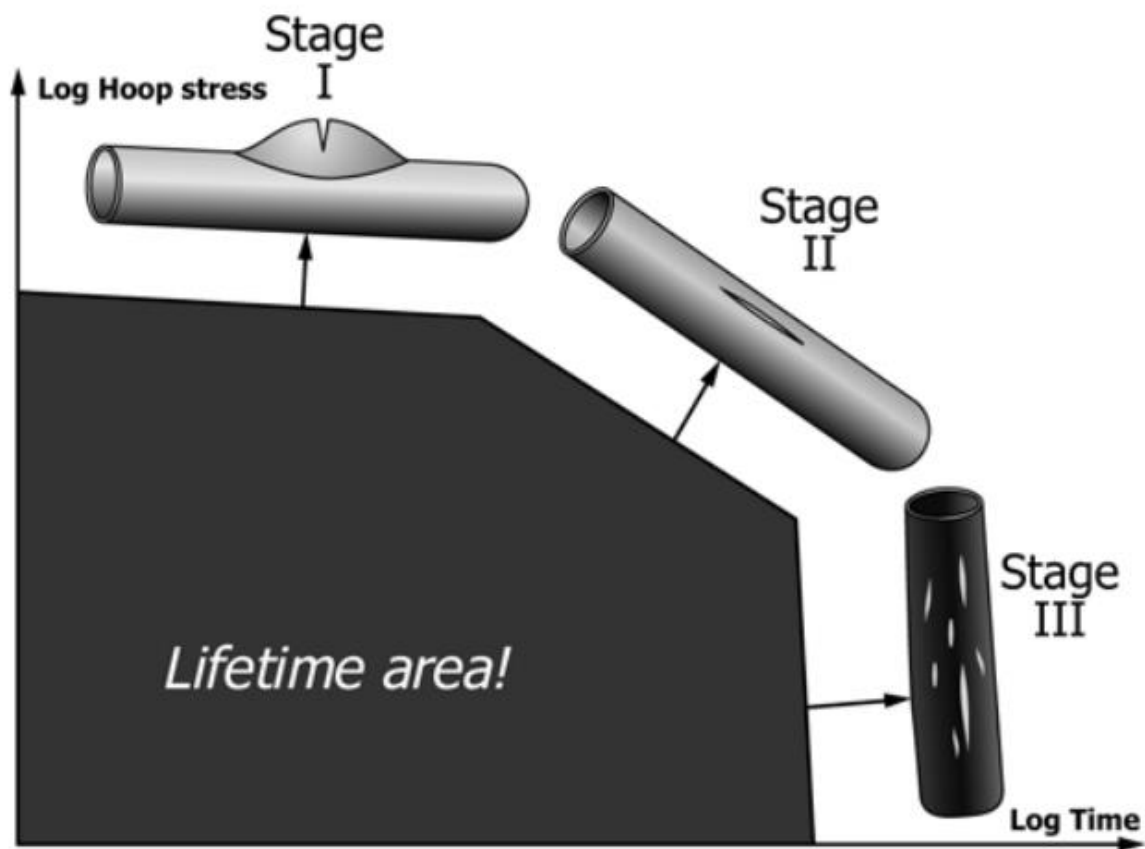
we considered only the first two PCs, since they explained 89% of the variance in the original data set, with PC1 and PC2 explaining 76% and 13% of the variance, respectively.

PCA has proved to be a very useful tool in PEX-a pipe analysis, allowing the identification of differences between various pipe formulations<sup>26</sup>. A major benefit of performing PCA on FTIR spectra of PEX-a pipes is the ability to use entire spectra in the analysis. As PCA is unsupervised and multivariate by nature, it can consider the changes to all the relevant spectral bands and condense them into fewer variables that explain the greatest variance in the data set, producing a concise, comprehensive representation of the data. It tends to be very difficult to incorporate more than just a few relevant bands into a concise discussion of the effects of ageing on multiple PEX-a formulations. This is because each formulation contains different additives at varying concentrations, each with several IR absorbing chemical groups. PCA simplifies the data interpretation. For example, PCA condenses correlated changes from two IR peaks which represent the same functional group into one variable, such as changes to the carbonyl and ester vibration peaks arising from an ester group. This allows us to visualize and quantify correlated changes to the chemical species present in the pipe. In this study, we employ PCA on a single PEX-a pipe formulation aged in different environments at 80° C, to identify similarities and differences between the effects of the different ageing environments.

### **2.3 American Standard Test Method (ASTM) for Ageing PEX-a pipes**

The American Standard Test Method (ASTM) provides many guides for different tests of the quality of a broad range of industrial products. Specifically, ASTM F2023 outlines a definitive guide for ageing PEX-a pipes with recirculating hot chlorinated water at high pressures<sup>24</sup>. We followed the procedure described in ASTM F2023 in all our ageing experiments,

with the aim of producing a so-called stage 3 failure. The different stages of failure of PEX-a pipe are shown in Figure 2.1: a burst of a flexible pipe (stage 1), a fracture of a pipe beginning to lose elasticity (stage 2), and cracking of brittle pipe with many small cracks (stage 3). The types of PEX-a ageing guidelines outlined in ASTM F2023 also include specifications on sample size and shape, temperature and test fluid. We generally followed these specifications for all our ageing experiments, as will be described in more detail in Chapter 3.



**Figure 2.7:** The logarithm of the hoop stress versus the logarithm of time in which the three stages of PEX-a pipe failure are indicated. The shaded region represents conditions to which PEX-a pipe can be subjected without failing. Conditions that lie outside the shaded area results in pipe failure, with different stages of failure indicated for the different directions shown in the figure. Image adapted from [24].

## 2.4 Previous Studies of Accelerated Ageing of PEX-a Pipes

Several research groups have attempted to develop in-house accelerated ageing experiments of PEX-a pipes and investigate the effects. Hirabayashi *et al.* conducted long-term hydrostatic and hydrodynamic pressure tests on PEX-a pipes<sup>20</sup>. Lundback *et al.* conducted immersion ageing in various environments including water and air on PEX plaques that they fabricated in-house<sup>21</sup>. Whelton *et al.* conducted immersion ageing of dog-bone shaped pieces cut from PEX-a pipes in chlorinated water<sup>16,22,23</sup>. Maria *et al.* performed hydrostatic pressure tests on polyethylene pipe segments, taking them almost to failure<sup>12</sup>. Bredács *et al.* conducted immersion tests on polyethylene pipes in aqueous chlorine dioxide at slightly elevated temperatures (40° C - 60° C)<sup>19</sup>. Duvall conducted chlorinated water recirculating ageing of polypropylene pipes.<sup>25</sup> The work of each of these groups helped to inform our process of developing our own accelerated ageing experiments.

As well as ageing their own samples, these groups each had their own protocol for investigating the effects of accelerated ageing. Hirabayashi *et al.* performed differential scanning calorimetry (DSC) measurements on small pieces of their samples under oxygen atmosphere at 210° C<sup>20</sup>. These measurements provided a quantification of the samples' oxidative induction time (OIT) which could then be compared for the different samples. In addition to these measurements, the group conducted proton NMR measurements over the melting point of polyethylene, allowing them to measure the cross-linking density of the material. They concluded that certain additive packages present in the PEX-a samples were much more effective than others<sup>20</sup>. They also found that the OIT was not a good predictor of PEX-a pipe failure; instead, the cross-linking density was more suitable<sup>20</sup>.

Similarly, Lunback *et al.* measured the OIT of their samples using DSC to determine the levels of antioxidants present<sup>21</sup>. These measurements were coupled to high performance liquid chromatography (HPLC) to ensure proper quantification of the additive concentration<sup>21</sup>. Their main goal was to investigate the difference between aerobic and anaerobic high temperature (75° C – 95° C) ageing environments on the PEX plaques studied. Their key conclusion was that both oxygen-rich and oxygen-free environments induced similar levels of additive depletion, confirmed to be migrating to the surrounding environment using HPLC<sup>21</sup>.

Whelton *et al.* conducted a thorough investigation of the chemical equilibrium of ageing solutions involving chlorine ions and they used the results of this investigation to age dog-boned shaped pieces of PEX pipes<sup>16,22,23</sup>. To determine the effects of their ageing process, they conducted DSC measurements and infrared (IR) spectroscopy on their dog-boned shaped samples<sup>14,23</sup>. They concluded that the solution properties of their chlorinated water must be carefully monitored throughout the ageing process to obtain reproducible results<sup>24</sup>. They were able to quantify the degree of diffusion of chlorinated water through a large variety of polyethylene-based pipes, including PEX-a, all of which were exclusively surface level effects (~ 200µm)<sup>23</sup>.

Maria *et al.* conducted DSC, IR microscopy and HPLC measurements to understand the effect of high temperature (80° C) hydrostatic pressure tests on PEX-a pipes<sup>12</sup>. Combining the decrease in OIT and IR absorbance, they determined that antioxidants were depleted from their PEX-a pipe samples. For their longest measurement time of 12,000 hours, they found that all the original antioxidants had been removed from the product<sup>12</sup>.

Bredács *et al.* conducted typical DSC and FTIR measurements, as well as SEM measurements of their dog-boned shaped polyethylene samples after full immersion in aqueous

chlorine dioxide<sup>19</sup>. As for Whelton *et al.*, they noted that precise control of the chemical equilibrium was paramount to the success of their experiments<sup>19</sup>. At their slightly elevated temperatures of 40° C - 60° C and slightly elevated chlorine content of 5 ppm – 10 ppm ClO<sub>2</sub>, they noticed severe surface damage within the first week of ageing<sup>19</sup>. They tested 0.3 mm and 1 mm thickness dog-boned shaped samples and noticed the thinner samples experienced substantially more damage. From the reduction in OIT and increase in carbon-chlorine IR absorbance peaks, they inferred that the ClO<sub>2</sub> was reacting with both the antioxidant and the polyethylene, primarily through a surface effect<sup>19</sup>.

Duvall designed and constructed a recirculating system with the capabilities of ageing polypropylene pipe samples at high temperatures and pressures (~100 °C & ~100 psi) with chlorinated water<sup>25</sup>. Using optical microscopy, he observed brittle cracks penetrating the pipe wall on samples aged for 1500 hours<sup>25</sup>, which he attributed to substantial levels of oxidative damage. ATR-FTIR measurements revealed an increase in oxidative products within the spectra<sup>25</sup>.

Each of these previous studies helped to influence the experiments we conducted, which started with immersion studies of pipe samples and extended to the design, construction and implementation of our own recirculating water system.

### 3 Materials and Methods

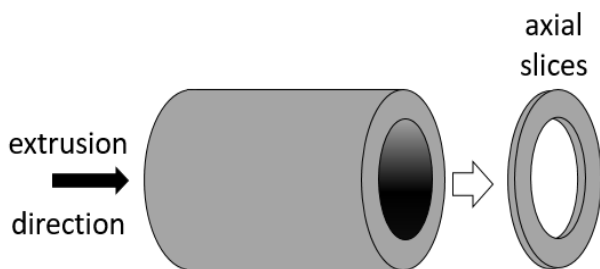
#### 3.1 PEX-a Pipe Samples

Several formulations of PEX-a pipes, manufactured using different additive packages and crosslinking peroxides, were provided by PexCor Manufacturing Company, Calgary, AB. These PEX-a pipes were used in in-house accelerated ageing experiments and characterized using FTIR microscopy. The diameter of most pipe samples used in the accelerated ageing experiments was 1/2", with a 2 mm wall thickness, but we also used some pipe samples with 3/4" diameter and a 3 mm wall thickness. In addition, we used FTIR microscopy to characterize pipe samples that had experienced in-service use.

Prior to ageing, PEX-a pipe segments were cut perpendicular to the extrusion direction using a standard pipe cutter. The lengths of the pipe samples used for the various ageing protocols are listed in Table 3.1.

Type of Accelerated Ageing	Temperature Range	Medium	Flow?	Nominal Length of Pipe Sample
UV/Ozone	20-25	Ozone gas	No	2 cm
Air Immersion	80-85	Air	No	4 cm
Water Immersion	60-85	Milli-Q Water	No	4 cm
Recirculating Water	70-90	Distilled Water	Yes	60 cm

**Table 3.1:** Tabulated accelerated ageing conditions including the specified temperature range, ageing medium and length of PEX-a pipe sample used.



**Figure 3.1:** Schematic diagram of PEX-a pipe showing the extrusion direction of the pipe and the slicing of the pipe to create thin axial slices ( $\sim 100 \mu\text{m}$  in thickness).

### 3.2 Accelerated Ageing of PEX-a Pipe

In-service potable hot water PEX-a pipes operate at pressures of 50 psi and are exposed to chlorinated water at elevated temperatures (testing and certification at  $60^\circ\text{C}$  for domestic hot water lines and  $82^\circ\text{C}$  for commercial hot water lines<sup>28</sup>) on the inner wall surface with the outer surface exposed to air. Prolonged exposure to these conditions causes gradual degradation of the pipe properties and, in some cases, catastrophic failure.

To develop a better understanding of the PEX-a ageing process, we subjected PEX-a pipe samples to different environmental stresses. Our goal was to use environmental conditions that mimicked various aspects of in-service conditions for hot water pipes, e.g., high temperature, high pressure, exposure to water, but with more aggressive conditions. The basic idea behind accelerated ageing is to speed up the degradation of the pipes while still probing the same degradation processes.

In Table 3.1, we list the different accelerated ageing procedures used in the present study with a summary of the different environmental stresses imposed on the PEX-a pipe samples during each procedure.

### 3.2.1 Exposure to UV/Ozone

The UV/ozone ageing experiments were performed using a Jelight Company model 342 UVO-Cleaner (Figure 3.2). The samples were placed within UV/ozone chamber and exposed to UV light (wavelengths of 184.9 nm and 253.7 nm with an average intensity of 28-30 mW/cm<sup>2</sup> @ 253.7 nm). UV light at 184.9 nm is absorbed by oxygen gas within the chamber to form ozone gas, and therefore the samples were exposed to both UV and ozone in the experiments.

UV/ozone experiments were performed on thin axial slices of PEX-a pipe (thickness ~100  $\mu$ m) and on ~ 2 cm long PEX-a pipe samples, with the samples placed ~ 2 cm from the UV light source. The samples were exposed to UV/ozone for different times ranging from 5 min to 2 h. At different time points, the samples were removed from the chamber for measurement using FTIR microscopy. The axial slices were measured directly. For the 2 cm long samples, axial slices were produced using the microtome, after first removing ~ 500  $\mu$ m from the pipe end to ensure that the radial profiles measured using FTIR microscopy were not affected by UV/ozone exposure of the pipe ends. The pipe segments were then placed back in the chamber for further ageing.





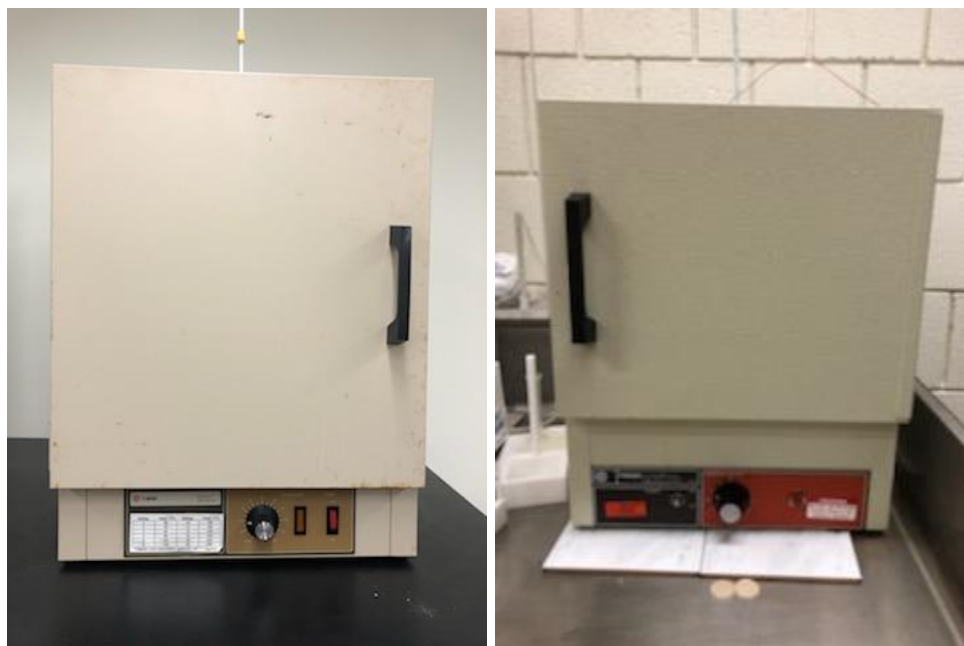
**Figure 3.2:** Images of the Jelight Company model 342 UVO-Cleaner used for the UV/ozone ageing of PEX-a pipe slices. The handle opens a drawer into which the samples are placed; the drawer is then closed to form a full seal. A timer is provided on the front with automatic shut-off capabilities.

### 3.2.2. Exposure to Elevated Temperature

#### 3.2.2.1 Immersion in Hot Air

PEX-a pipe segments ~ 4 cm in length were placed in a standard lab oven (Figure 3.3) and exposed to air at a fixed high temperature that was varied from 70 °C to 90 °C. Exposure to hot air simulated the environment of the outer surface of in-service pipes, which are at elevated temperature because of the flow of hot water through the inside of the pipes. Immersion ageing of pipes in hot air allowed us to isolate the effect of high temperature from the additional effects of hot water, pressure and chlorine. During the hot air immersion ageing experiments, the samples were removed from the oven at several time points within the first 4 weeks of ageing for measurement using FTIR microscopy. As for the pipe segments subjected to UV/ozone ageing,

axial slices were produced using the microtome, after first removing  $\sim 500\ \mu\text{m}$  from the pipe end to ensure that the radial profiles measured using FTIR microscopy were not affected by exposure of the pipe ends to the ageing environment. The pipe segments were then placed back into the oven for further ageing.



**Figure 3.3:** Lab ovens used to age PEX-a pipe samples immersed in high temperature air and Milli-Q water. The oven temperature was adjusted with a knob on the outside of the oven and monitored using a glass mercury thermometer.

### 3.2.2.2 Immersion in Hot Water

PEX-a pipe segments  $\sim 4\ \text{cm}$  in length were fully submerged in Milli-Q water in 600 mL glass beakers and placed in a standard lab oven (Figure 3.3) and exposed to a fixed high temperature that was varied from  $60\ ^\circ\text{C}$  to  $90\ ^\circ\text{C}$ . Since the pipe segments float in water, an inverted 50 mL beaker was placed on top of the pipe segments to ensure full submersion. A glass dish was placed on top of the 600 mL beaker to reduce evaporation of the water at elevated

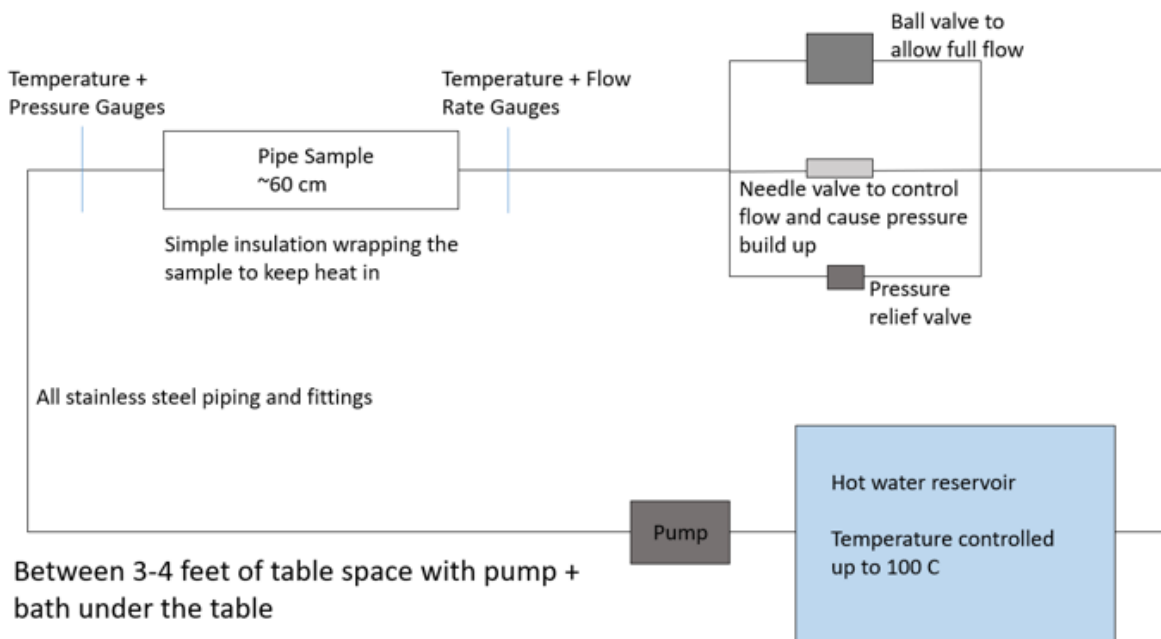
temperatures. Every 2-3 days during the ageing experiments, the water in the 600 mL beaker was removed and replaced with fresh Milli-Q water. Exposure of the pipe segments to hot water simulated the environment of the inner surface of in-service pipes, through which hot water flows. Immersion ageing of pipes in hot water allowed us to include the effects of both elevated temperature and exposure to water. During the hot water immersion ageing experiments, the pipe segments were removed from the oven at several time points within the first 4 weeks of ageing for measurement using FTIR microscopy. The pipe segments were cooled by placing them in room temperature water for ~ 15 min and then axial slices were produced using the microtome, after first removing ~ 3 mm from the pipe end to ensure that the radial profiles measured using FTIR microscopy were not affected by exposure of the pipe ends to the ageing environment. The pipe segments were then placed back in the water in the 600 mL beaker and covered by the inverted 50 mL beaker. The glass dish was replaced on the 600 mL beaker and the beaker was placed back into the oven for further ageing.

### **3.2.2.3 Recirculating Hot Water at High Pressure**

To more accurately simulate the ageing environment experienced by in-service PEX-a pipes, we designed and constructed a recirculating water system that was operated at elevated temperature and pressure (Figure 3.4). Our design was guided by ASTM F20237<sup>24</sup>. The system consisted of a circulating bath (Cole-Parmer, model number # RK-12122-32, 8 L capacity), a pump (McMaster-Carr extreme-head centrifugal pump, model number 43195K51) and various pressure and flow gauges and a pressure relief valve, connected by 304 stainless steel tubing (3/4" diameter) wrapped in thermal insulation. PEX-a pipe segments ~ 60 cm in length were placed into the system using quick connect fittings (McMaster-Carr Brass Push-to-Connect

fittings) that allowed quick removal and insertion of the pipe segments. In operation, hot distilled water was circulated at a flow rate of 2.6 GPM at a pressure of 80 psi, and a fixed temperature ranging from 70 °C to 90 °C was set in the circulating bath. To detect water leakage from the recirculating system, we used a water sensor (Wet Switch<sup>®</sup>, WS-1 from Diversitech, product number 3146992) placed on a tray underneath the PEX-a pipe segment. Following our successful operation of the recirculating system, we constructed a second nominally identical system that allowed us to conduct simultaneous ageing experiments under different conditions.

a)



b)



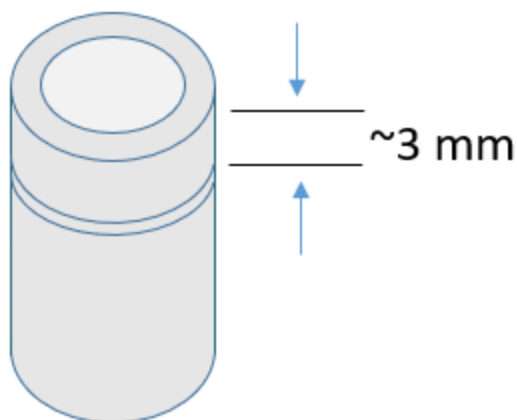
**Figure 3.4:** (a) Schematic diagram of the recirculating system shown in (b). This system was used to subject PEX-a pipe segments (~60 cm long) to high temperature distilled water at high pressure.

During the operation of the recirculating systems, ~ 35% of the distilled water in the system was removed each day and replaced with fresh distilled water, and 100% of the distilled water was removed and replaced with fresh distilled water each week. For ageing experiments performed at 90 °C, it was necessary to add water to the circulating bath once a day because of evaporation at this elevated temperature. In contrast to the immersion ageing experiments, the recirculating hot water experiments allowed us to achieve conditions that resembled in-service conditions, albeit in a more extreme fashion. During the hot water recirculating ageing experiments, the pipe segments were removed from the system at several time points within the

first 6 weeks of ageing for measurement using FTIR microscopy. Small segments ~ 3 cm in length were removed from the same side of the pipe segment and axial slices were produced using the microtome, after first removing ~3 mm from the pipe end to ensure that the radial profiles measured using FTIR microscopy were not affected by exposure of the pipe ends to the ageing environment. The remainders of the long pipe segments were then placed back into the recirculating system for further ageing.

### **3.3 Preparation of Axial Pipe Slices for Transmission FTIR Microscopy**

The UV/ozone and immersion ageing environments produced exposure of the pipe segments on all surfaces. Since we wanted to measure the effect of the ageing environments across the wall thickness of the pipe segments, it was necessary to remove a small length (~ 3 mm in length) from the pipe end before producing an axial slice (~100  $\mu\text{m}$  in thickness) by slicing the PEX-a pipe segments perpendicular to the extrusion direction using an American Optical model 820 rotary microtome. For PEX-a pipes aged in the hot water recirculating system, a pipe segment small enough to fit in the microtome (~ 3 cm in length) was cut from the end of the pipe using a standard pipe cutter and then the axial slice was produced using the microtome (Figure 3.5); the axial slices were always collected from the same end of the pipe segment.



**Figure 3.5:** Schematic diagram of the production of axial slices from UV/ozone and immersion aged PEX-a pipe segments. Since these ageing environments expose all surfaces of the pipe segments, including the pipe ends, ~ 3 mm of the pipe end was removed before producing an axial slice using the microtome for use in the FTIR microscopy experiments.

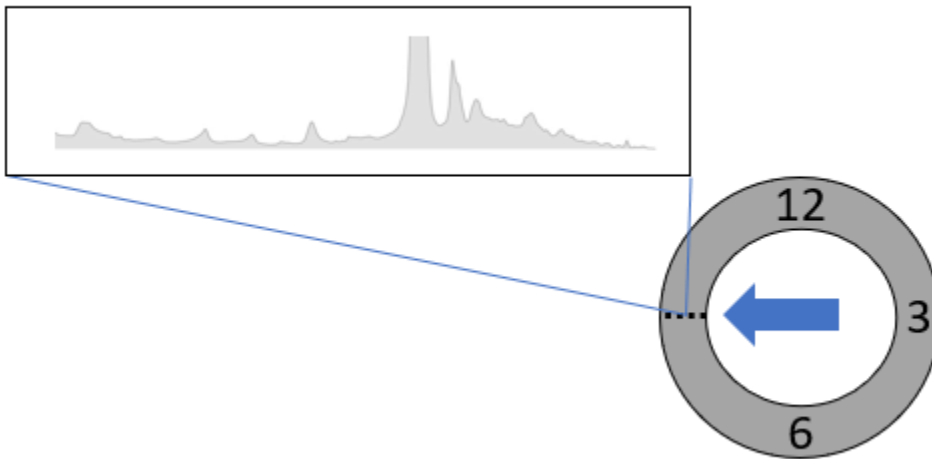
### 3.4 Transmission Infrared (IR) Measurements of Axial Slices of PEX-a Pipe

A Thermo/Nicolet Continuum Infrared Microscope equipped with a liquid-nitrogen cooled MCT detector was used for the collection of transmission IR absorption spectra on axial slices. Each collected spectrum corresponded to the sum of 32 scans in the wavenumber range 4000-650  $\text{cm}^{-1}$  with a 4  $\text{cm}^{-1}$  resolution. Spectra were collected across the pipe wall thickness with a 100  $\mu\text{m}$  separation between scans, corresponding to between 20 and 30 spectra collected across the pipe wall thickness. Each individual spectrum represented the average IR absorption in a 50  $\mu\text{m} \times 50 \mu\text{m}$  area surrounding the specific point of measurement. Absorption of IR light is represented in absorbance units

$$A = -\log\left(\frac{I}{I_0}\right) \quad (7)$$

where  $I$  and  $I_0$  are the single beam intensities transmitted through the thickness of the axial slice and air, respectively.

As the slicing action of the microtome slightly warped the axial slice at the beginning and end of the slice (6 o'clock and 12 o'clock in Figure 3.3), line-profiles across the wall thickness were collected along the perpendicular direction (3 o'clock and 9 o'clock in Figure 3.6). A minimum of two slices were cut in directions  $90^\circ$  from each other to ensure all locations around the clock could be measured, i.e., one slice was cut from the 6 o'clock location to the 12 o'clock location with the 3 o'clock location and the 9 o'clock location measured, and the other slice was cut from the 3 o'clock location to the 9 o'clock location with the 6 o'clock location and the 12 o'clock location measured.



**Figure 3.6:** Schematic diagram of an axial slice of a PEX-a pipe showing the direction of a measured line profile. Spectra were collected across the pipe wall thickness with a spacing between spectra of  $100\ \mu\text{m}$ . The numbers indicate the locations “around the clock”, with the measurement corresponding to 9 o'clock.



### **3.5 Analysis of FTIR Microscopy Data**

#### **3.5.1 Mapping of the IR Indices Across Pipe Wall**

FTIR spectroscopy has been used previously to characterize PEX-a pipe<sup>19,22,23,25</sup>. In the present study, we combine FTIR spectroscopy with optical microscopy to achieve a significant improvement in spatial resolution. FTIR microscopy offers a spatial resolution of 10  $\mu\text{m}$ , allowing us to investigate localized chemical fingerprints across the thickness of the PEX-a pipe wall.

PEX-a pipes vary in diameter, typically from ½” up to 2”. In the present study, we characterize pipes that were primarily of ½” diameter, with a wall thickness of 2 mm, together with several pipes of 1” diameter, with a wall thickness of 3 mm. By collecting closely spaced FTIR spectra across the wall thickness of the pipe, we can characterize and track the distribution of different chemical species across the pipe wall thickness. We plot various metrics related to different characteristic IR indices and IR bands as a function of the radial distance in which the inner surface of the pipe corresponds to 0% radial distance and the outer surface corresponds to 100% radial distance (Figure 4.1).

#### **3.5.2 PCA of FTIR Spectra**

We performed PCA on raw FTIR spectra in Python using the data visualization framework Orange 3 equipped with a spectroscopy plug-in. Orange has many built-in Python functions, which simplifies the importing, processing, and visualization of data. This allowed us to develop a fairly automated process for performing a principal component analysis of the FTIR spectra. Full spectra were imported as CSV files into a combined data table, which included spectra collected on PEX-a pipe of the same formulation, both virgin and aged, in the different

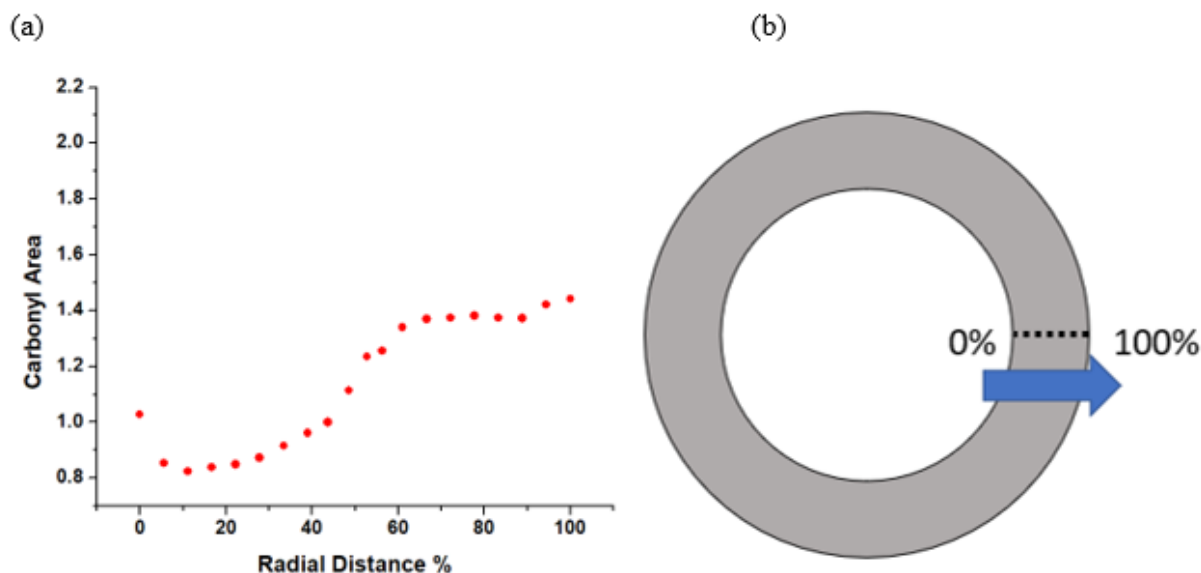
ageing environments. For some of the analyses, data collected within the central portion of the pipe walls (25%-75% of the pipe wall thickness) was averaged. For other analyses in which the radial dependence of the FTIR spectra was considered, data across the entire wall thickness was included. The database used in the analysis included spectra collected on PEX-a pipe of the PW formulation that was aged at 80° C in the hot air immersion, hot water immersion and recirculating water environments, for time points spanning 3 – 42 days. Also included in the dataset for the PCA calculation, was in-service PEX-a pipe of the same PW formulation, which was subjected to lower temperatures for much longer times. In total, the PCA was calculated using 11 spectral bands on over 1000 FTIR spectra. For the PCA to be free from statistical bias, centering and scaling was performed on the data set such that the mean and standard deviation of each variable was as close as possible to 0 and 1, respectively, with double floating-point precision. This is done by replacing the values in each variable (wavenumber in our case) with standardized variables by subtracting the average value and dividing by the standard deviation. The centering and scaling of the data was performed easily using the built-in Orange function “preprocessing”, ensuring that biases were not introduced into the results from background noise in the spectra. The resulting principal component (PC) scores were visualized in two dimensions by plotting the two leading principal component values PC1 vs PC2. The first two principal components together represent 89% of the variance in the original dataset, 76% and 13% respectively. As each subsequent PC represented less variance, the set of PC1 and PC2 was considered to be sufficient to represent the effects of various ageing environments on PEX-a pipe over time.

## 4 Results and Discussion

### 4.1 FTIR Microscopy Measurements of PEX-a Pipe Subjected to Accelerated Ageing

FTIR spectroscopy has been used previously to characterize PEX-a pipe, as summarized in Section 2.4. In the present study, we combined FTIR spectroscopy with optical microscopy to achieve a significant improvement in spatial resolution. FTIR microscopy offers a spatial resolution of 10  $\mu\text{m}$ , allowing us to investigate localized chemical fingerprints across the wall thickness of PEX-a pipes.

PEX-a pipes vary in diameter, typically from  $\frac{1}{2}$ " up to 2". In the present study, we characterized pipes that were primarily of  $\frac{1}{2}$ " diameter, with a wall thickness of 2 mm, together with several pipes of  $\frac{3}{4}$ " diameter, with a wall thickness of 3 mm. By collecting closely spaced FTIR spectra across the pipe wall thickness, we were able to characterize and track the distribution of different chemical species across the pipe wall thickness. We plot various metrics related to different characteristic IR indices and IR bands as a function of the radial distance in which the inner surface of the pipe corresponds to 0% radial distance and the outer surface corresponds to 100% radial distance (Figure 4.1).



**Figure 4.1:** (a) Representative radial distance profile of a characteristic IR index (carbonyl area) determined from FTIR measurements of a ½” PW PEX-a pipe aged with recirculating 80°C hot water for 21 days, shown as a function of the percentage of the radial distance across the pipe wall thickness. The inner surface of the pipe wall corresponds to 0% and the radial distance increases radially outward, as indicated schematically in (b).

#### 4.1.1 Exposure to Elevated Temperature

##### 4.1.1.1 PEX-a Pipe Ageing in Hot Air Immersion Environment

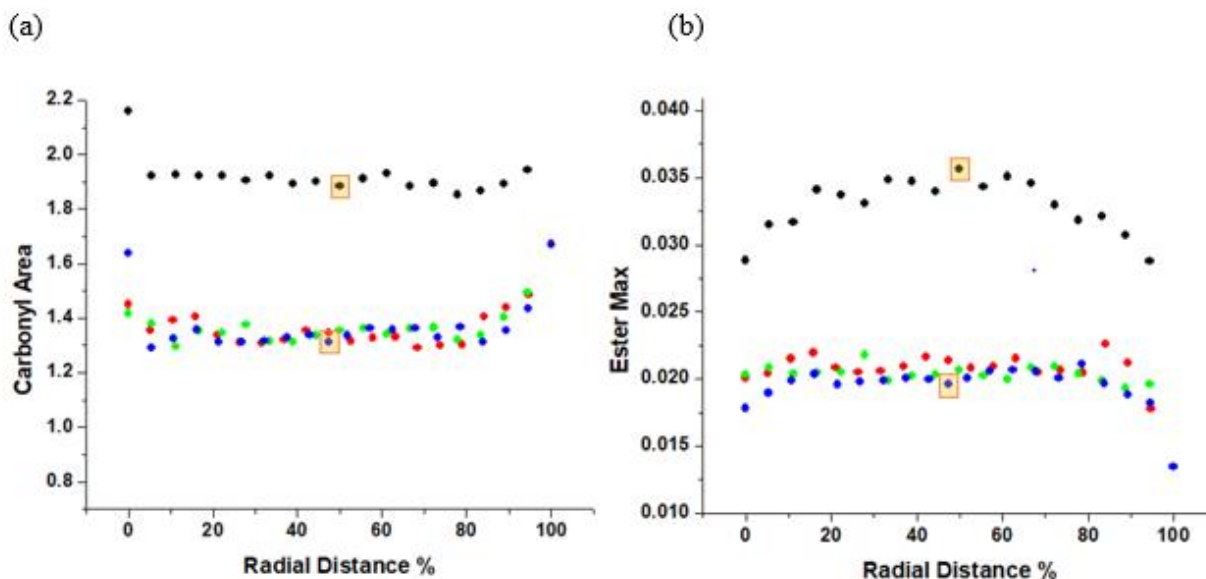
The simplest of our elevated temperature experiments were conducted in ovens with the pipe samples immersed in hot air. The hot air immersion environment, in which the pipe samples were exposed to hot air at both the inner (0%) and outer (100%) surfaces of the pipe wall, allowed us to investigate the effects of high temperature on PEX-a pipe without the presence of water. In Figures 4.2 and 4.3, we show radial distance profiles of the carbonyl area and ester max IR indices and representative spectra for the ½” RFH and T301 pipe formulations, with data points collected once per week of exposure to hot air at 80° C. As discussed in Section 2.1.1.1,

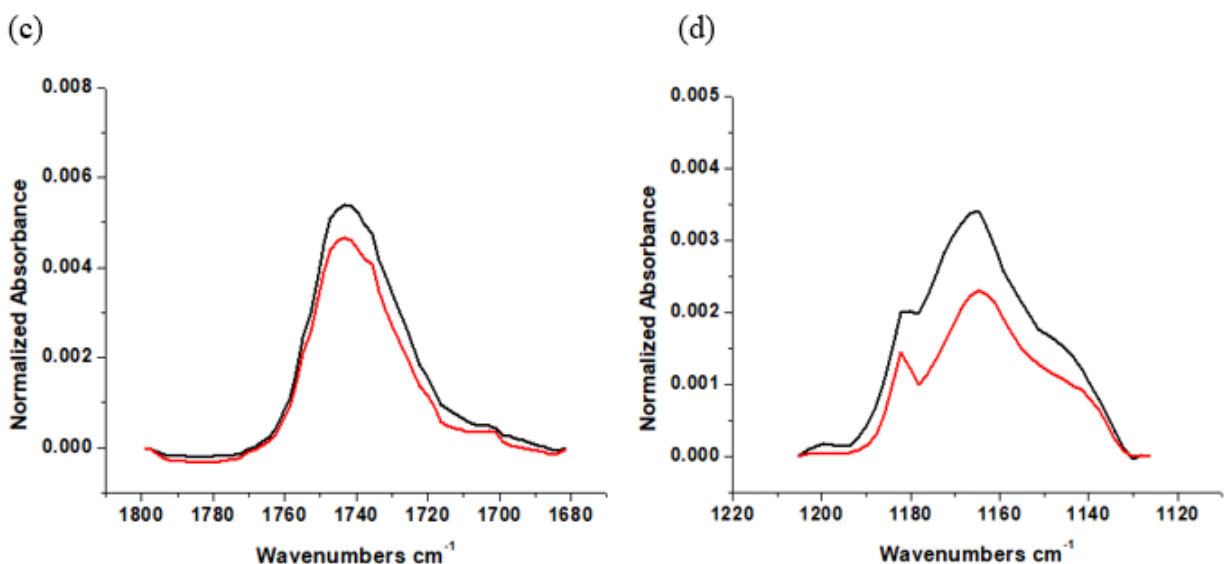
the carbonyl band has contributions from both protective stabilizing additives and compounds that result from oxidative damage, so that changes in the carbonyl band with ageing can provide indications of the loss of stabilizing additives and oxidative degradation of PEX-a pipes. Ester groups occur commonly in commercial stabilizing additives, and they can also occur in degradation products. Therefore, decreases in the ester max absorbance can indicate either the loss of ester moieties in the stabilizing additives, or a loss of degradation products containing ester moieties.

The data shown for the RFH formulation in Figure 4.2 is representative of the behaviour that we observed in all our hot air immersion experiments: a decrease in the absorbance for both the area under the carbonyl peak ( $1760\text{ cm}^{-1}$ - $1680\text{ cm}^{-1}$ ) and the maximum absorbance of the ester peak ( $1160\text{ cm}^{-1}$ ) compared with that measured for virgin pipe samples. Figure 4.2 (c) shows a representative carbonyl peak, taken from ~50% of the radial distance, which exhibits no substantial increase at the lower wavenumber shoulder. This indicates that there are no degradation products formed in this environment. Changes in the carbonyl peak and ester peak are slightly asymmetric, with larger decreases observed for the ester peak. The changes can be attributed to ester-containing volatile compounds that are removed quickly at high temperature. These decreases occurred very quickly with ageing time (before the collection of the first time point at one week of exposure); additional exposure to the hot air immersion environment did not produce further decreases of these IR metrics. The radial distance line profiles in Figure 4.2 show that there is a relatively uniform distribution across the pipe wall of the carbonyl and ester functional groups from the additive compounds.

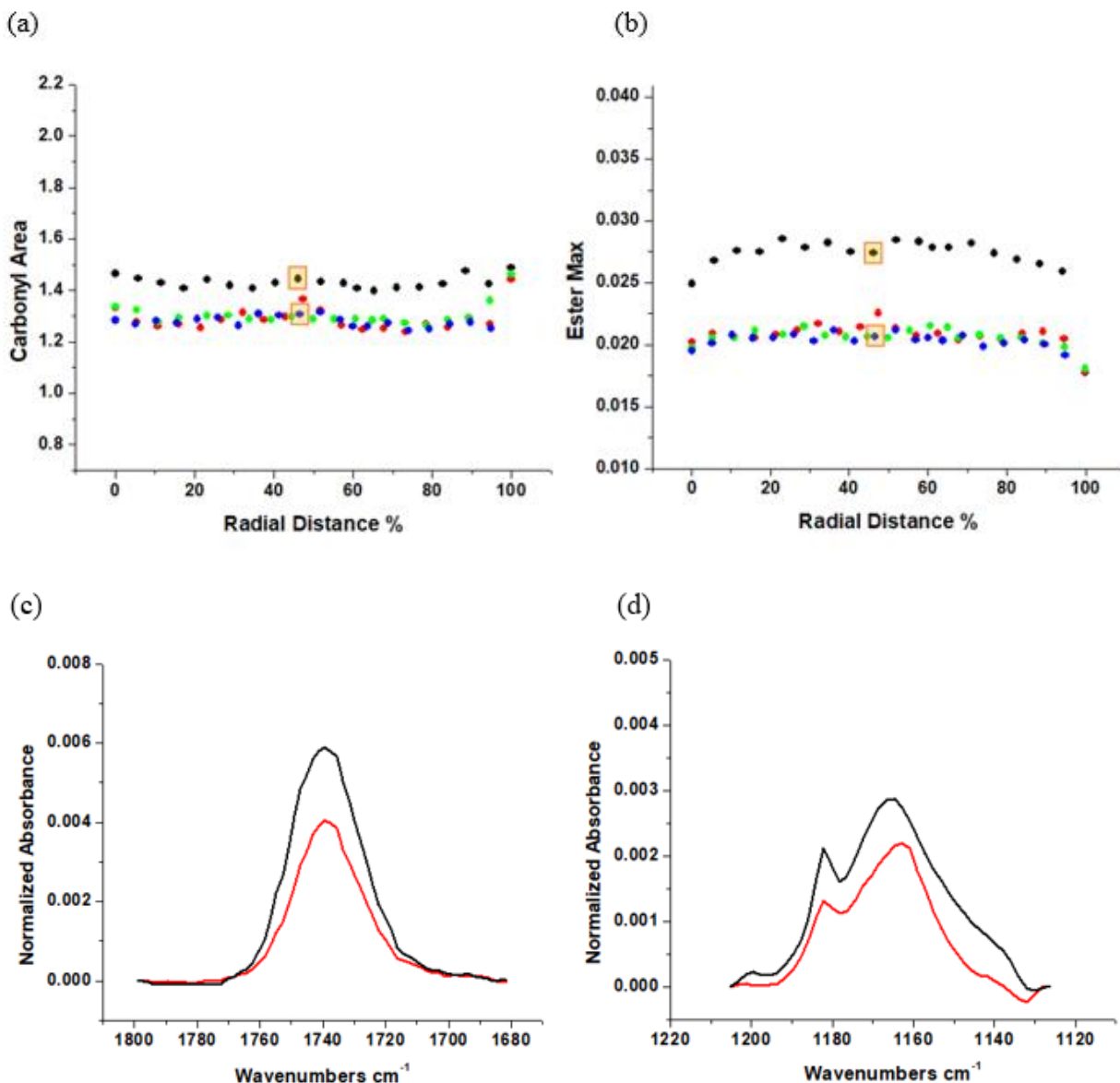
Similar changes were also observed in pipes with the T301 formulation, as shown in Figure 4.3, albeit to a lesser degree. The average decrease in the carbonyl area index for the aged

T301 sample over 3 weeks in 80° C air was ~10% of the original value, compared to ~25% for that of the RFH sample in the same environment. For the ester max index, we observed an average decrease of 25% over the ageing time for the T301 formulation, compared to an average decrease of 40% for the RFH sample. The representative spectra in Figure 4.3 show an asymmetric decrease in the carbonyl and ester peaks for this formulation as well, with no lower wavenumber increase in the carbonyl peak. The hot air environment seemed to cause a small loss of the ester moieties in the stabilizing agents in the PEX-a pipes samples, as both the carbonyl and ester peaks decreased, with the larger decrease in the ester peak attributed to the loss of volatile ester containing compounds. With exposure of the PEX-a pipe samples to oxygen at high temperature, they exhibited no measurable increase in the lower wavenumber carbonyl absorbance, indicating that no degradation products were being produced within the bulk of the pipe wall.





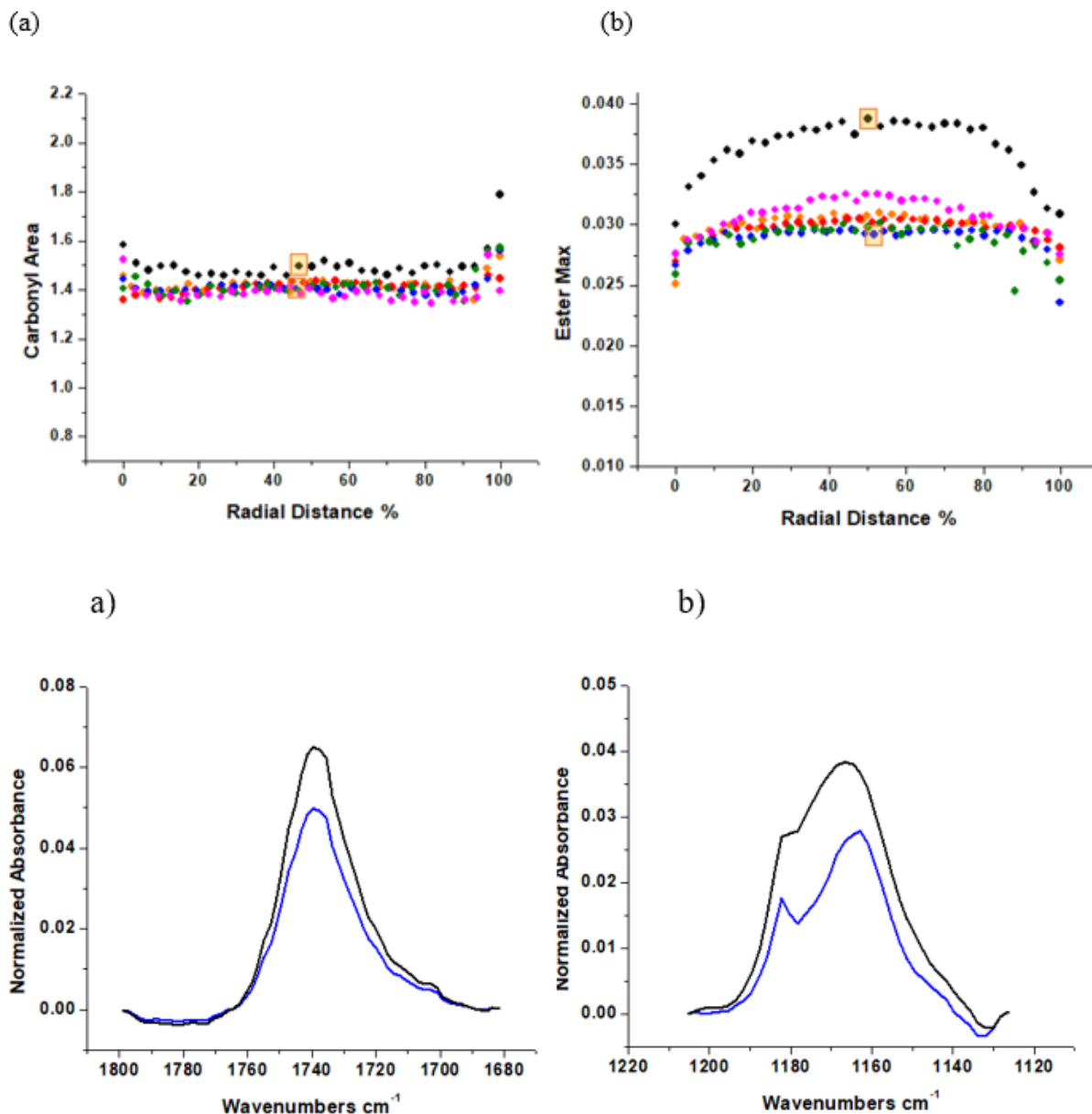
**Figure 4.2:** (a) and (b): Radial distance line profiles for virgin ½” RFH PEX-a pipes (black) and RFH pipes exposed to the 80°C hot air immersion ageing environment for different ageing times: 1 week (red), 2 weeks (green) and 3 weeks (blue). Index values are average values of data points measured within 3% of the radial distance values over four line profiles. (c) and (d): Representative IR spectra, from points highlighted in orange on a) and b), of virgin RFH PEX-a pipes (black) and RFH pipes exposed to the 80°C hot air immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region.



**Figure 4.3:** (a) and (b): Radial distance line profiles for virgin  $\frac{1}{2}$ " T301 PEX-a pipes (black) and T301 pipes exposed to the 80°C hot air immersion ageing environment for different ageing times: 1 week (red), 2 weeks (green) and 3 weeks (blue). Index values are average values of data points measured within 3% of the radial distance values over four line profiles. (c) and (d): Representative IR spectra, from points highlighted in orange on a) and b), of virgin T301 PEX-a pipes (black) and T301 pipes exposed to the 80°C hot air immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region.

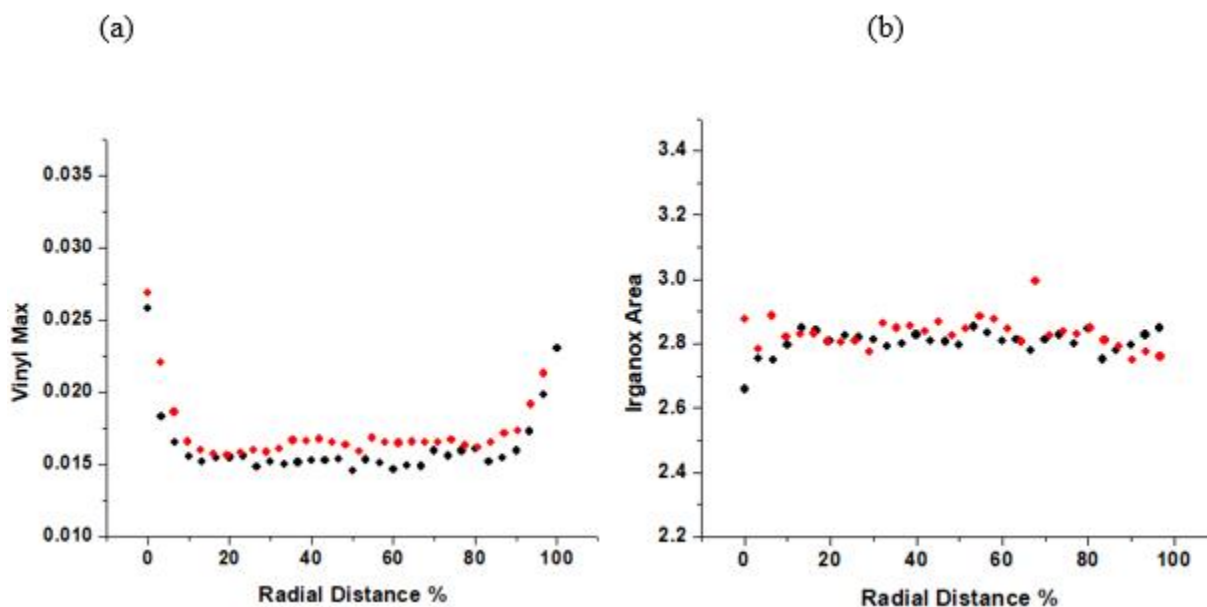


Since decreases in the carbonyl and ester IR bands were observed to occur within the first week for both RFH and T301 pipe formulations, we conducted an additional hot air immersion ageing experiment on a PEX-a pipe with a 1" PW formulation and collected IR spectra at several time points during the first week of exposure. This experiment was performed at a slightly higher temperature of 85° C. In Figure 4.4 we show radial distance line profiles of two IR metrics collected at different time points, beginning at three days of exposure. Changes in the carbonyl area with ageing time (Figure 4.4a) were small; decreases in the ester max absorbance with ageing time (Figure 4.4b) were larger (maximum decrease of 25%), with most of the changes occurring during the first three days of ageing. As discussed in Section 2.1.1.1, decreases in the ester max absorbance may indicate the loss of ester moieties in the stabilizing additives, or a loss in ester-containing degradation products produced during or after manufacturing. The lack of exposure to water in the hot air immersion environment precludes leaching of the stabilizing agents; instead, the loss of volatile ester-containing compounds likely results from thermal decomposition and evaporation at high temperature.



**Figure 4.4:** (a) and (b): Radial distance line profiles for virgin 1" PW PEX-a pipes (black) and PW pipes exposed to the 85°C hot air immersion ageing environment for different ageing times: 3 days (pink), 6 days (orange), 8 days (green), 10 days (red) and 14 days (blue). (c) and (d): Index values are average values of data points measured within 3% of the radial distance values over three line profiles. Representative IR spectra, from points highlighted in orange on a) and b), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 85°C hot air immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region.

In Figure 4.5, we show representative radial distance profiles of two other characteristic IR indices: the vinyl max index, and the Irganox area index. Exposure of the pipe sample to the hot air immersion environment for two weeks produced a measurable increase in the vinyl max index throughout the pipe (average increase of 5%), indicating that the hot air environment resulted in scission of some of the polymer chains within the PEX-a matrix that increased the amount of carbon-carbon double bonds. The Irganox area index, which is a measure of the absorbance of the phenolic O-H stretching vibration shows no significant changes with ageing time at high temperatures, suggesting that the hot air environment does not provide sufficient oxidative potential to consume the Irganox additive in this short period of time.



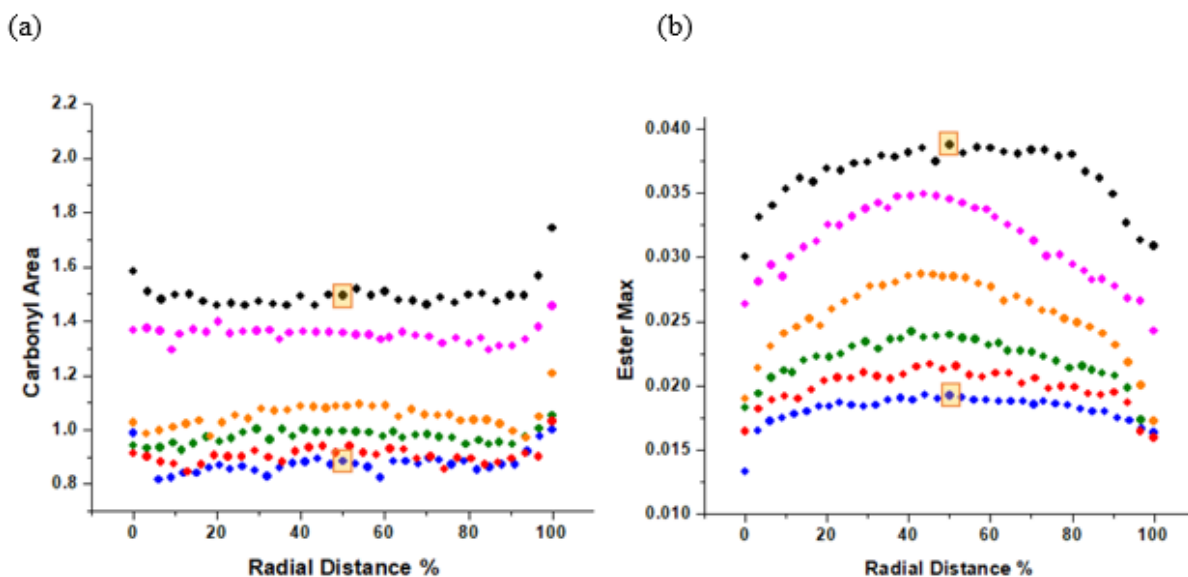
**Figure 4.5:** Representative radial distance profiles of characteristic IR indices for virgin 1” PW PEX-a pipe (black) and PW pipe exposed to 85° C air for 3 weeks (red): (a) vinyl max index and (b) Irganox area index.

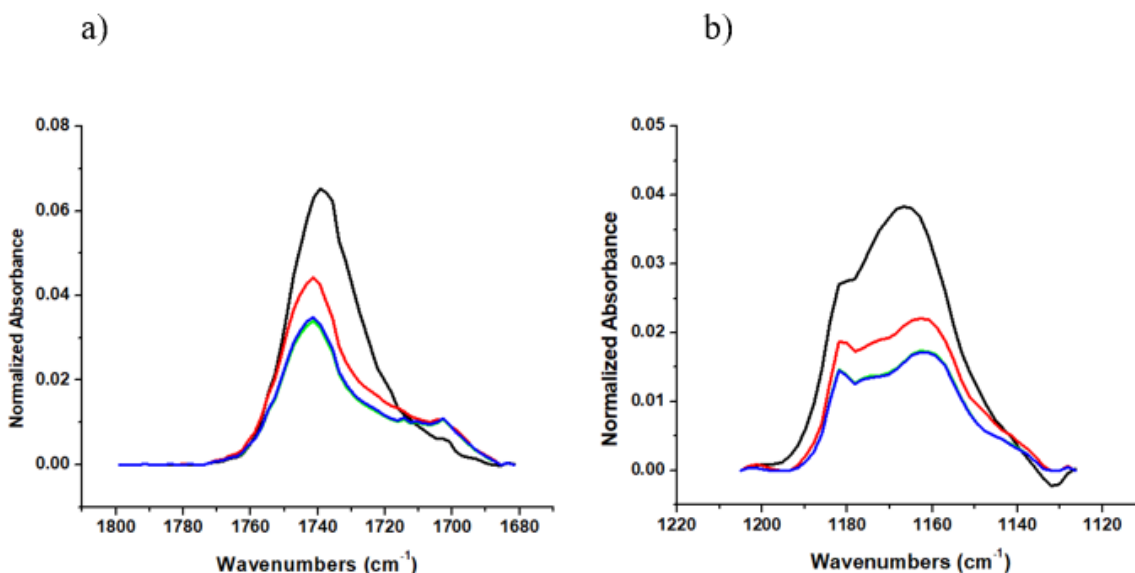
#### **4.1.1.2 PEX-a Pipe Ageing in Hot Water Immersion Environment**

We performed ageing experiments on segments of 1" PEX-a pipe immersed in hot water; this ageing environment mimicked that experienced by the inside of an in-service PEX-a pipe, allowing us to investigate the effects of high temperature and the presence of water on the pipes. This contrasts with the ageing experiments on PEX-a pipes immersed in hot air in which the presence of hot air can result in oxidation of the pipes. As shown in the previous section, immersion in hot air resulted in decreases in the absorbance of the carbonyl and ester peaks because of the high temperature. In the present section, we compare results obtained for the hot air and hot water immersion ageing experiments.

For PEX-a pipes with the 1" PW formulation aged in Milli-Q water at 85° C, we observed significant decreases in both the carbonyl area and ester max indices (Figure 4.6). Significant decreases of ~10 % and ~15% occurred in the carbonyl area and ester max indices for the first time point (3 days) with the changes penetrating the entire pipe wall, as can be seen in the radial distance profiles shown in Figure 4.5. Both indices track the integrity of the ester linkages within the additive molecules and decreases in the absorbance are associated with the breaking of these bonds. The carbonyl area and ester max indices decrease further after the first few days, reaching stable values of decreases of ~40% and ~55%, respectively, at approximately 2 weeks of ageing. As shown for ageing in the hot air immersion environment in section 4.1.1.1, part of the decreases in the indices can be attributed to the high temperature of the environment. However, with exposure to water, the indices decrease beyond the constant values measured for

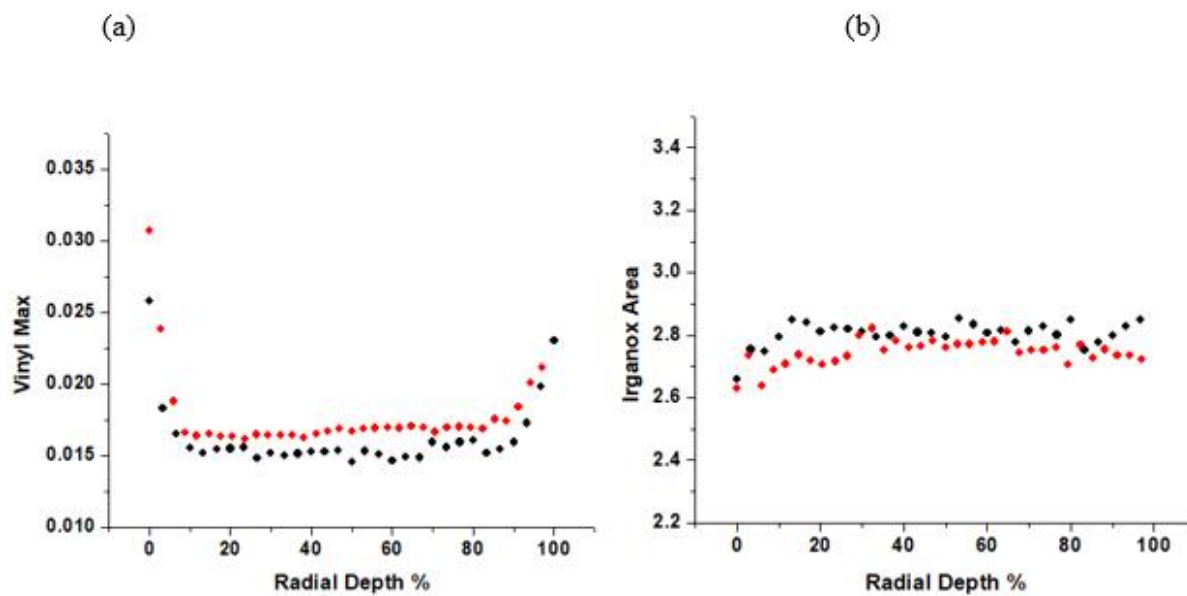
long ageing times in the hot air ageing experiments. Also, we observed a small increase of ~15% on the lower wavenumber shoulder of the carbonyl peak centered at  $1700\text{ cm}^{-1}$  (Figure 4.6c), which we attribute to degradation products in the form of carboxylic acids; this increase is not due to oxidation since the pipe samples are fully immersed in water. Despite this small increase associated with the degradation products, the peak area shows a net decrease because of the large decrease of the peak centered at  $1740\text{ cm}^{-1}$ . We propose that the decrease, which is large compared to that for PEX-a pipe aged in hot air, is due to hydrolysis of the ester linkages in the additive compounds. Although hydrolysis of the ester linkages does not prevent the additives from performing their function, it fragments the additives into smaller molecules that can then diffuse more easily through the polymer matrix and be leached from the pipe into the surrounding water.





**Figure 4.6:** (a) and (b): Radial distance line profiles for virgin 1" PW PEX-a pipes (black) and PW pipes exposed to the 85°C Milli-Q water immersion ageing environment for different ageing times: 3 days (pink), 6 days (orange), 8 days (green), 10 days (red) and 14 days (blue). (c) and (d): Index values shown are average values of data points measured within 3% of the radial distance values over three line profiles. Representative IR spectra, from points highlighted in orange on a) and b), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 85°C Milli-Q water immersion ageing environment for 3 weeks (red). The spectrum in (c) corresponds to the carbonyl peak, and the spectrum in (d) corresponds to the fingerprint region.

The hot water immersion environment also has a larger effect on other characteristic IR indices than the hot air immersion environment (Figure 4.7). A small degree of chain scission occurred in both high temperature environments, and this effect was larger in the presence of water, as highlighted by a ~10% increase in the vinyl max index after 21 days of ageing (Figure 4.7a), compared to only a ~5% increase for the hot air environment. The Irganox area index was not significantly different for hot air and hot water immersion ageing.



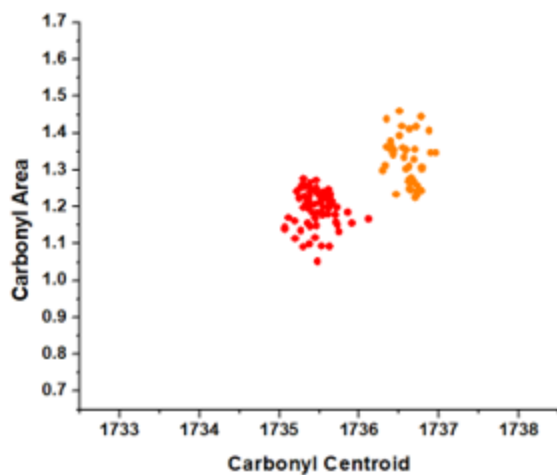
**Figure 4.7:** Representative radial distance profiles of characteristic IR indices for virgin 1” PW PEX-a pipe (black) and PW pipe exposed to 85° C Milli-Q water for 3 weeks (red): (a) vinyl max, (b) Irganox index.

We also studied the effect of high temperature Milli-Q water on three different 1/2” diameter PEX-a pipe formulations (PW, RFH and T301) in the hot water immersion environment, each aged at 80° C for 4 weeks. Each formulation exhibited a decrease in additive levels due to this environment, as can be seen in Figure 4.8 by both the decreasing carbonyl area and carbonyl centroid index values and the decreasing absorbance at  $\sim 1740\text{ cm}^{-1}$ . Because the ester max index simply tracks the other side of the oxygen – carbon – oxygen functional group, without the generation of degradation products, it does not bring new relevant information. Instead, the carbonyl area versus carbonyl centroid plots can be used to distinguish between contributions to the carbonyl area from additive depletion versus generation of degradation

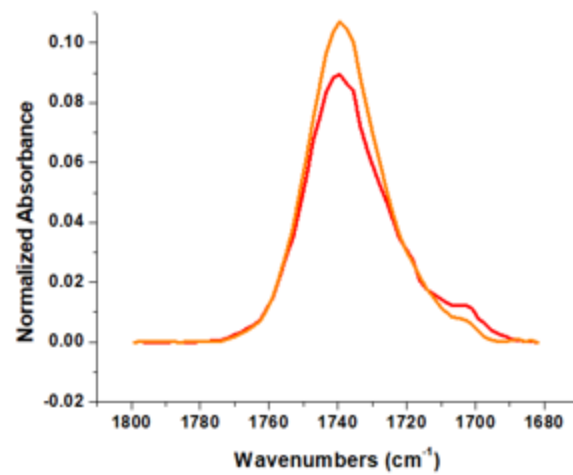
products. The carbonyl centroid index value, defined in section 2.1.1.2, is the area-weighted centre of the carbonyl peak, and shifting of the carbonyl centroid index to lower values corresponds to an increase of degradation products. In Figure 4.8, it can be seen that the RFH formulation exhibits the largest increase in degradation products of the three formulations and T301 exhibits the smallest increase. In Figure 4.8g, we show the average values of the carbonyl area and carbonyl centroid indices for each virgin formulation as well as each formulation aged at 80° C for 4 weeks, and it can be seen that the RFH formulation started at a higher centroid value and, with increasing ageing time in this environment, reached a lower centroid value than the other two formulations. Although the T301 sample exhibited little carbonyl absorbance associated with degradation products, associated with a small shift in the centroid, it experienced the largest decrease in the carbonyl area, associated with the loss of additives during the ageing process. Each PEX-a pipe formulation tested exhibited additive depletion over time for immersion in hot water, rendering them more susceptible to oxidative failure.



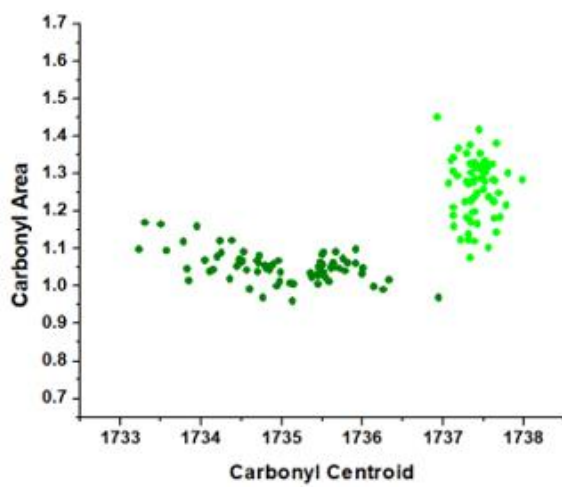
(a)



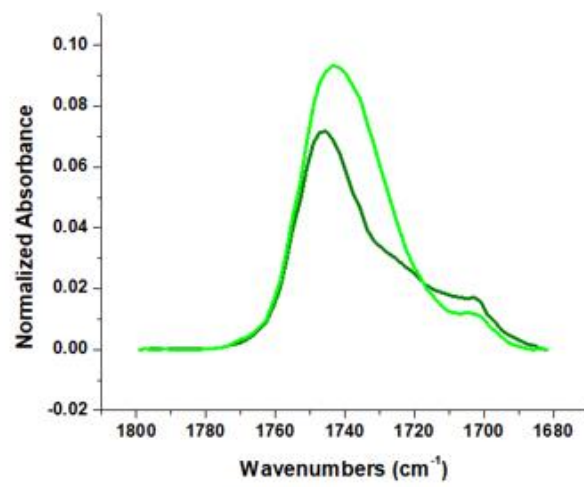
(b)



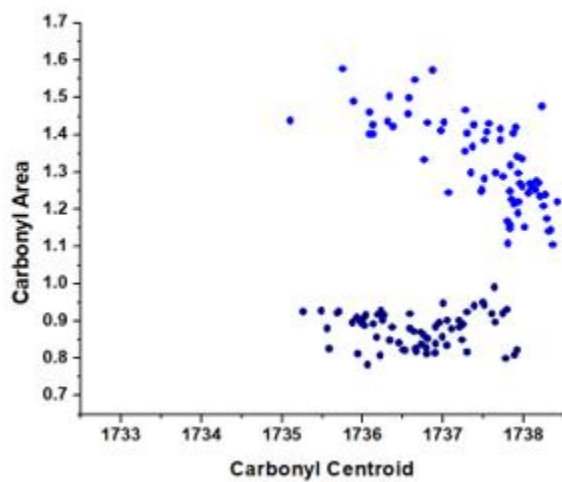
(c)



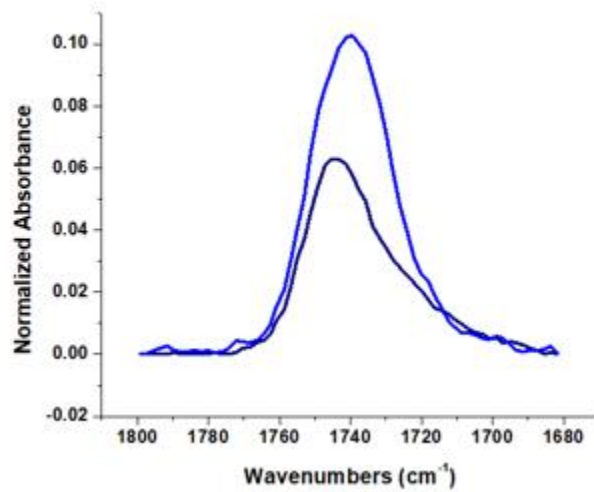
(d)

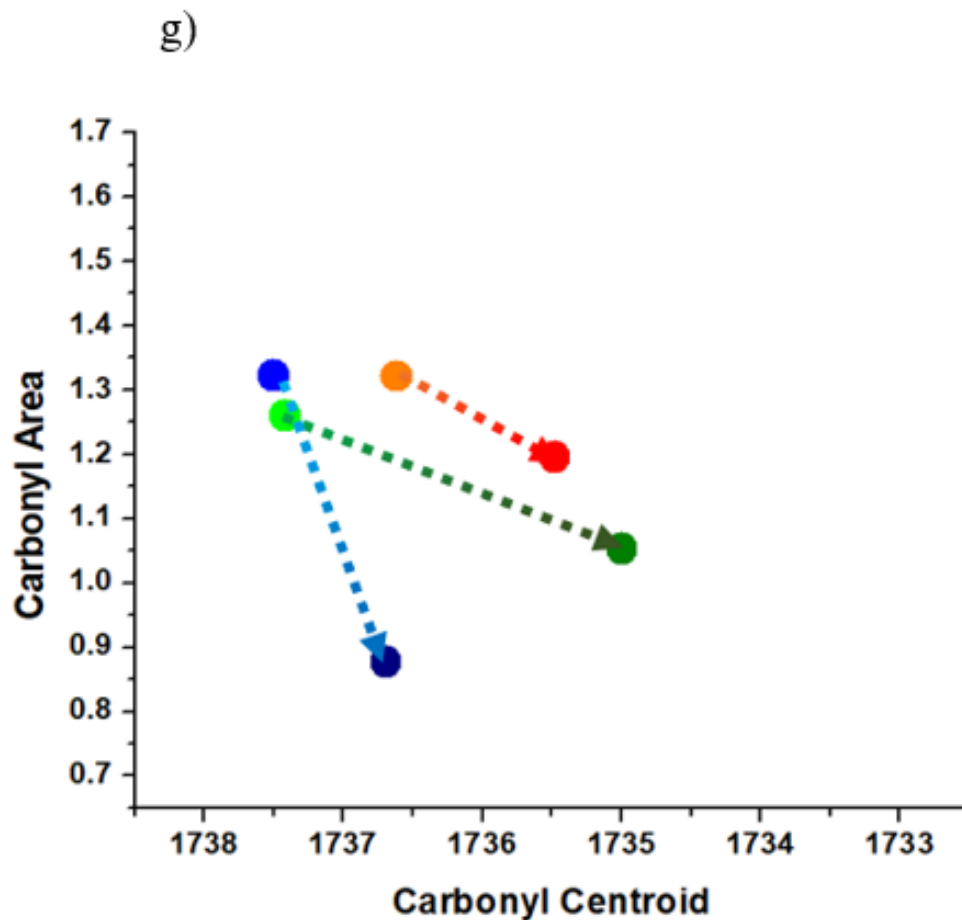


(e)



(f)





**Figure 4.8:** (a) Carbonyl area versus carbonyl centroid graph of virgin ½” PW PEX-a pipe (orange) and PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red). (b) Average spectra calculated from the inner 80% of three line profiles of virgin PW PEX-a pipe (orange) and PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red). (c) Carbonyl area versus carbonyl centroid graph of virgin ½” RFH PEX-a pipe (light green) and RFH PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (dark green). (d) Average spectra calculated from the inner 80% of three line profiles of virgin RFH PEX-a pipe (light green) and RFH PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (dark green). (e) Carbonyl area versus carbonyl centroid graph of virgin ½” T301 PEX-a pipe (blue) and T301 PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (navy). (f) Average spectra calculated from the inner 80% of three line profiles of virgin T301 PEX-a pipe (blue) and T301 PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (navy). g) Average carbonyl area versus carbonyl centroid graph of virgin PW (orange), RFH (light

green) and T301 (blue) PEX-a pipe and PW (red), RFH (dark green) and T301 (navy) PEX-a pipe aged 80° C Milli-Q water for 4 weeks. Dashed arrows indicate the trajectories for each formulation within the plot over the 4 weeks of ageing.

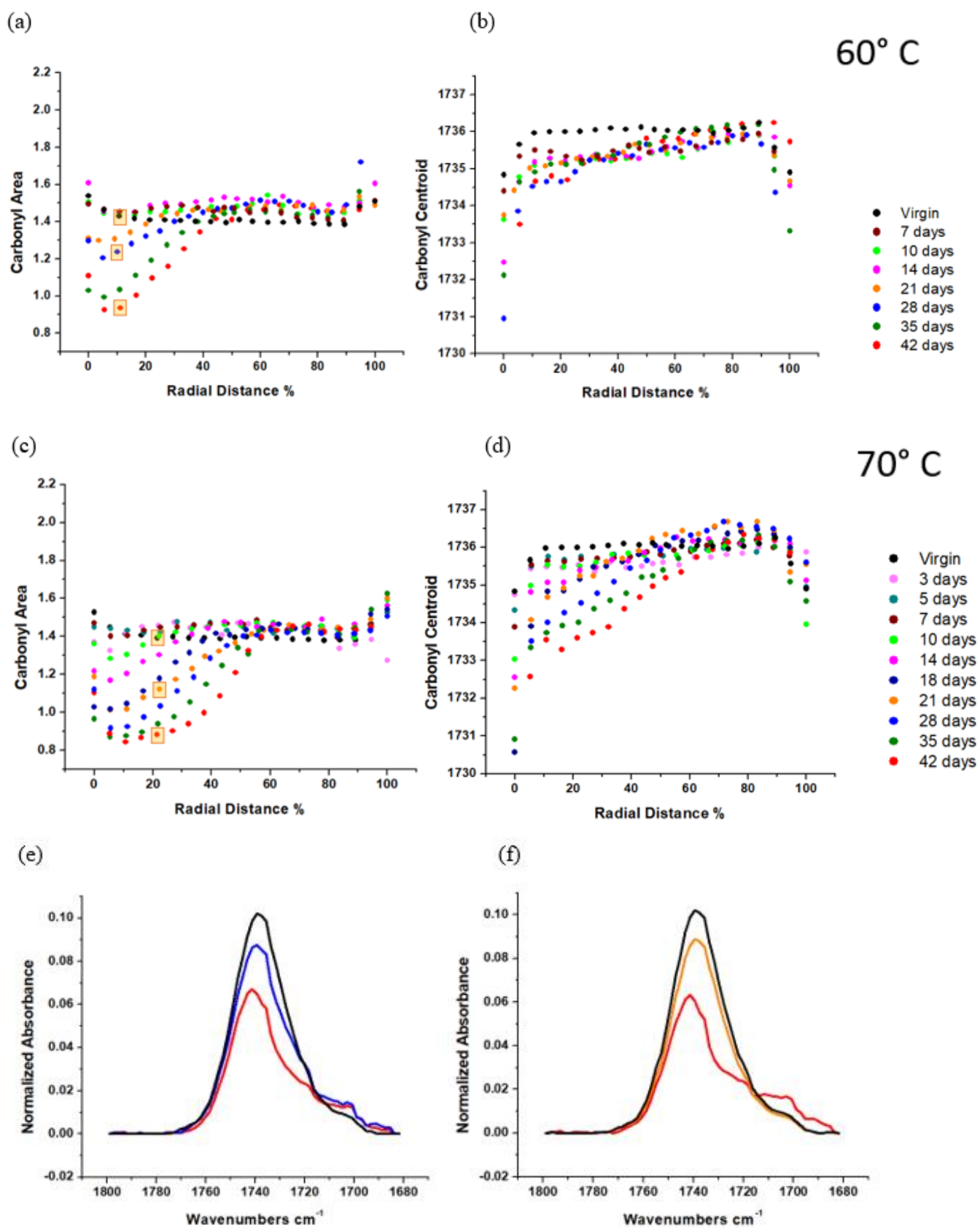
#### **4.1.1.3 PW PEX-a Pipe Ageing in Recirculating Hot Water at Elevated Pressure**

Flowing hot water through PEX-a pipes most closely mimics in-service conditions. Our custom recirculating systems, described in Section 3.2.2.3, can be used to age PEX-a pipes at temperatures up to 90° C and pressures up to 120 psi, which are both larger than typical in-service conditions. For the present experiments, we chose a pressure of 80 psi and constant temperatures ranging from 60° C to 90° C. This environment allowed us to investigate the effects of exposure to high temperature water from the inside of the pipe and air from the outside as well as the added effect of elevated pressure.

We performed trials of PEX-a pipes with the ½” PW formulation using four different temperatures – 60° C , 70° C, 80° C and 90° C – and the radial distance profiles are shown in Figures 4.9 and 4.10 for ageing times ranging from 3 days to 42 days. In addition, the radial distance profiles for virgin PW PEX-a pipe are shown for reference. The effect of ageing in this environment is similar to that observed for hot water immersion ageing: decreases in the carbonyl area with increasing ageing time, with the decrease in the index occurring faster at higher temperatures. In addition, these datasets show well defined propagation of the ageing effect from the inner pipe wall (0% radial distance) that is exposed to hot water toward the outer pipe wall (100% radial distance) that is exposed to air. The propagation of the ageing effect with

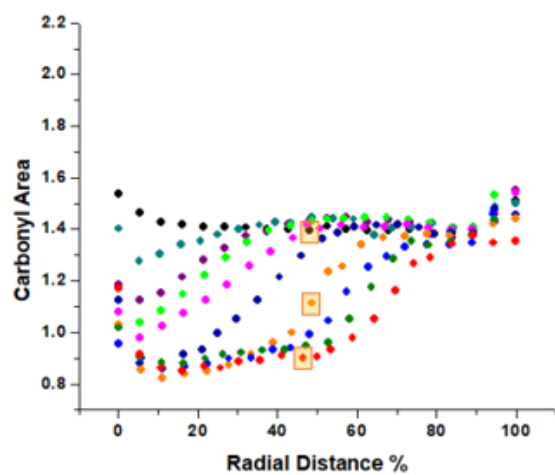
ageing time was observed for both the carbonyl area and the ester max indices for which it occurred on approximately the same time scale.

The decreases in the carbonyl area and ester max indices with increasing ageing time are associated with the breaking of the ester bonds present in the additives in an ester hydrolysis reaction, resulting in a decrease in the absorbance in these spectral ranges. With exposure of the PEX-a pipe to the recirculating hot water environment, the decreases in the indices began at the inner surface of the pipe wall and penetrated through the pipe wall as ageing proceeded. At the inner surface, the decreases in the carbonyl area and ester max indices reached plateau values that were comparable to those measured for pipe exposed to the hot water immersion environment, shown in Figure 4.4. These decreases of the indices to the plateau values occurred at the inner pipe surface over short time scales that depended on the ageing temperature: at 60° C, the plateau values at the inner surface were reached after 42 days of ageing, whereas, at 90° C, they were reached much more quickly (after 7 days). Not surprisingly, the penetration of the decreases in the indices into the pipe wall was much slower at 60° C than at 90° C: after 28 days, the ageing effect penetrated to only ~25% of the pipe wall thickness at 60° C, whereas it penetrated to ~80% of the pipe wall thickness at 90° C.

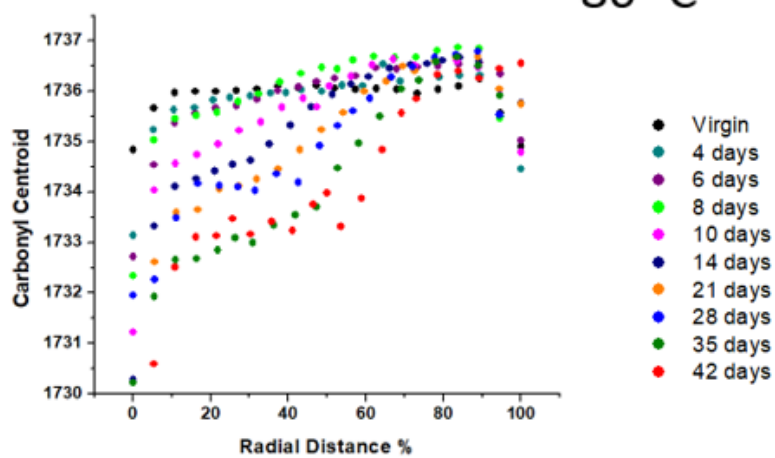


**Figure 4.9:** (a) and (b): Average radial distance profiles for virgin ½” PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 60°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. (c) and (d): Average radial distance profiles for virgin PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 70°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. For each figure, we show the average values of data points measured within 3% of the radial distance values for three line profiles collected at each ageing time. (e): Representative IR spectra, from points highlighted by the orange rectangles in a), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 60°C recirculating water ageing environment at 80 psi for 28 days (blue) and 42 days (red). (f): Representative IR spectra, from points highlighted by the orange rectangles in c), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 70°C recirculating water ageing environment at 80 psi for 21 days (orange) and 42 days (red).

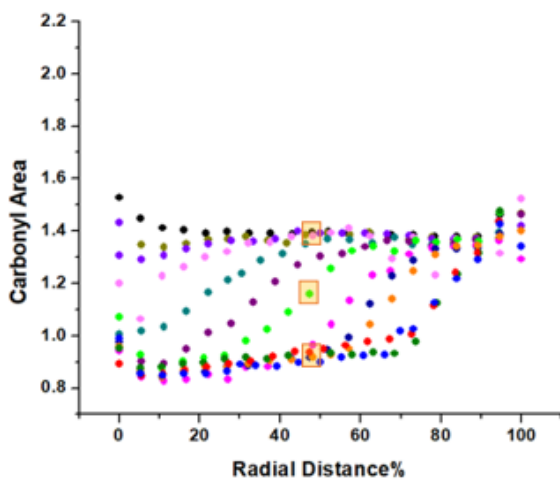
(a)



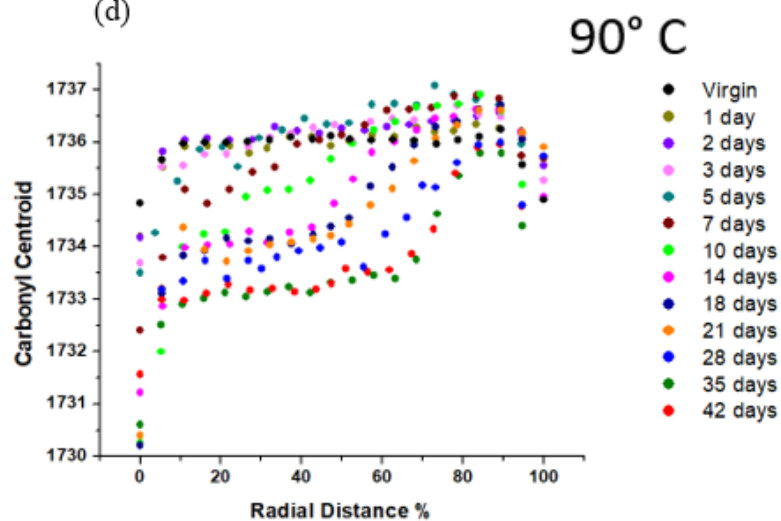
(b)



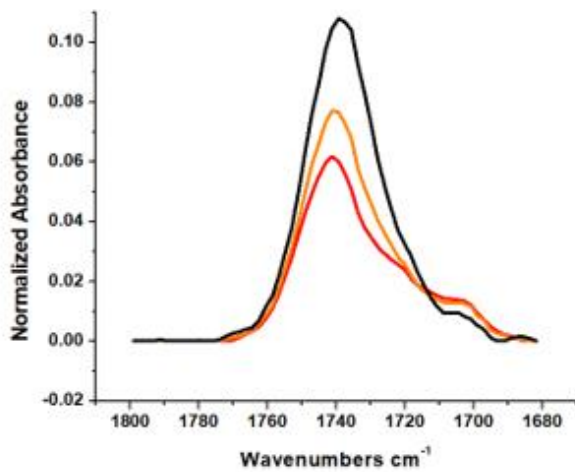
(c)



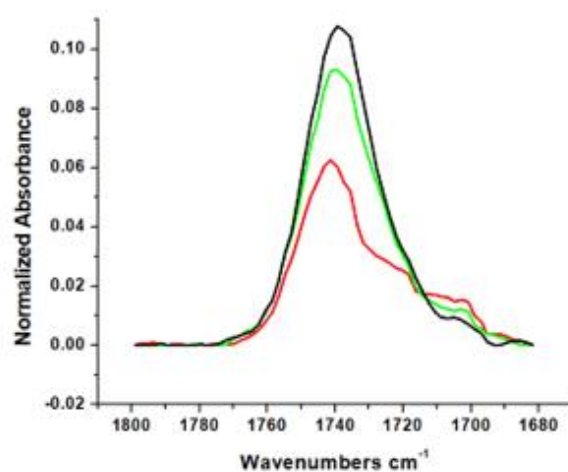
(d)



(e)



(f)

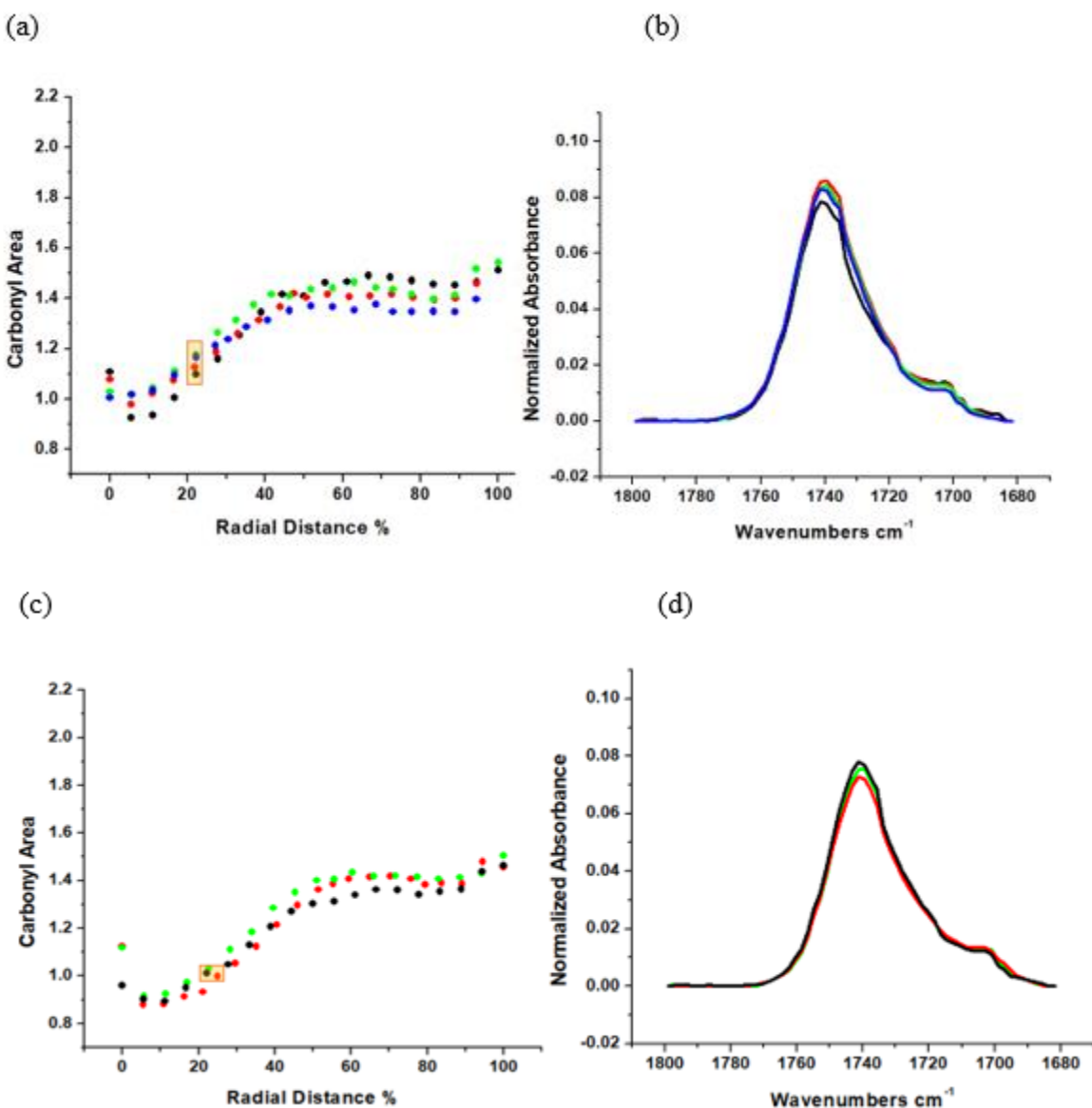


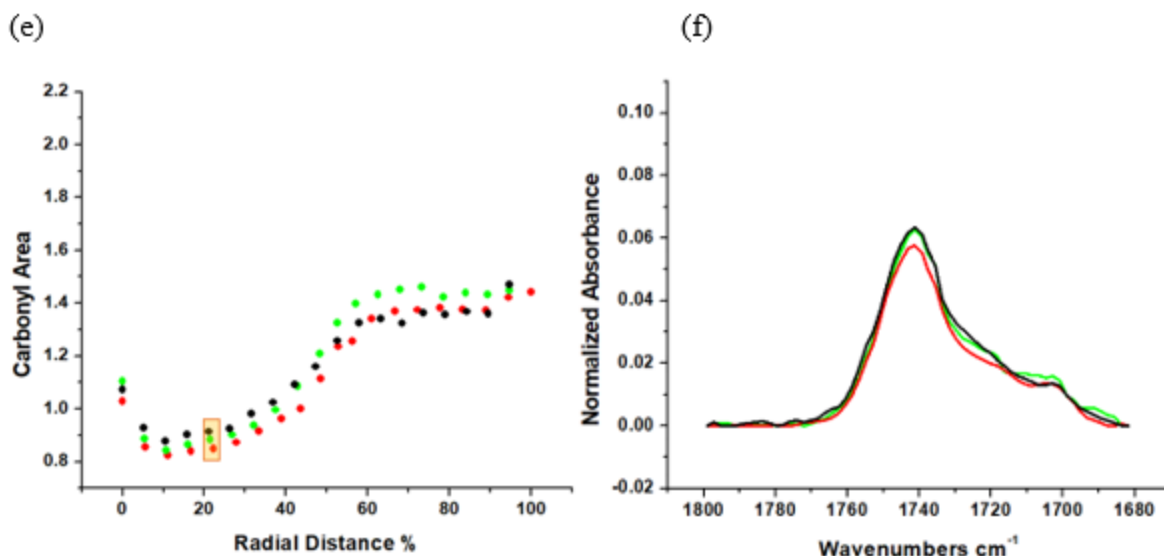
**Figure 4.10:** (a) and (b): Average radial distance profiles for virgin ½” PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 80°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. (c) and (d): Average radial distance profiles for virgin PW PEX-a pipes (black) and PW PEX-a pipes exposed to the 90°C recirculating water ageing environment for different ageing times as shown in the legend on the right-hand side. For each figure, we show the average values of data points measured within 3% of the radial distance values for three line profiles collected at each ageing time. (e): Representative IR spectra, from points highlighted by the orange rectangles in a), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 80°C recirculating water ageing environment at 80 psi for 21 days (orange) and 42 days (red). (f): Representative IR spectra, from points highlighted by the orange rectangles in c), on virgin PW PEX-a pipes (black) and PW pipes exposed to the 90°C recirculating water ageing environment at 80 psi for 10 days (green) and 42 days (red).

For the small (30 °C) temperature range that we measured in these ageing experiments, it is reasonable to assume that we are probing the same degradation processes. We can then relate the degree of degradation measured at different ageing times and temperatures by using the concept of time-temperature superposition. If successful, we will be able to achieve an overlap between radial distance profiles measured at long ageing times at low temperature with profiles measured at shorter ageing times and higher temperature. We can obtain a crude estimate of the validity of time-temperature superposition by comparing radial profiles of carbonyl area values at four different temperatures, which represent the degree of ester hydrolysis during the ageing process. We found that we could achieve excellent overlap of the radial profiles measured at different temperatures for ageing times that increased with decreasing temperature, as shown in



Figure 4.11. Specifically, we found that the best overlap of the radial profiles was achieved by choosing a factor of 2 increase in ageing time for a decrease in ageing temperature of 10° C. For example, a PW PEX-a pipe aged at 90° C for 7 days exhibited a radial distance profile of the carbonyl area index that was very similar to those measured for a PW PEX-a pipe aged at 80° C for 14 days and 70° C for 28 days (Figure 4.11c).





**Figure 4.11:** (a): Average radial distance profiles for 1/2" PW PEX-a pipes exposed to the 60° C (blue) 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for 42 (blue) 21 (green), 10 (red) and 5 (black) days. b): Representative IR spectra, from points highlighted in orange on a), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 60° C for 42 days (blue), 70° C for 21 days (green), 80°C for 10 days (red) and 90° C for 5 days (black). (c): Average radial distance profiles for PW PEX-a pipes exposed to the 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for 28 (green), 14 (red) and 7 (black) days. (d): Representative IR spectra, from points highlighted in orange on c), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 70° C for 28 days (green), 80° C for 14 days (red) and 90° C for 7 days (black). (e): Average radial distance profiles for PW PEX-a pipes exposed to the 70° C (green), 80° C (red) and 90° C (black) recirculating water ageing environment for 42 (green), 21 (red) and 10 (black) days. f): Representative IR spectra, from points highlighted in orange on e), on PW pipes exposed to the recirculating water ageing environment at 80 psi at 70° C for 42 days (green), 80° C for 28 days (red) and 90° C for 14 days (black). For a), c) and e), the average value was calculated from points within 3% radial distance of one another, from three line profiles collected at each ageing time.

This method of simply lining up carbonyl index radial profiles is a fairly crude way of determining a time-temperature superposition of our data. A more refined method involves calculating a shift factor that can be used to scale measured quantities from several temperatures to a single temperature.<sup>29</sup> We started this process by determining the penetration depth of the ester hydrolysis at each time point over our ageing experiments. This was done by determining the midpoint between the maximum and minimum carbonyl area values at each time point, and identifying the pipe wall radial distance corresponding to the midpoint as the penetration depth. In Figure 4.12 a) we show a log-log plot of the penetration depth  $\delta$  versus ageing time  $t$  for all the recirculating ageing experiments that we performed on 1/2" PW pipe. On a log-log plot, a power law function of the form:

$$\delta = At^m \quad (8)$$

is a straight line of the form:

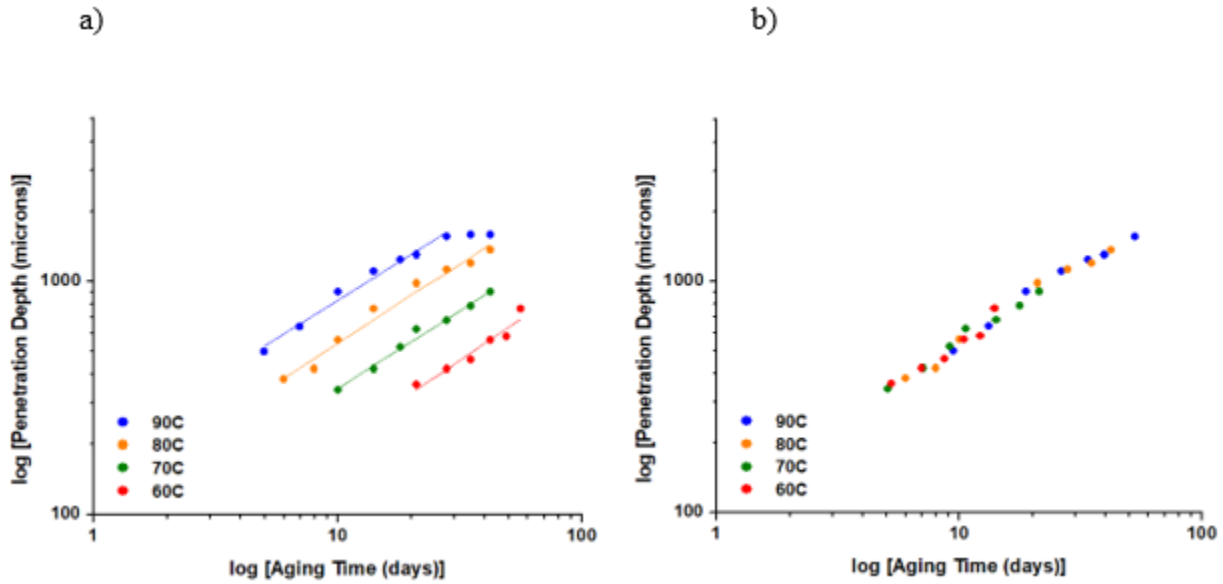
$$\log \delta = m \log t + A \quad (9)$$

where the exponent  $m$  is the slope of the straight line. In the present case, we fit plots of  $\log \delta$  versus  $\log t$  at each measurement temperature to Eqn. 4, and the best-fit values of the exponent  $m$  were: 0.66, 0.68, 0.67 and 0.70 for 90 °C, 80 °C, 70 °C and 60 °C respectively. Since all the best-fit values of  $m$  were very close, we are confident that we are probing the same degradation process at the different temperatures  $T$ . To scale all the data to a single measurement temperature of  $T = 80$  °C, we used the relationship:

$$\log t_{80^\circ\text{C}} = \log t(T) + \log a_{80^\circ\text{C}}(T) \quad (10)$$

where  $\log t_{80^\circ\text{C}}$  are the logarithm of the time values scaled to the reference temperature of 80 °C,  $\log t(T)$  are the logarithm of the time values measured at a different temperature  $T$ , and

$\log a_{80^{\circ}\text{C}}(T)$  is the logarithm of the shift factor referred to  $T = 80^{\circ}\text{C}$ . For this comparison, we chose a common values of the penetration depth  $\delta = 0.60\text{ cm}$  (30% of the pipe wall thickness). The resulting master plot of all the data is shown in Figure 4.12 b), showing the overlap of the scaled data sets on a log-log plot. The shift factors for each temperature are tabulated in Figure 4.1. Therefore, the concept of time-temperature superposition applies to our ageing data.



**Figure 4.12:** a) Log-log plot of penetration depth  $\delta$  in microns against ageing time in days for 1/2" PW PEX-a pipe samples aged at 80 psi and the temperatures outlined in the legend. The solid lines correspond to best fits of each data set to a straight line. Since the 90 °C data set reaches a plateau of penetration effect, the last two data points were not included in the fit. The best-fit power law equations were;  $\delta = 182t^{0.657}$ ,  $\delta = 115t^{0.677}$ ,  $\delta = 73.76t^{0.671}$  and  $\delta = 40.34t^{0.705}$  for the 90 °C, 80 °C, 70 °C and 60 °C respectively, with  $R^2$  values of 0.982, 0.976, 0.986 and 0.918. b) Master plot of the time-temperature superposition of all the data sets measured at the four different temperatures, shifted to coincide with the 80 °C set.

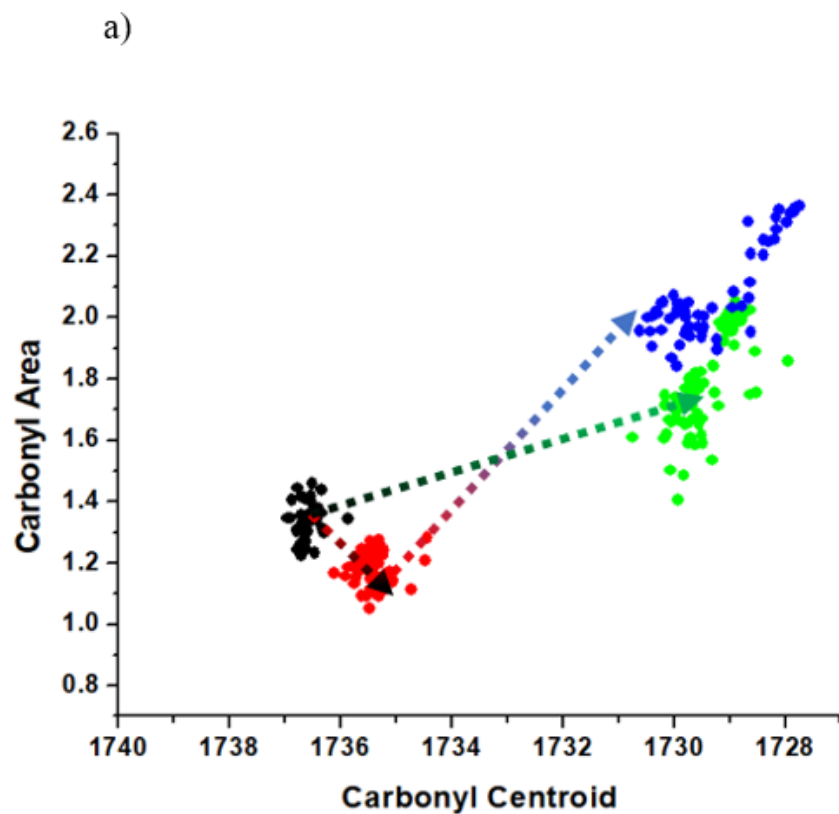
Temperature (°C)	Shift factor (a <sub>80</sub> (T))
60	4.01
70	1.97
80	-
90	0.53

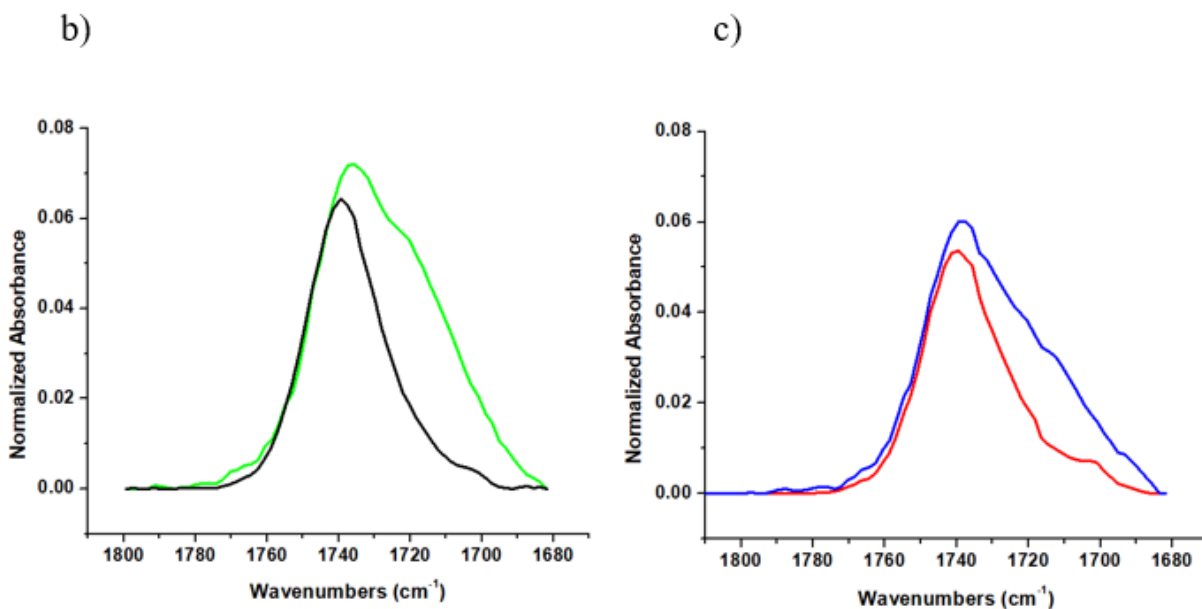
**Figure 4.1:** Tabulated shift factors for each temperature tested.

#### 4.1.2 PW PEX-a Pipe Ageing in UV/Ozone Environment

In the UV/ozone exposure experiments, we compared the effect of a highly oxidizing environment on virgin pipe and pipe that had been aged in the hot water immersion environment. We have shown in the hot water immersion experiments in section 4.1.1.1, as well as the hot water recirculating experiments shown in sections 4.1.1.2 and 4.1.1.3, that hot water can break some of the ester linkages in the additives incorporated into PEX-a pipes. These additives are designed to prevent oxidative damage; however, the ester linkages are not critical to their preventative role, as outlined in section 1.3. We propose that the cleavage of these bonds can result in an increased likelihood of the additives diffusing out of the polyethylene matrix, rendering the pipe more susceptible to oxidative damage. The substantially larger amount of oxidation exhibited by water aged pipes (Figures 4.6 and 4.8), when compared to air aged pipes (Figures 4.2 – 4.4) seems to corroborate this proposition. We conducted UV/ozone experiments on both virgin ½” PW pipes and those aged in hot 80 °C water for four weeks, to investigate their degree of oxidation (Figure 4.13). An axial slice taken from a virgin PW pipe and aged in the UV/ozone chamber for 2 hours exhibited a ~ 0.005 – 0.01 absorbance unit increase in the 1690 cm<sup>-1</sup> – 1740 cm<sup>-1</sup> region, whereas an axial slice taken from a pipe aged in 80 °C water for four weeks subjected to the same UV/ozone conditions increased by ~ 0.03 – 0.04 absorbance units in the same spectral range. This larger increase in carbonyl absorbance, specifically at

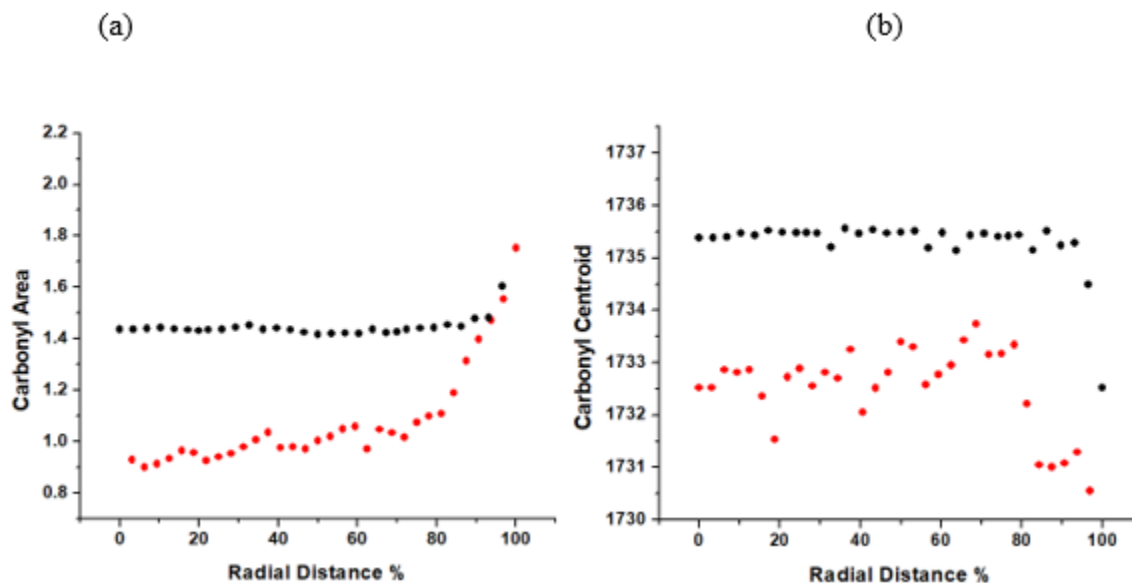
lower wavenumbers where oxidative products absorb, corresponds to more oxidative damage produced in the PEX-a sample that was previously aged in hot water. This is an indication that the additives lose their ability to prevent oxidation after experiencing hot water ageing for long times, likely due to their leeching from the pipe by the surrounding water.





**Figure 4.13:** a) Carbonyl area index versus carbonyl centroid index of virgin PW PEX-a (black), PW PEX-a pipe after 2 hours of UV/ozone exposure (green), PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks (red) and PW PEX-a pipe after 4 weeks of 80° C Milli-Q water followed by 2 hours of UV/ozone exposure (blue). The dashed lines indicate the trajectories of the data with UV/ozone exposure. (b) and (c): Representative spectra of the carbonyl region of (b) virgin PW PEX-a pipe and (c) PW PEX-a pipe aged in 80° C Milli-Q water for 4 weeks. The black and red curves were measured before exposure to UV/ozone, and the green and blue curves were measured after 2 hours of exposure to UV/ozone. The spectra were collected midway through the pipe wall thickness (~50% radial distance).

## 4.2 FTIR Microscopy Measurements of In-Service PW PEX-a Pipes



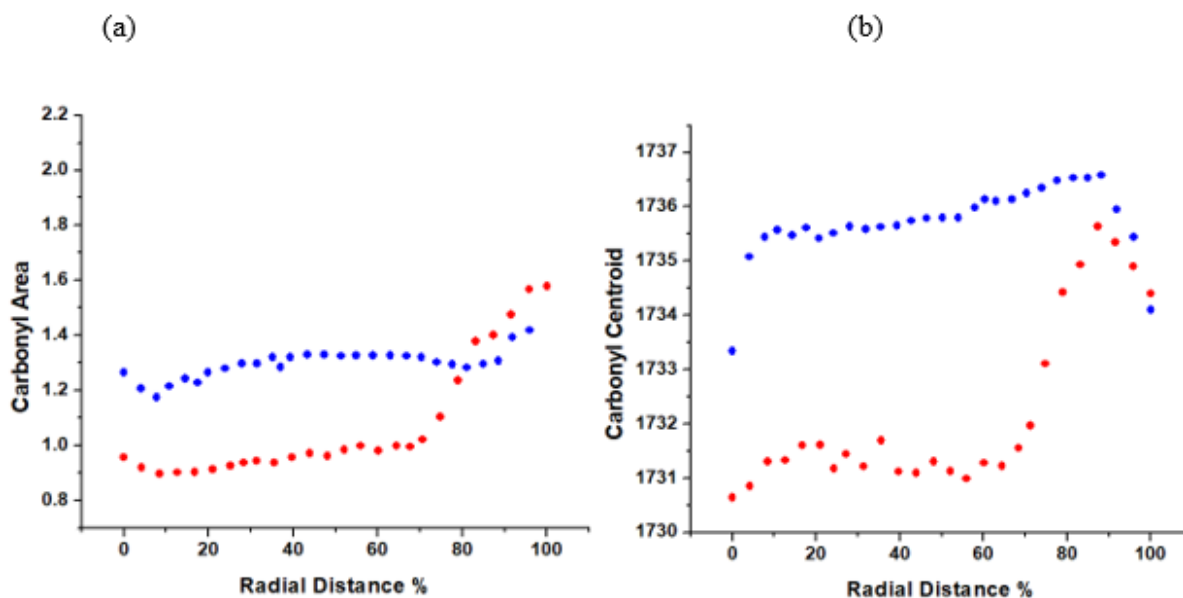
**Figure 4.14:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for a virgin 1” PW PEX-a pipe (black) and a PW pipe exposed to in-service conditions for more than 4 years, which experienced pipe failure (red). Index values shown are average values of data points measured within 3% of the radial distance values for three line profiles.

We conducted measurements on PEX-a pipes exposed to in-service conditions for different lengths of time, to better understand the properties of pipes installed in the field so that we can compare these results with those for our in-house aged pipes. The first sample was a 1” PW pipe denoted the “Yukon” sample, which had been installed in a home application for more than 4 years and had exhibited significant cracking leading to pipe failure. In Figure 4.14, we show the carbonyl area index and carbonyl centroid index profiles across the pipe wall for the failed sample (red) and the virgin retainer (black). Both indices exhibited trends that were similar to those for our recirculating water aged pipes shown in section 4.1.1.3, with the carbonyl area



index decreasing from the value of ~1.4 for the virgin pipe at the inner surface to a plateau value of ~0.9, and this effect penetrated the pipe wall by about 80% – 90% of the pipe wall thickness. We attribute this effect to the decrease of the Tinuvin additive after exposure to high temperature water, caused by the hydrolysis of the ester bonds within the additives and the leaching of these molecular fragments from the pipe by the water.

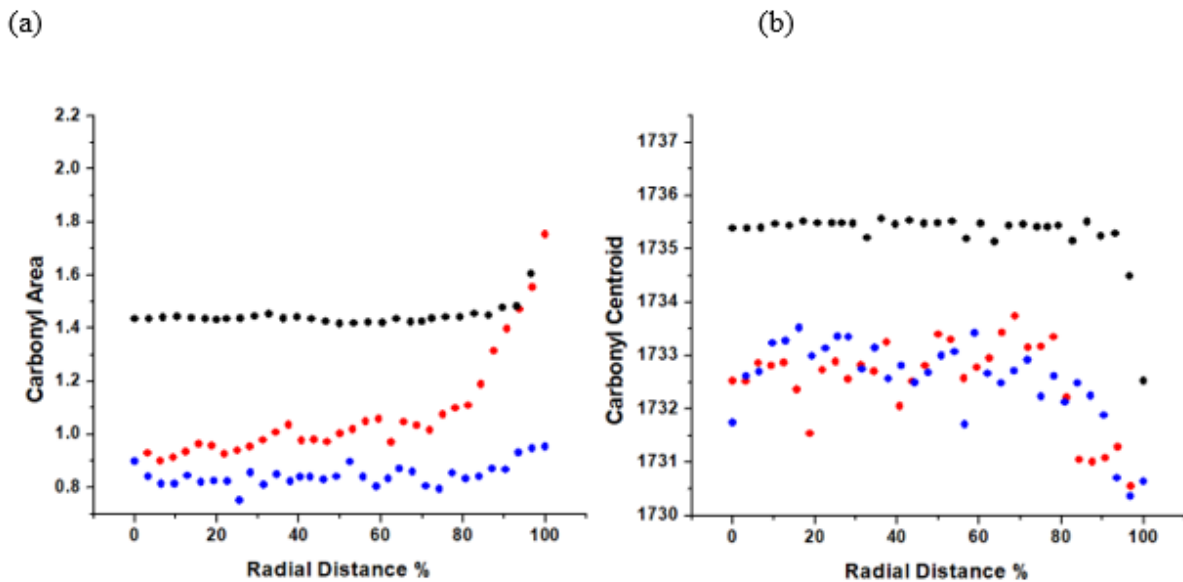
In-service pipes differ from our in-house aged pipes with respect to the operating temperature and length of time in service. The in-service pipes would experience a maximum temperature of ~60° C, with fluctuations occurring based on user needs, compared to our constant exposure to higher temperatures. The water quality in the field can vary greatly, with various ions present in different concentrations, whereas we exclusively used Milli-Q or distilled water. The in-service samples we received were subjected to in-service conditions for lengths of time between 1 and 5 years and our in-house experiments are completed within 6 weeks. Nevertheless, the results shown in Figures 4.14 and 4.15 are very similar results to those for the in-house recirculating hot water ageing experiments described in Section 4.1.1.3. Both profiles shown in Figure 4.15 were measured on ½” pipes that had been exposed to in-service conditions, at the same installation location, denoted the “43P1” and “43P0” samples, for 1 (blue) and 3 (red) years respectively. A reduction in the additive due to exposure to high temperature water can be seen by comparing the 3 years aged sample to the 1 year aged, as determined by the reduction in the carbonyl area from the inner surface. The pipe aged for 3 years exhibited substantial cracking which led to pipe failure, similar to the “Yukon” sample shown in Figure 4.14. The reduction in the carbonyl area index penetrated ~70% - 80% through the pipe wall thickness for the “43P0” sample, compared to ~80% - 90% of the pipe wall thickness for the “Yukon” sample. However, cracking that led to pipe failure occurred in both samples.



**Figure 4.15:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for 1” PW PEX-a pipes that were subjected to the same in-service conditions for 1 year (blue), which did not experience pipe failure, and 3 years (red), which did experience pipe failure. Index values are average values of data points measured within 3% of the radial distance values for six line profiles.

Our in-house ageing experiments discussed in sections 4.1.1.2 and 4.1.1.3 showed that the largest effect on the chemical properties of PEX-a pipes in hot water environments is the depletion of additives. This is determined by the correlated decrease in carbonyl and ester absorbance, which both arise from the same functional groups within the additives. Absorbance in both these peaks decreased over time in hot water, corresponding to the cleavage of the ester bonds present in the additives. Our goal with the ageing experiments was to accelerate the same ageing process that the pipes would experience in the field. If successful, the final values measured for both environments should be the same. This seems to be the case, as can be seen in Figure 4.16, which shows radial profiles of the carbonyl area index and carbonyl centroid index

for both in-service aged and in-house immersion aged samples of the same 1" PW pipe. The carbonyl area and carbonyl centroid indices measured after 3 weeks at 80° C agree quite closely with the corresponding index values measured on the in-service pipe at the inner surface, with both indices decreasing by ~40%. As the in-service sample was aged by flowing water through the pipe, only the index values at the inner surface were significantly affected. Throughout the bulk of the pipe, both samples showed similar values of the carbonyl index values, with the decrease in the indices slightly larger for the immersion environment than for the in-service sample. These results indicate that our in-house accelerated ageing experiments at elevated temperatures affected the PW PEX-a pipe in a manner that was similar to the in-service conditions, albeit in a much shorter period of time.



**Figure 4.16:** (a) and (b): Radial distance profiles of the carbonyl area index (a) and the carbonyl centroid index (b) for a virgin 1" PW PEX-a pipe (black), a PW PEX-a pipe exposed to in-service conditions for more than 4 years, inducing pipe failure (red), and a PW PEX-a pipe aged in a hot water immersion environment at 80° C (blue). Index values are average values of data points measured within 3% of the radial distance values for three line profiles.

## **4.3 PCA of FTIR Measurements of PW PEX-a Pipe Subjected to Accelerated Ageing at Elevated Temperature**

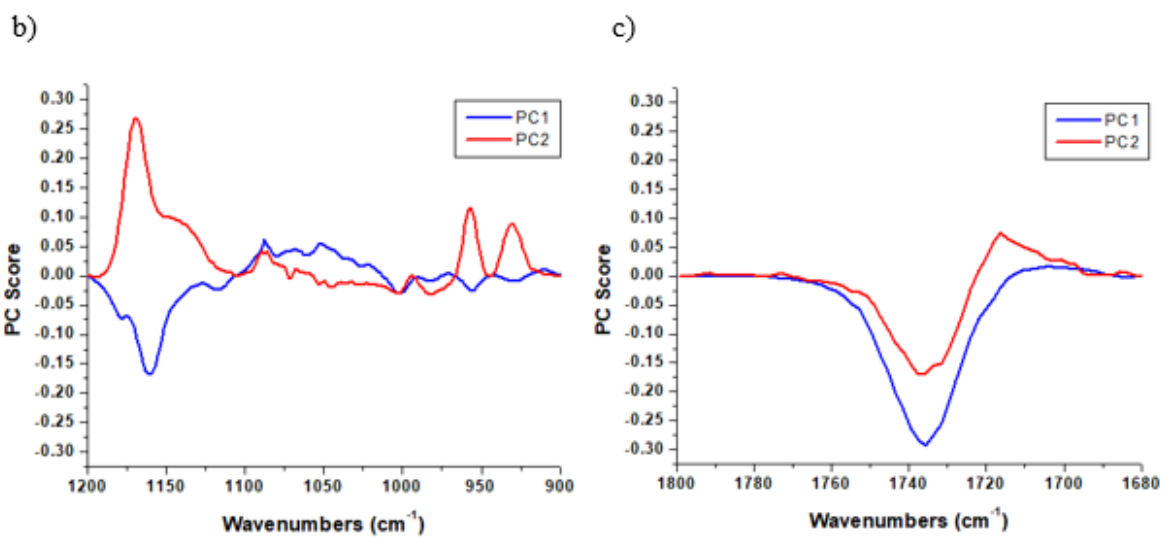
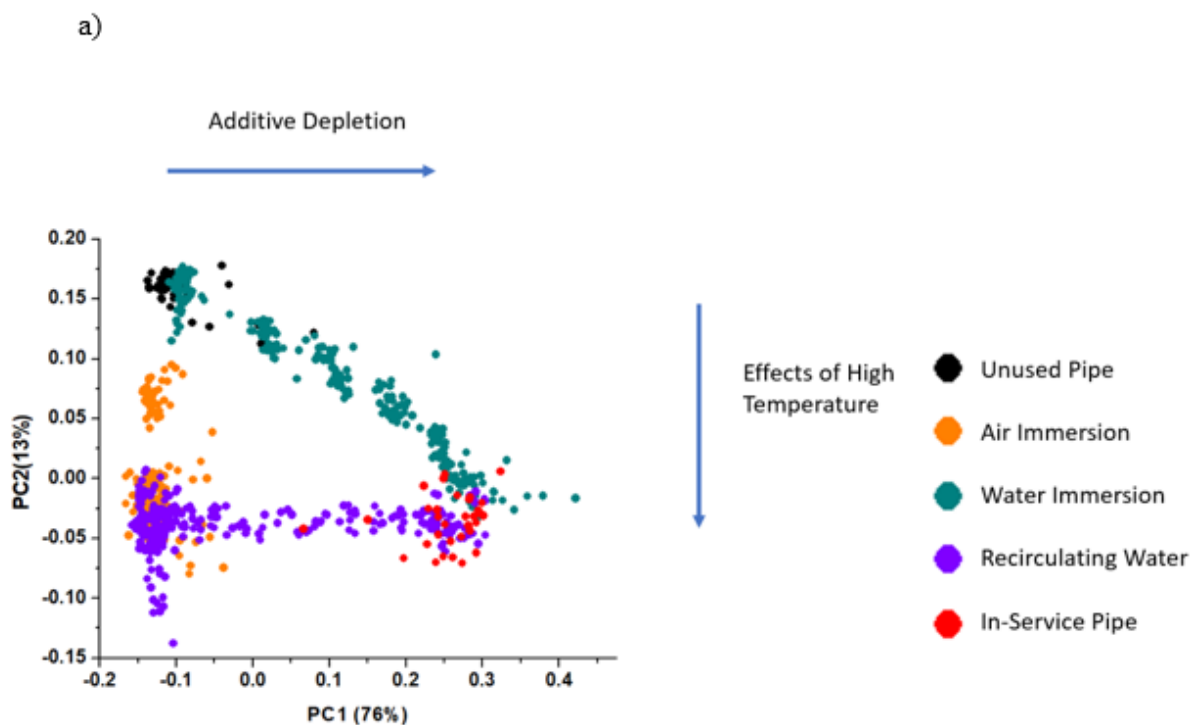
### **4.3.1 Tracking Accelerated Ageing Pathways in PC Space**

In the Dutcher Lab, Michael Grossutti has developed a systematic and thorough principal component analysis of the FTIR spectra collected on PEX-a pipe. In this analysis, PCA was performed on a large data set of 1104 spectra, including the spectral regions from  $900\text{ cm}^{-1}$  to  $1200\text{ cm}^{-1}$  and  $1680\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$ . The results are shown in Figure 4.17 in a plot of PC2 versus PC1. In the PCA, we included PW PEX-a pipe ageing data for: virgin/unused pipe, hot air immersion data at  $80^\circ\text{ C}$  for ageing times up to 3 weeks, hot water immersion data at  $80^\circ\text{ C}$  for ageing times up to 4 weeks, recirculated hot water data at  $80^\circ\text{ C}$  for ageing times up to 6 weeks, and in-service conditions. All data measured within the inner and outer 25% of the pipe wall thickness were not included in the PCA to avoid surface-related effects. The first two principal components (PCs) explained 89% of the spectral variance within the dataset, with PC1 and PC2 explaining 76% and 13% of the variance, respectively. The clustering of the data within the PC1-PC2 plot for each ageing environment and their evolution with ageing time provides insight into the effects of each ageing environment on the PEX-a pipes. The virgin pipe spectra, which serve as the starting point for the ageing process, correspond to large negative values of PC1 and large positive values of PC2. With increasing ageing time, exposure to the hot air immersion environment resulted primarily in the decrease of the PC2 values until a plateau value was reached after 10 days. In contrast, exposure to the hot water immersion environment resulted primarily in an increase in the PC1 values with ageing time, with almost constant values obtained

after 14 days. Therefore, immersion in hot air and hot water resulted in very different ageing pathways. Exposure to the recirculating ageing environment resulted in the data proceeding from the region corresponding to hot air immersion ageing to ending in the region corresponding to late stage hot water immersion ageing. This result can be understood in terms of relatively quick changes to the pipes due to the hot air on the outside of the pipes (as discussed in section 4.1.1.1), with the effect of the hot water flowing within the pipe dominating at longer ageing times.

In Figure 4.17 b) and c), we show the loading spectra used in the PCA for PC2 and PC1, respectively. The loading spectra represent the correlations in the spectral variance that describe each PC. In these spectra, positive correlations correspond to peaks pointing in the same direction and vice versa for negative correlations<sup>30,31</sup>. We see that the carbonyl and ester peaks associated with ester linkages in the additives were highly correlated in the negative direction with PC1, meaning that as these peaks decrease, the PC1 value increases. This allows PC1 to be a correlated measure of the loss of ester moieties associated with additives during the aging process. The vinyl peak, peaks arising from polyethylene and the lower wavenumber region of the carbonyl peak (associated with degradation) were highly correlated with PC2. Because of this, we suggest that PC2 is a general measure of the effects of high temperature on the PEX-a material.

We note that the PC data for in-service pipe coincides closely with both hot water immersion and recirculating ageing data points at long ageing times. This suggests that our in-house hot water ageing has closely reproduced changes within the central portion of the wall of the in-service pipes, validating our in-house ageing protocols.



**Figure 4.17:** a) PC1 versus PC2 plot for PW pipes aged in the various 80 °C ageing environments. The colours correspond to different data sets as listed in the legend. The PC space

was calculated using 1000+ IR spectra of 11 absorbance peaks, from the middle 50% of the pipe wall thickness. The first two principal components explain 89% of the variance in the dataset, with PC1 and PC2 explaining 76% and 13%, respectively. Each point in the plot corresponds to one spectrum. b) Fingerprint region loading spectrum for PC1 and PC2. c) Carbonyl region loading spectrum for PC1 and PC2.

## 5 Summary and Future Work

### 5.1 Summary of Findings

In this thesis, I describe our development of a robust set of experimental procedures to expose PEX-a pipes to accelerated ageing and quantify the effects of the ageing process on the pipes using IR microscopy. We introduced several different ageing environments, including hot air immersion, hot water immersion, recirculating hot water, and exposure to UV/ozone, which allowed us to isolate and combine various environmental factors. In addition to designing and testing the recirculating hot water systems, I performed many accelerated ageing experiments on various PEX-a pipe sizes and formulations under various ageing conditions. Through this, I have contributed significantly to an extensive database consisting of tens of thousands of IR spectra on virgin and aged PEX-a pipe.

We found that the most pronounced changes to the IR spectra due to ageing were the peaks associated with oxidation as well as the ester linkages within the antioxidant additives. In every high temperature environment, we found that the additive content was depleted, with this effect more pronounced in the presence of hot water. Exposure to UV light and ozone produced a significant amount of oxidation, which was larger than that produced by ageing in hot water. Flowing recirculated hot water through the pipes produced changes in the IR spectra that were consistent with those measured for pipe that was in-service for much longer periods of time, validating this accelerated ageing procedure. We found that exposure to flowing hot water produced an ageing effect that gradually penetrated through the pipe wall. By measuring this effect at different temperatures within the range 60-90 °C and at different ageing times, we were able to determine that the ageing process can be described by time-temperature superposition,



determining that increasing the ageing temperature by 10 °C was equivalent to decreasing the ageing time by a factor of 2. We observed that exposure to high temperature water significantly depleted the stabilizing additive levels in the PEX-a pipes. This is a concern since the loss of the stabilizing additives by ageing in hot water leaves the PEX-a pipe susceptible to oxidative degradation by other environmental factors.

## **5.2 Future Work**

It would be very interesting to extend our in-house ageing environments to include exposure to hot chlorinated water. Chlorine ions have a stronger oxidizing potential than pure water and can be an important factor in the failure of in-service PEX-a pipes<sup>16,22,23</sup>. The chemical equilibrium of free chlorine in water is rather sensitive, and careful monitoring and control is required to perform this experiment properly. This would involve preparing new solutions daily with constant monitoring of its properties, but it is an important step towards achieving a more realistic simulation of in-service ageing of PEX-a pipe.

All data shown in this thesis is in the form of line profiles measured from the inner surface to the outer surface of the pipe wall, with 100 µm step sizes. Our preliminary work measuring IR spectra within 200 µm of both the inner and outer surfaces showed significant differences compared to the central portion of the pipe wall. Quantifying the effect of ageing at the inner and outer surfaces is essential to developing a full understanding of the effects of ageing on PEX-a pipe.

In addition, chemical analyses of cracks formed from the ageing process on both in-service and in-house aged samples will be conducted with our in-house FTIR microscope as well as the high-resolution mid-IR spectromicroscopy facility at the Canadian Light Source (CLS).

Understanding the mechanisms leading to the formation of cracks as well as the propagation of these cracks is essential to preventing them and extending pipe lifetime. This will be done by examining cracks of various sizes with significant improvements in signal-to-noise and spatial resolution afforded by the CLS facility.

## References

1. Kumar, S., & Pandya, M. V. (1997). Thermally recoverable crosslinked polyethylene. *J. App. Poly. Sci.* 64(5), 823–829.
2. Khonakdar, H. A., Morshedian, J., Wagenknecht, U., & Jafari, S. H. (2003). An investigation of chemical crosslinking effect on properties of high-density polyethylene. *Polymer*, 44(15), 4301–4309.
3. Chodák, I. (1998). High modulus polyethylene fibres: Preparation, properties and modification by crosslinking. *Prog. Poly. Sci. (Oxford)*, 23(8), 1409–1442.
4. Thakare, K. A., Vishwakarma, H.G., Bhawe, A.G. (2015). Experimental Investigation of Possible Use of HDPE As Thermal Storage Material in Thermal Storage Type Solar Cookers. *Int. J. Res. Eng. Tech.*, 04(12), 92–99.
5. Gedde, U. W., & Ifwarson, M. (1990). Molecular structure and morphology of crosslinked polyethylene in an aged hot-water pipe. *Poly. Eng. Sci.*, 30(4), 202–210.
6. Chodák, I., Romanov, A., Rätzsch, M., & Haudel, G. (1987). Influence of the additives on polyethylene crosslinking initiated by peroxides. *Acta Polymerica*, 38(12), 672–674.
7. Gedde, U. W., Viebke, J., Leijstrom, H., & Ifwarson, M. (1994). Long-Term Properties of Hot-Water Polyolefin Pipes - A Review. *Poly. Eng. Sci.* 34(24), 1773–1787.
8. Gardette, M., Perthue, A., Gardette, J. L., Janecska, T., Földes, E., Pukánszky, B., & Therias, S. (2013). Photo- and thermal-oxidation of polyethylene: Comparison of mechanisms and influence of unsaturation content. *Poly. Deg. and Stab.* 98, 2383-2390.

9. Yang, R., Liu, Y., Yu, J., & Wang, K. (2006). Thermal oxidation products and kinetics of polyethylene composites. *Poly. Deg. and Stab.* 91(8), 1651–1657.
10. Luongo, J. P. (1960). Infrared study of oxygenated groups formed in polyethylene during oxidation. *J. Poly. Sci.* 42(139), 139–150.
11. Lundbäck, M., Strandberg, C., Albertsson, A. C., Hedenqvist, M. S., & Gedde, U. W. (2006). Loss of stability by migration and chemical reaction of Santonox ® R in branched polyethylene under anaerobic and aerobic conditions. *Poly. Deg. Stab.* 91(5), 1071–1078.
12. Maria, R., Rode, K., Schuster, T., Geertz, G., Malz, F., Sanoria, A., Oehler, H., Brüll, R., Wenzel, M., Engelsing, K., Bastian, M., & Brendlé, E. (2015). Ageing study of different types of long-term pressure tested PE pipes by IR-microscopy. *Poly.* 61, 131–139.
13. Step, E. N., Turro, N. J., Gande, M. E., & Klemchuk, P. P. (1994). Mechanism of Polymer Stabilization by Hindered-Amine Light Stabilizers (HALS). Model Investigations of the Interaction of Peroxy Radicals with HALS Amines and Amino Ethers. *Macromolecules*, 27(9), 2529–2539.
14. Reingruber, E., & Buchberger, W. (2010). Analysis of polyolefin stabilizers and their degradation products. *J. Sep. Sci.* 33(22), 3463–3475.
15. Jiang-Qing, P., & Song, C. (1993). A study of the photolysis of a commercial hindered amine light stabilizer. *Poly. Deg. Stab.*, 40(3), 375–378.
16. Whelton, A. J., Dietrich, A. M., & Gallagher, D. L. (2010). Contaminant diffusion, solubility, and material property differences between hdpe and pex potable water pipes. *J. Enviro. Eng.*, 136(2), 227–237.

17. Nouman, M., Saunier, J., Jubeli, E., & Yagoubi, N. (2017). Additive blooming in polymer materials: Consequences in the pharmaceutical and medical field. *Poly. Deg. Stab.*, 143, 239–252.
18. Millet, P., Humeau, P., Correc, O., Aguinaga, S., Couzinet, A., Cerru, F., & Le Cloirec, P. (2016). Diffusion of chemicals from the surface of pipe materials to water in hydrodynamic conditions: applications to domestic drinking water installations. *Water Pollution XIII*, 1, 161–172.
19. Bredács, M., Frank, A., Bastero, A., Stolarz, A., & Pinter, G. (2018). Accelerated aging of polyethylene pipe grades in aqueous chlorine dioxide at constant concentration. *Poly. Deg. and Stab.*, 157, 80–89.
20. Hirabayashi, H., Iguchi, A., Yamada, K., Nishimura, H., Ikawa, K., & Honma, H. (2013). Evaluation of durability and structure of peroxide cross-linked polyethylene pipes with several stabilizers. *Annual Technical Conference - ANTEC, Conference Proceedings*, 2(September), 1494–1499.
21. Lundbäck, M., Strandberg, C., Albertsson, A. C., Hedenqvist, M. S., & Gedde, U. W. (2006). Loss of stability by migration and chemical reaction of Santonox ® R in branched polyethylene under anaerobic and aerobic conditions. *Poly. Deg. Stab.*, 91(5), 1071–1078.
22. Whelton, A. J., & Dietrich, A. M. (2009). Critical considerations for the accelerated ageing of high-density polyethylene potable water materials. *Poly. Deg. Stab.*, 94(7), 1163–1175.
23. Whelton, A. J., Dietrich, A. M., & Gallagher, D. L. (2011). Impact of chlorinated water exposure on contaminant transport and surface and bulk properties of high-density

- polyethylene and cross-linked polyethylene potable water pipes. *J. Enviro. Eng.*, 137(7), 559–568.
24. American Stand Test Method Int. (2003). Standard Test Method for Evaluating the Oxidative Resistance of Crosslinked Polyethylene (PEX) Pipe, Tubing and Systems to Hot Chlorinated Water.
  25. Duvall, D. (2014). Oxidation resistance of polypropylene random copolymer pipe to chlorinated water. *J. Fail. Anal. Prev.*, 14(3), 336–342.
  26. Hiles, M., Grossutti, M., & Dutcher, J. R. (2019). Classifying formulations of crosslinked polyethylene pipe by applying machine-learning concepts to infrared spectra. *J. Poly. Sci.*, 57(18), 1255–1262.
  27. Wold, S., Esbensen, K., & Geladi, P. (1987). Principal Component Analysis. *Chemometrics Int. Lab. Sys.*, 2(1–3), 37–52.
  28. Plastic Pipes In. (2017). Guide To Chlorine Resistance Ratings of Pex Pipes and Tubing for Tn-53.
  29. Fukushima, K., Cai, H., Nakada, M., & Miyano, Y. (2009). Determination of time-temperature shift factor for long-term life prediction of polymer composites. *ICCM International Conferences on Composite Materials*.
  30. Modugno, C., Peltier, C., Simonin, H., Dujourdy, L., Capitani, F., Sandt, C. and Perrier-Cornet, J.M. (2020) Understanding the effects of high pressure on bacterial spores using synchrotron infrared spectroscopy. *Front. Microbiol.*, 10, 3122.
  31. Cordella, Christophe BY. (2012) PCA: the basic building block of chemometrics. *Anal. Chem.*, 47.