

Understanding the Mechanical Properties of Fibre-Matrix Interfaces in Flexible Composite Pipe Materials

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ABSTRACT

There is an increasing demand for flexible thermoplastic composite pipes to be used in subsea oil and gas fields where production fluid temperatures and hydrostatic pressures are high. However, there is also concern that under those conditions, fibre-matrix interfaces within the pipes will gradually degrade, causing the pipe to become prone to collapse under hydrostatic pressure. Therefore, this thesis reports investigations of how the strength of interfaces in thermoplastic composite pipes changes due to prolonged exposure to water, oil, and elevated temperatures.

The primary materials of this investigation were glass fibre-reinforced polypropylene (G/PP) and carbon fibre-reinforced polyamide 12 (C/PA12). Those materials were studied as they were received, as well as after they had been aged in water and oil (represented by a 50/50 pentane/toluene solution). In one approach, interfaces within the composites were incrementally damaged through single fibre push-out tests to simulate the effects of kink band propagation during the compressive failure of unidirectional composite laminates. In another approach, hereby named the hybrid-push test, fibres were pushed into a soft substrate to evaluate novel ways of analysing the strength of interfaces.

A key finding was that the strength of a fibre-matrix interface may decline or improve depending upon the type of materials from which it is comprised and the environment in which the host composite is aged. Also, the rate at which axial load was applied to fibres in G/PP was positively correlated with the shear stress required to cause interface failure. Another finding was that the interfacial shear strength of G/PP reduced at elevated temperatures and recovered at room temperature. Moreover, interface shear strength values were lower in regions of high fibre density, interfaces degraded asymmetrically around the circumference of fibres, also distinct interface failure modes were observed and named as pulloff and pulldown failure modes.

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TABLE OF CONTENTS

<u>ABSTRACT.....</u>	<u>2</u>
<u>ACKNOWLEDGEMENTS.....</u>	<u>3</u>
<u>LIST OF SYMBOLS AND ABBREVIATIONS</u>	<u>8</u>
<u>LIST OF FIGURES.....</u>	<u>2</u>
<u>LIST OF TABLES</u>	<u>6</u>
<u>1. INTRODUCTION</u>	<u>7</u>
1.2 OUTLINE OF THE THESIS	9
<u>2. LITERATURE REVIEW.....</u>	<u>10</u>
2.1 HISTORY AND APPLICATIONS OF FLEXIBLE COMPOSITE PIPES	10
2.1.1 <i>Applications of steel catenary risers.....</i>	<i>11</i>
2.1.2 <i>Applications of flexible risers</i>	<i>13</i>
2.1.3 <i>Conclusions.....</i>	<i>17</i>
2.2 CLASSIFICATION OF HIGH PRESSURE, HIGH-TEMPERATURE WELLS	17
2.2.1 <i>Conclusions.....</i>	<i>19</i>
2.3 MODES OF PIPE FAILURE UNDER COMPRESSIVE STRESS	20
2.3.2 <i>Conclusions.....</i>	<i>25</i>
2.4 PROPERTIES OF POLYMER COMPOSITES AND SOLVENTS.....	26
2.4.1 <i>Properties of polymer matrices, polypropylene and polyamide 12</i>	<i>26</i>
2.4.2 <i>Properties of polypropylene.....</i>	<i>28</i>
2.4.3 <i>Properties of polyamide 12.....</i>	<i>30</i>
2.4.4 <i>Structure and properties of fibre-matrix interfaces.....</i>	<i>33</i>
2.4.5 <i>Chemical composition of interfaces in polymer composites.....</i>	<i>34</i>
2.4.6 <i>Thickness of interfaces in polymer composites.....</i>	<i>35</i>
2.4.7 <i>Viscoelastic behaviour of interfaces</i>	<i>38</i>
2.4.8 <i>Properties of engineered fibres.....</i>	<i>39</i>

2.4.9	<i>Influence of fibre arrangements in matrices.....</i>	43
2.4.10	<i>Properties of solvents, pentane and toluene</i>	45
2.4.11	<i>Conclusions.....</i>	47
2.5	AGEING PROCESSES THAT AFFECT POLYMER COMPOSITES.....	48
2.5.1	<i>Thermal ageing processes</i>	49
2.5.2	<i>Mechanical ageing processes</i>	51
2.5.3	<i>Chemical ageing processes.....</i>	52
2.5.4	<i>Conclusions.....</i>	57
2.6	TECHNIQUES USED TO DETERMINE INTERFACIAL SHEAR STRENGTH	58
2.6.1	<i>Single fibre fragmentation test method.....</i>	59
2.6.2	<i>Single fibre pull-out and microbond test methods.....</i>	61
2.6.3	<i>Single fibre push-out and push-in test methods.....</i>	63
2.6.4	<i>Influence of local fibre density on interface shear strength</i>	67
2.6.5	<i>Conclusions.....</i>	70
2.7	HIGH-TEMPERATURE NANOINDENTATION	71
2.8	TENSILE TESTING	73
2.9	LITERATURE REVIEW CONCLUSIONS.....	76
3.	<u>EXPERIMENTAL METHODS</u>	77
3.1	MATERIALS OF INVESTIGATION.....	77
3.1.1	<i>Distribution, diameter, and volume fraction of fibres in specimens.....</i>	79
3.2	PROCEDURES USED TO AGE POLYMER AND COMPOSITE SPECIMENS.....	82
3.2.1	<i>Vapour pressure within climactic chambers</i>	85
3.3	FABRICATION OF SPECIMENS FOR MICROMECHANICAL TESTS.....	88
3.3.1	<i>Procedures used to mount composites to substrates</i>	90
3.4	INTERFACE TEST APPARATUS AND EXPERIMENT PROCEDURES.....	93
3.4.1	<i>Interface shear strength tests conducted at elevated temperatures.....</i>	96
3.4.2	<i>Fibre selection criteria for interface shear strength tests</i>	97
3.4.3	<i>Induction and analysis of incremental interface damage.....</i>	99
3.4.4	<i>Differential scanning calorimetry analysis of polypropylene.....</i>	100
3.4.5	<i>Tensile tests conducted on polyamide 12.....</i>	102

3.5	DATA TREATMENT	103
4.	<u>CHARACTERISTICS OF POLYMER COMPOSITES AT ROOM TEMPERATURE.....</u>	105
4.1	TACTICITY OF GLASS/POLYPROPYLENE AND POLYPROPYLENE	105
4.2	FIBRE CONSTRAINT REDUCED INTERFACE SHEAR STRENGTH VALUES.....	108
4.2.1	<i>Conclusions.....</i>	<i>110</i>
4.3	INVESTIGATION OF THE HYBRID-PUSH TEST METHOD	111
4.3.1	<i>Hybrid-push tests conducted on G/PP.....</i>	<i>111</i>
4.3.2	<i>Substrate modelling technique.....</i>	<i>113</i>
4.3.3	<i>Conclusions.....</i>	<i>116</i>
4.4	VISCOELASTIC BEHAVIOUR OF GLASS/POLYPROPYLENE INTERFACES	118
4.4.1	<i>Conclusions.....</i>	<i>120</i>
4.5	INDUCTION AND MEASUREMENT OF INCREMENTAL INTERFACE DAMAGE	121
4.5.1	<i>Conclusions.....</i>	<i>124</i>
5.	<u>CHARACTERISTICS OF POLYMER COMPOSITES AT ELEVATED TEMPERATURES.....</u>	125
5.1	INTERFACIAL SHEAR STRENGTH OF C/PA12 AT ELEVATED TEMPERATURES.....	125
5.2	INTERFACIAL SHEAR STRENGTH OF G/PP AT ELEVATED TEMPERATURES	129
5.2.1	<i>Conclusions.....</i>	<i>131</i>
6.	<u>CHARACTERISTICS OF AGED POLYMER COMPOSITES</u>	132
6.1	EFFECTS WATER ON THE CHARACTERISTICS OF GLASS/POLYPROPYLENE.....	132
6.1.1	<i>Glass/polypropylene: Kinetics of water absorption</i>	<i>132</i>
6.1.2	<i>Effects of water on the interfacial shear strength of G/PP.....</i>	<i>136</i>
6.1.3	<i>Conclusions.....</i>	<i>137</i>
6.2	EFFECTS OF OIL (PENTANE/TOLUENE) ON THE CHARACTERISTICS OF G/PP	138
6.2.1	<i>Glass/polypropylene: Kinetics of pentane/toluene absorption.....</i>	<i>138</i>
6.2.2	<i>Effects of pentane/toluene on the interfacial shear strength of G/PP</i>	<i>141</i>
6.2.3	<i>Conclusions.....</i>	<i>142</i>
6.3	EFFECTS WATER ON THE CHARACTERISTICS OF CARBON/POLYAMIDE 12.....	143
6.3.1	<i>Carbon/polyamide 12: Kinetics of water absorption</i>	<i>143</i>
6.3.2	<i>Effects of water on the interfacial shear strength of C/PA12.....</i>	<i>144</i>

6.3.3	<i>Conclusions.....</i>	<i>146</i>
6.4	EFFECTS OF OIL (PENTANE/TOLUENE) ON THE CHARACTERISTICS OF C/PA12	147
6.4.1	<i>Carbon/polyamide 12: Kinetics of pentane/toluene absorption.....</i>	<i>147</i>
6.4.2	<i>Effects of pentane/toluene on the interfacial shear strength of C/PA12.....</i>	<i>148</i>
6.4.3	<i>Conclusions.....</i>	<i>154</i>
6.5	LOCATION OF INTERFACE FAILURE IN AGED COMPOSITES UNDER SHEAR STRESS.....	156
6.5.1	<i>Conclusions.....</i>	<i>159</i>
<u>7.</u>	<u>CONCLUSIONS AND FURTHER WORK.....</u>	<u>160</u>
7.1	FURTHER WORK	163
<u>8.</u>	<u>REFERENCES.....</u>	<u>164</u>

LIST OF SYMBOLS AND ABBREVIATIONS

AFM	Atomic force microscopy
ASTM	American Society for Testing and Materials
CFRP	Carbon fibre-reinforced polymer
C/PA12	Carbon fibre-reinforced polyamide 12
CO ₂	Carbon dioxide
DSC	Differential scanning calorimetry
FEG	Field emission gun
G/PP	Glass fibre-reinforced polypropylene
GFRP	Glass fibre-reinforced polymer
HCl	Hydrochloric acid
H ₂ S	Hydrogen sulfide
H ₂ SO ₄	Sulfuric acid
IFSS	Interfacial/Interface shear strength
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
PA12	Polyamide 12
PP	Polypropylene
RTP	Reinforced thermoplastic pipe
SCS-6/Ti-24-11	Silicon-carbide-fibre-reinforced titanium alloy
SiO ₂	Silicon dioxide, also known as silica
SEM	Scanning electron microscope
SiC/RBSN	Silicon-carbide-fibre-reinforced reaction-bonded silicon nitride
TCP	Thermoplastic composite pipe
TEM	Transmission electron microscope

A	Area
A_{vd}	Actual vertical distance
α	Kink band orientation angle
α_L	Linear coefficient of thermal expansion
d	Fibre diameter
d_i	Fibre diameter that has undergone interface failure
E_f	Longitudinal elastic fibre modulus.
h	Specimen thickness
l_c	Critical fibre length
L_0	Specimen length
P	Load applied
P_c	Critical load applied to the fibre at the onset of nonlinearity
P_f	Load applied to the fibre
P_s	Load applied to the substrate
τ	Shear stress at the interface
τ_f	Frictional shear stress
τ_c^{SL}	Shear stress at the interface (determined from push-in tests)
τ_f	Frictional shear stress the interface
τ_m	Semi-empirically determined shear stress at the interface
τ_i	Total shear stress across debonded interfaces
T	Temperature
T_c	Crystallisation temperature
S_0	Slope of the load-displacement curve in the linear region
σ	Engineering stress
v_f	Fibre volume fraction
$W_{\%}$	Percentage change in specimen weight
W_i	Initial specimen weight
W_t	Weight of specimen at immersion time

LIST OF FIGURES

Figure 2.1 Offshore platform and flexible risers	11
Figure 2.2 Spooled flexible composite flowline	11
Figure 2.3 Typical riser configurations.....	12
Figure 2.4 Classification system for high pressure, high-temperature wells (Schlumberger).18	
Figure 2.5 Sonar image of a lateral buckle in a pipe	20
Figure 2.6 Upheaval buckling of a pipe.....	20
Figure 2.7 Illustration of buckle propagation during pipe collapse	21
Figure 2.8 Pipe exhibiting buckle propagation after a collapse test in a hyperbaric chamber 22	
Figure 2.9 Stress contour map of a pipe cross-section undergoing compression	22
Figure 2.10 Diagram of compressive failure in the extension mode	23
Figure 2.11 Diagram of compressive failure in the shear mode	23
Figure 2.12 Stages of kink band growth in a composite under compressive stress.....	24
Figure 2.13 Kink band in a composite plate	24
Figure 2.14 Microbuckling and kinking in a CFRP composite	25
Figure 2.15 Interface failure in a CFRP composite	25
Figure 2.16 Illustration of a semicrystalline polymer.....	28
Figure 2.17 Molecular structure of polypropylene	29
Figure 2.18 Molecular structure of polyamide 12	31
Figure 2.19 Relative proportion of typical dry components in a GFRP size formulation.....	34
Figure 2.20 Diagram of components in a carbon fibre-reinforced polymer composite.....	37
Figure 2.21 Illustration of a cross-section of carbon fibre.....	40
Figure 2.22 Illustration of graphite	40
Figure 2.23 Common fibre arrangements used in engineered composites	43
Figure 2.24 Continuous unidirectional fibres in laminates, oriented in various directions	44
Figure 2.25 Molecular structure of toluene.....	46
Figure 2.26 Molecular structure of n-pentane.....	47
Figure 2.27 Single fibre interface shear strength test methods.....	58
Figure 2.28 Diagram illustrating the single fibre fragmentation test.....	59
Figure 2.29 Illustrations of single fibre (a) pull-out and (b) microbond test methods.....	61
Figure 2.30 Illustration of the push-in test.....	63

Figure 2.31 The position of a flat punch at successive stages of the push-out test	64
Figure 2.32 Typical load-displacement plot of a push-out test.....	64
Figure 2.33 Square (a) and (b) hexagonal fibre packing in unidirectional composites	68
Figure 2.34 Illustration of a tensile testing machine.....	73
Figure 2.35 Typical stress-strain response of a semicrystalline thermoplastic polymer	74
Figure 3.1 Cross-section of C/PA12 flexible pipe specimen.....	77
Figure 3.2 Cross-section of G/PP flexible pipe specimen	77
Figure 3.3 Photograph of G/PP tape specimen	78
Figure 3.4 Photograph of C/PA12 tape specimen.....	78
Figure 3.5 Cross-section of the C/PA12 layer in the C/PA12 pipe specimen	79
Figure 3.6 Cross-section of the G/PP layer in the G/PP pipe specimen	79
Figure 3.7 Original (a) and modified (b) image of a G/PP sample surface	80
Figure 3.8 Dimensions the samples used in (a) ageing and (b) micromechanical tests.....	84
Figure 3.9 Procedure used to produce thin composite samples from flexible pipe	89
Figure 3.10 Procedure used to produce thin composite samples from composite tape	89
Figure 3.11 Composites mounted using the (a) conventional and (b) improved method.....	91
Figure 3.12 Aged and as-received G/PP samples, mounted using carbon tape.....	91
Figure 3.13 G/PP sample mounted on wax.....	92
Figure 3.14 G/PP sample mounted using silver-epoxy paste	93
Figure 3.15 Alemn timer instrument and details of its components	94
Figure 3.16 Schematic of the nanoindenter setup within the SEM.....	95
Figure 3.17 Common nanoindenter geometries.....	96
Figure 3.18 C/PA12 sample mounted for push-out tests at elevated temperatures	97
Figure 3.19 Fibre packing in (a) C/PA12 and (b) G/PP specimens.....	98
Figure 3.20 Regions of low (a) and high (b) fibre density in a G/PP composite.....	98
Figure 3.21 C/PA12 before fibres were pushed-out in numerical order 1 to 7.....	99
Figure 3.22 C/PA12 after fibres 1, 2 & 3 were pushed out	99
Figure 3.23 G/PP before fibres were pushed out in numerical order 1 to 7	99
Figure 3.24 G/PP after fibres 1, 2 & 3 were pushed out.....	99
Figure 3.25 Diagram of the differential scanning calorimetry technique.....	100
Figure 3.26 Dimensions of the polyamide 12 specimens that were tensile tested.....	102
Figure 3.27 Polymer sample in the tensile testing machine.....	102
Figure 3.28 Illustration of how data treatment was performed.....	103

Figure 3.29 (a) original and (b) extrapolated IFSS profiles of G/PP, push-out tested at 30°C and 70°C	104
Figure 4.1 DSC heating scans of G/PP, extracted from a G/PP pipe.....	106
Figure 4.2 DSC heating scans of PP, that was extracted from the jacket of a G/PP pipe.....	106
Figure 4.3 DSC heating scans of G/PP tape	107
Figure 4.4 DSC heating scans of PP standard sheet material	107
Figure 4.5 IFSS profiles of G/PP pushed-out tested in high and low fibre density regions ..	109
Figure 4.6 IFSS profiles of G/PP, during hybrid-push and conventional push-out tests.....	111
Figure 4.7 IFSS profiles of hybrid-push tested G/PP. Also, extrapolated IFSS profiles of push-out tested G/PP.....	112
Figure 4.8 Indentation of the wax substrate which was used for hybrid-push tests	113
Figure 4.9 Load-displacement curves of G/PP generated from hybrid-push tests. Also, load-displacement curves of the wax substrate.....	113
Figure 4.10 Graph of G/P hybrid-push tests results, with and without substrate modelling .	115
Figure 4.11 Graph of G/PP push-out tests results with and without substrate modelling	116
Figure 4.12 IFSS profiles of G/PP tape that was push-out tested at 0.1, 5 and 10 $\mu\text{m/s}$	118
Figure 4.13 Underside view of a glass fibre pushed out from G/PP specimen	122
Figure 4.14 Underside view of a carbon fibre pushed out from C/PA12 specimen	122
Figure 4.15 Underside view: glass fibre pushed out from G/PP.....	122
Figure 4.16 IFSS profiles of push-out tested (a) G/PP and (b) C/PA12 composites.....	123
Figure 5.1 C/PA12 sample expanded and bowed when heated to 120°C.....	126
Figure 5.2 C/PA12 matrix expanded when heated to 120°C (close view)	126
Figure 5.3 IFSS profiles of thermally aged C/PA12.....	127
Figure 5.4 Indentation of C/PA12 matrix at 30, 80 and 120°C	128
Figure 5.5 Micrograph of G/PP, at room temperature (25°C)	129
Figure 5.6 Micrograph of G/PP, exhibiting expansion at 70°C.....	129
Figure 5.7 Micrograph of G/PP, exhibiting expansion at 70°C (close view)	129
Figure 5.8 IFSS profiles of G/PP that was push-out tested at 30°C and 70°C	130
Figure 5.9 Load displacement profile of the G/PP matrix at 30°C and 70°C.....	130
Figure 6.1 Photograph of G/PP sample as received.....	132
Figure 6.2 Photograph of G/PP sample after it was aged in water	132
Figure 6.3 Surface of G/PP (from tape) after it was aged in water for 35 days at 80°C	133
Figure 6.4 Weight change of G/PP (from tape) and polypropylene, both aged in water at 50°C and 80°C	134

Figure 6.5 Illustration of capillary action, as well as positive and negative contact angles in large and small bore capillaries.....	135
Figure 6.6 Liquid wetting on (a) hydrophobic solid and (b) hydrophilic solid surface.....	135
Figure 6.7 Interface shear strength profiles of G/PP that was extracted from G/PP tape and aged in water at 80°C for 35 days	136
Figure 6.8 Weight change of PP (from PP sheet), aged in pentane/toluene at 25°C and 85°C	138
Figure 6.9 Weight change profile of G/PP, aged in pentane/toluene at 25, 85, and 100°C...	139
Figure 6.10 Surface condition of G/PP as received	140
Figure 6.11 Surface of G/PP aged in pentane/toluene at 85°C for 51 days	140
Figure 6.12 Surface of G/PP aged in pentane/toluene at 100°C for 51 days	140
Figure 6.13 Top-down view of G/PP aged in pentane/toluene at 100°C for 51 days.....	140
Figure 6.14 Distribution of degradation in a hygrothermally aged composite	140
Figure 6.15 C/PA12 as received	143
Figure 6.16 C/PA12 that was aged in water for 72 hours at 130°C (top-down view).....	143
Figure 6.17 C/PA12 as received (side view)	143
Figure 6.18 C/PA12 that was aged in water for 72 hours at 130°C (side view).....	143
Figure 6.19 Interfacial shear strength profiles of C/PA12 (from flexible pipe) as received and after hydrothermal ageing at 130°C for 72 hours	145
Figure 6.20 C/PA12 as received	147
Figure 6.21 C/PA12 aged in pentane/toluene for 51 days at 100°C	147
Figure 6.22 C/PA12 aged in pentane/toluene for 51 days at 130°C	147
Figure 6.23 Weight change of PA12 aged in pentane/toluene at 100°C and 130°C for 35 days	148
Figure 6.24 IFSS profile of C/PA12 aged in pentane/toluene at (a) 100°C and (b) 130°C...	148
Figure 6.25 DSC. First heating scan, PA12 aged in pentane/toluene	149
Figure 6.26 DSC. Cooling scan, PA12 aged in pentane/toluene	149
Figure 6.27 DSC. Second heating scan, PA12 aged in pentane/toluene.....	149
Figure 6.28 Polymorphic transformation behaviours of polyamide 12 from a melt	151
Figure 6.29 Polymorphic transformation behaviours of polyamide 12 from a solution.....	151
Figure 6.30 G/PP push-out tested (a) and exhibiting the pulloff failure mode (b and c).....	156
Figure 6.31 G/PP (from tape) aged in water at 80°C for 13 days, then ground and polished	157
Figure 6.32 IFSS profiles of G/PP (from tape), aged in water at 80°C for 13 days	158

LIST OF TABLES

Table 2.1 Examples of commercial flexible pipeline designs	14
Table 2.2 Classification system for high pressure, high-temperature wells (Halliburton)	19
Table 2.3 Physical and thermal properties of polypropylene	29
Table 2.4 Molecular structure of isotactic, syndiotactic and atactic polypropylene.....	30
Table 2.5 Physical and thermal properties of polyamide 12.....	32
Table 2.6 Indenter displacement rates which external research groups have used when analysing polymer composites through push-out tests	38
Table 2.7 Representative physical properties of two grades of carbon fibre.....	41
Table 2.8 Representative physical and thermal properties of E-glass and S-glass.....	42
Table 2.9 Thermal and chemical properties of toluene.....	46
Table 2.10 Thermal and chemical properties of pentane.....	47
Table 3.1 Volume fraction of fibres in the composite specimen	81
Table 3.2 Environmental conditions that specimens were aged under	83
Table 3.3 N-pentane. Coefficients for vapour pressure in Equation 3.4.....	85
Table 3.4 Toluene. Coefficients for vapour pressure in Equation 3.4	85
Table 3.5: Thermal program that was used for DSC analysis of specimens	101
Table 4.1 DSC peak temperature (melting point) of polypropylene-based specimens	107
Table 6.1 DSC analysis, peak temperatures of PA12 aged in pentane/toluene for 51 days ..	150

1. INTRODUCTION

Global demand for oil and gas is increasing, while oilfields that are easy to access have begun to deplete. That has driven oil and gas companies to explore oilfields located in hostile environments. In offshore fields, production fluids (such as water, oil, and gas) are transported from below the seabed up to sea-level production and storage facilities through pipelines. However, those fluids may contain strong acids such as HCl and H₂SO₄, which will gradually corrode steel pipelines. As a solution, flexible pipes which consist of a substantial proportion of polymer composite materials, are used for a diverse range of subsea applications. Those composite materials are made from a polymer (e.g. polypropylene) that is reinforced by engineered fibres (e.g. carbon fibres or glass fibres). Because of that, flexible composite pipes are corrosion-resistant, as well as straightforward to install in dynamic subsea environments due to their flexibility and lightweight. Hence, oil and gas companies are increasingly using flexible composite pipes to explore and develop offshore fields.

The mechanical behaviour of a composite is highly dependent on the condition of the fibre-matrix interfaces that it contains. However, there is little information regarding how the strength of an interface will change as its host composite ages in offshore production conditions. There is also a lack of information regarding how slight mechanical damage to an interface will affect its overall shear strength. Furthermore, it is unclear how far the mechanical behaviour of an interface will revert after the host composite is exposed to an elevated temperature and then returned to room temperature. That temperature fluctuation may occur, for example, when a composite pipeline is used offshore and subsequently recovered for inspection, maintenance, or redeployment in another field.

Therefore, the main aim of this investigation was to assess the micromechanical properties of fibre-matrix interfaces within composite materials that are used in flexible pipes, namely glass fibre-reinforced polypropylene (G/PP) and carbon fibre-reinforced polyamide 12 (C/PA12). Then to find out how and why those properties change as the composites are exposed to the water, oil, and elevated temperatures that flexible pipes typically encounter during service.

Aims and Objectives

The aims and objectives of this investigation were to:

- Collect samples of G/PP and C/PA12 from flexible pipes, then hygrothermally age the samples, as well as their nonreinforced matrices, in water and oil (represented by a 50/50 pentane/toluene solution).
- Determine where the composites begin to degrade as they age in water and oil (fibre, matrix, or interface) and how that progresses with time.
- Understand how the properties of thermoplastic composites change over time in subsea oil and gas production environments, at both macro and molecular scales.
- Identify how far fibre-matrix interfaces can recover their shear strength after the host composite is heated to 70°C and then returned to room temperature.
- Find how the behaviour of interfaces is affected by:
 - Shear stress which is applied at different strain rates
 - The host composite undergoing hygrothermal ageing in water and oil
 - The proximity of neighbouring fibres
 - Gradual mechanical damage to the interface

1.2 Outline of the thesis

Chapter 1 gives an introduction to this thesis by explaining why there is an intense and growing demand for flexible pipes to be made from composite materials. It describes the advantages and limitations of those technologies, the rationale for the present research, plus the key objectives of this investigation.

Chapter 2 is a literature review. It covers discussions regarding the applications of polymer composites in flexible pipes as well as environmental conditions that can cause composites to age, and the effects that ageing can have on their characteristics. Furthermore, it describes popular single fibre interface shear strength test methods and provides evaluations of their suitability for being used to complete the aims and objectives of the present work.

Chapter 3 covers the experimental apparatus and procedures that were used to conduct primary research in the present work. It introduces the polymer and composite materials of this investigation. Then it explains the procedures that were used to age those specimens, test the strength of interfaces, and analyse the thermochemical and tensile properties of the materials.

Chapters 4 to 6 describe primary research that was conducted on polypropylene and polyamide 12, as well as C/PP and C/PA12. It presents findings regarding the characteristics of those materials at room temperature (Chapter 4) and at elevated temperatures (Chapter 5). Chapter 6 presents findings regarding the characteristics of those materials after they had been aged in water and oil (pentane/toluene).

Chapter 7 provides a conclusion to this thesis. It also suggests further work that could be carried out to extend the research presented in this thesis.

2. LITERATURE REVIEW

2.1 History and applications of flexible composite pipes

Polymer composites are renowned for being materials that have high strength and light weight. Due to those advantages, they are often used to improve the performance of products, such as sports equipment, automobiles, aircraft, boats, and spacecraft. Additionally, composite materials are frequently used to construct critical structures on offshore platforms such as staircases, tanks, handrails and firewater piping. The most successful offshore applications for composite materials have been in pipework for the transport of aqueous liquids [1, 2].

Flexible composite pipes began to be used in the offshore oil and gas industry during the 1970s. Reinforced thermoplastic pipes (RTP) have been around since the 1990s and were first produced in long-lengths by Pipelife Nederland B.V. in 1998. Thermoplastic composite pipes (TCP) were first deployed for use in deep sea applications during the late 2000s [3]. Today flexible pipes are used for a wide array of pipework infrastructure, such as flowlines, water extraction lines, jumpers and risers.

A riser is one of the most important load-bearing structures on offshore production facilities. A riser is a specially constructed vertical or near-vertical segment of a pipe which transfers materials between subsea equipment and a sea-level facility, such as a platform or a floating production storage and offloading unit (FPSO) (see Figure 2.1). Risers transport materials such as oil, gas, control fluids, injection fluids and injection gases. Riser-base gas injection systems provide gas lift for the transportation of materials.

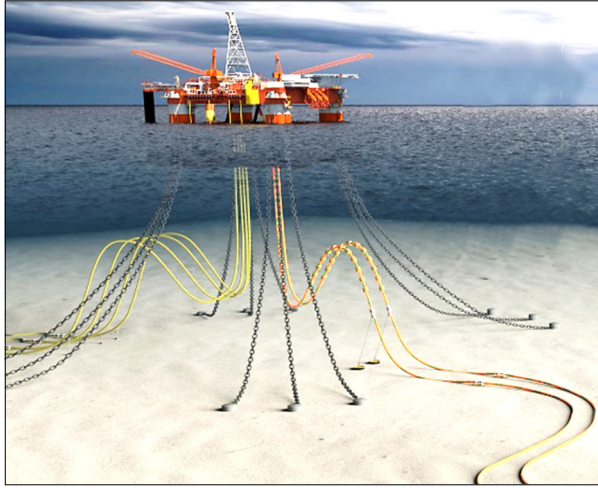


Figure 2.1 Offshore platform and flexible risers [4]



Figure 2.2 Spooled flexible composite flowline [5]

2.1.1 Applications of steel catenary risers

Steel catenary risers (SCRs) are the most common type of riser used for deepwater applications. A steel catenary riser is a riser that hangs from a sea-level facility. The riser hangs with a catenary or catenary-like curve in its structure. It is also usually free-hanging, such that it operates without support from floating intermediary devices, e.g. buoys [6]. Steel lazy-wave risers (SLWRs) are a variant of the steel catenary riser design. SLWRs have added buoyancy near the touchdown point of the riser to isolate motions of the sea-level facility (see Figure 2.3). Other configurations are also available such as steep wave designs [7]. In general, steel catenary risers cost 20% to 30% less than flexible risers of a similar size, although they are not always the most cost-effective option because they require sophisticated planning and extensive supplementary infrastructure to be installed and utilised [8]. Steel catenary risers must be resistant to fatigue, and the thickness of the pipe wall must be carefully balanced to avoid excessive weight or buoyancy. Abelanet et al. [9] noted that steel catenary risers usually require a fatigue life that is ten times longer than their service life, which equals around 250 years of fatigue life in total.

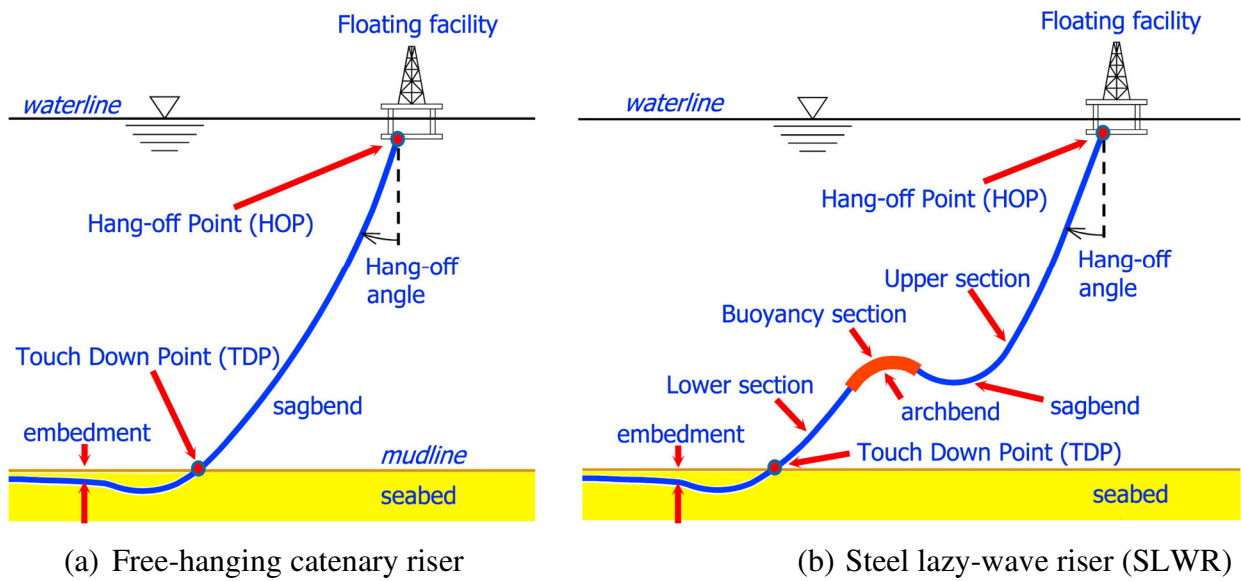


Figure 2.3 Typical riser configurations [10]

2.1.2 Applications of flexible risers

Flexible composite pipes consist of bonded or unbonded layers of polymers and polymer composites. They may also contain metallic layers. Bonded pipelines contain layers that are bound together and fixed in place, which prevents each layer from moving independently. Nevertheless, the term ‘bonded’ does not specify the use of an adhesive because thermoplastic composites can be melt-fused together. Unbonded flexible pipes contain layers that can move independently to one another, which extends the flexibility of the pipe [11].

The cross-section of an unbonded flexible riser, in order from its inner to outer surface, typically consists of the following components [12, 13]:

- Steel carcass, which prevents the build-up of gases in the annulus of the pipe. It also prevents collapse of the pressure sheath, which may otherwise occur due to external pressure, decompression, mechanical crushing loads, or tensile armour pressure.
- Pressure sheath, which acts as a barrier to maintain the integrity of the bore fluid. Polymers that are used to construct the pressure sheath include polyamide 11 (PA11), polyamide 12 (PA12), high-density polyethylene (HDPE), polyethylene (PE), and polyvinylidene difluoride (PVDF).
- Pressure armour layer (also referred to as the hoop layer). This layer resists the hoop stress within the pipe wall that is caused by the pressure of the bore fluid. It is often made from high strength carbon steel.
- Tensile armour layers. The tensile armour layers are made from carbon steel and entirely or partially sustain tensile loads which are exerted on the pipe.
- Outer sheath. The outer sheath is a polymeric layer which acts as a barrier to seawater ingress. It also protects the tensile armour layers from corrosion, abrasion and impact damage.

According to the American Petroleum Institute (2002) [12], composites are solely used as a replacement for carbon steel in the tensile armour layers of flexible pipelines. Since that time, commercial designs akin to those presented in Table 2.1 have become well-established. A challenge for the oil and gas industry is to develop advanced flexible risers solely from layers of polymers and composites, or even from a single layer of one of those materials.

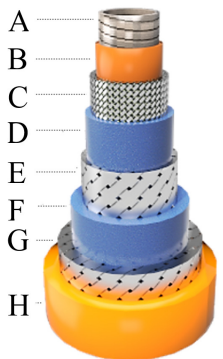
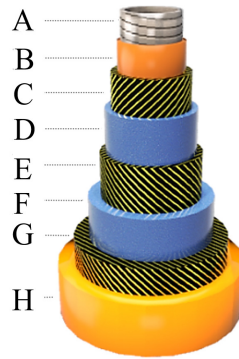
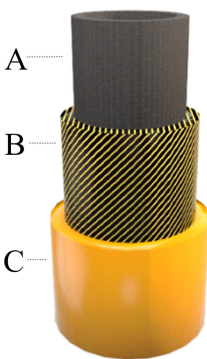
	Flexible pipe (Conventional design)	Hybrid flexible pipe (HFP)	Thermoplastic pipe (RTP or TCP)	Thermoplastic composite pipe (Single layer design)
				
A	Carcass (S)	Carcass (S)	Liner (P)	Pipe (C)
B	Pressure sheath (P)	Pressure sheath (P)	Reinforcement (C or C & S)	
C	Pressure armour (S)	Pressure armour (C)	Jacket (P)	
D	Anti-wear tape (P)	Anti-wear tape (P)		
E	Tensile armour (S)	Tensile armour (C)		
F	Anti-wear tape (P)	Anti-wear tape (P)		
G	Tensile armour (S)	Tensile armour (C)		
H	Outer sheath (P)	Outer sheath (P)		

Table 2.1 Examples of commercial flexible pipeline designs

where S= Steel, C= Polymer composite, P= Polymer

Reinforced thermoplastic pipe (RTP) is also referred to as flexible composite pipe (FCP) and non-metallic pipe (NMP). Reinforced thermoplastic pipes contain unbonded layers of polymer and composite materials. Additionally, they are often reinforced with high strength steel wire, polyester fibre, or aramid fibre, although other combinations are also used (see Table 2.1). In 2010, major industry associations changed the name 'reinforced thermoplastic pipe' to the generic name 'flexible composite pipe' due to the increasing variety of flexible pipes and the need for comprehensive certificates [14].

SoluForce[®] is the originator of high-pressure flexible composite pipe systems [3]. They have installed over 3500 km of flexible composite pipes since the year 2000. The SoluForce Heavy HT flexible pipe has an operating temperature of 85°C and a design temperature of 105°C, which is a level of performance that is unmatched by any other flexible composite pipe available today. The pipe is reinforced with high-strength steel wire, and the 4-inch H415 version of the pipe has a minimum burst pressure of 450 bar (6527 psi, 45 MPa) [15]. Nonetheless, reinforced thermoplastic pipes typically have a burst pressure of up to 70 bar (1015 psi, 7 MPa) [16].

Airborne Oil & Gas developed and deployed the first downline offshore thermoplastic composite pipes in 2009 (downline pipes are used to pump fluids down to the seabed for injection into subsea wellheads or subsea pipelines) [17]. Reinforced thermoplastic pipes (RTP) consist of unbonded layers, whereas thermoplastic composite pipes (TCP) consist of bonded layers that have been melt-fused together. Because of that fully bonded design, thermoplastic composite pipes have been qualified for use at pressures of up to 689 bar (10,000 psi, 69 MPa), which exceeds the normal burst pressure of reinforced thermoplastic pipes by a factor of 10. As such, reinforced thermoplastic pipes are mainly used onshore or at a maximum depth of 30 m whereas thermoplastic composite pipes have been qualified for use at 3000 m and have been deployed at a depth of 2100 m [16].

Advantages of flexible composite pipes

The main advantages that flexible composite pipes have over their steel counterparts are:

- **Excellent corrosion resistance.** That can extend the service life of the pipe, as well as reduce maintenance costs that are associated with protecting a pipe from corrosion.
- **High strength-to-weight ratio.** High strength enables flexible pipes to be used in deep reservoirs. Furthermore, the low weight of a composite riser reduces the cost of equipment that is required to support its weight at the hang-off point of a floater. It also enhances the pay-load carrying capacity of floaters [16].

- **Low bending stiffness relative to axial stiffness.** That enhances the ability of flexible pipes to endure repetitive stress caused by motions of sea level facilities, alternating stresses caused by production startup and shutdown, and vortex-induced vibrations [18]. Furthermore, it enables flexible pipes to be transported on a reel to an oil and gas field, then continuously unreeled for installation. That allows the pipe to be installed rapidly, even on uneven surfaces [19].
- **Cost reductions.** Glass fibre-reinforced plastic (GRP) piping is 0.5 to 0.2 times more cost-effective than similar piping which is made of stainless steel or copper-nickel. Composites are also often a cost-effective option when used as a replacement for steel in heavy riser pipe or complex offshore piping systems that consist of several fittings (i.e. bends, elbows, tees and flanges). Those cost advantages grow when composites are used to replace expensive corrosion-resistant metals such as copper-nickel alloys, and duplex or super duplex stainless steel [1]. Glass-reinforced plastic piping becomes an increasingly competitive alternative to steel piping as the required diameter of the pipe increases [20].

Limitations of flexible composite pipes

- **Low resistance to high temperatures.** A polymer will naturally change from being a hard, glassy material to a soft, rubbery material when it is heated to a temperature that is above its glass transition temperature [21]. At the glass transition temperature, the amorphous regions in polymers experience a transition from a rigid state to a flexible state. Accordingly, polymers within flexible pipes will soften when exposed to a temperature above their glass transition temperature. That is around 35 to 36°C in the case of PA12 [22, 23] and -1°C in the case of isotactic polypropylene [24]. In contrast, conventional metal pipelines remain rigid at those temperatures. For example, carbon steel melts at approximately 1425 to 1540°C, and stainless steel melts at about 1510°C [25].
- **Moisture absorption.** Flexible pipes consist of polymeric layers that will gradually absorb fluids such as crude oil and seawater. That may cause the pipe to soften or become brittle, depending on the chemical makeup of the pipe and the polymer.

2.1.3 Conclusions

The main design challenge which restricts the use of flexible pipes in ultra-deep waters is related to the high hydrostatic pressure present at those depths [26]. Typically, a steel riser will be constructed with a greater thickness to increase its strength. Unfavourably, the weight of steel in a conventional riser will increase loading on its structure which becomes a significant hindrance at depths exceeding 1500 m because the pipe will need external support [27]. For example, a heavy riser will require a stronger top-tension force to support its weight. Also, the thicker pipe will be more expensive to manufacture and install. Consequently, the installation cost of the riser will increase. A modern solution is to use polymer composite risers instead of steel risers.

Nonetheless, polymer composites have a relatively low resistance to high temperatures and can absorb fluids. Hence, there is concern that those factors may cause flexible pipes to significantly lose their resistance to external loads and hydrostatic pressure over time. That uncertainty could be alleviated with new and direct scientific research.

2.2 Classification of high pressure, high-temperature wells

In 2015, Total S.A. installed a well platform to develop the Maharaja Lela Jamalulalam South well (MLJ3-03). External pressures at the well exceeded 17,000 psi (117 MPa), and it had a downhole temperature of 165°C. At that time, it was regarded as the most challenging ultra high pressure, high-temperature (HPHT) well that had ever been drilled [28]. However, there is no industry-wide definition of HPHT conditions. Even so, The Society of Petroleum Engineers (SPE), Schlumberger, and Halliburton use guidelines to classify HPHT wells. Those guidelines are summarised in this chapter. They were used to help select the conditions under which the polymer and composite specimens were aged in the present work.

Schlumberger is well renowned as being the world's leading oilfield services provider. They have operations in over 120 countries and around 105,000 employees [29]. Their guidelines separate HPHT wells into three categories, as illustrated in Figure 2.4. Those categories are based on the stability of well-service-tool components such as elastomeric seals and electronic devices at high temperatures and pressures. Electronic devices must be shielded from the severe temperatures present in ultra-HPHT wells. Plastic and polymer composite materials may be

vulnerable to high temperatures in HPHT wells, which can exceed 150°C. In the abbreviation HPHT-hc, the term ‘hc’ refers to the French phrase ‘hors catégorie’ which means beyond classification. Those pressure conditions are unlikely to be seen soon, although bottomhole temperatures in geothermal and thermal-recovery wells can exceed 260°C [30] (The bottomhole is the deepest or lowest part of a well). This classification system is not restricted to wells that satisfy the temperature and pressure criteria simultaneously. Because if the pressure or temperature of a well falls into one of the HPHT regions, the well will be classified according to the most severe condition encountered. For example, a well with temperatures below 150°C and pressures ranging from 10,000 to 20,000 psi (69 to 138 MPa) will be classified as a HPHT well due to the high pressures.

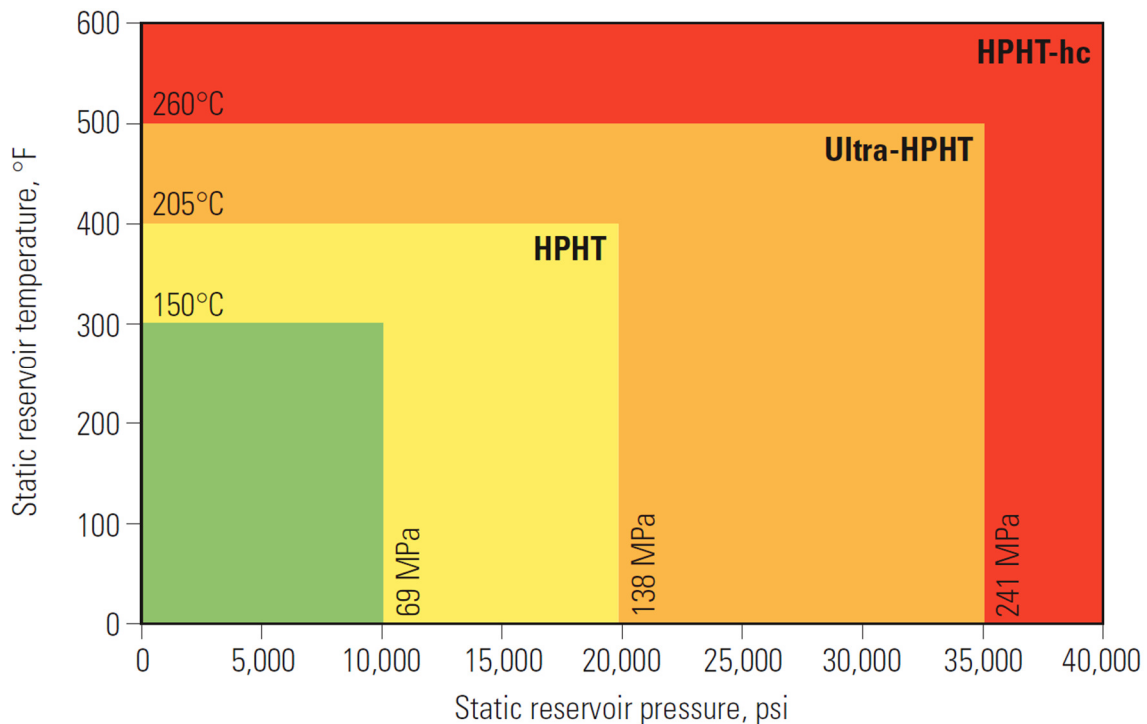


Figure 2.4 Classification system for high pressure, high-temperature wells [30] (Schlumberger)

Halliburton is one of the largest oilfield service companies on Earth. The company has operations in more than 80 countries and employs approximately 55,000 people [31]. Halliburton develop HPHT technologies and processes that help oil and gas operators execute well constructions and completions, plus improve efficiency, safety, and reliability. A definition of HPHT wells that has been provided by Halliburton is stated in Table 2.2.

Borehole temperature	
HT	>150°F (150°C) – 350°F (175°C)
Extreme HT	>350°F (175°C) – 400°F (200°C)
Ultra HT	>400°F (200°C)
Borehole pressure	
HP	>10,000 psi (69 MPa) – 15,000 psi (103 MPa)
Extreme HP	>15,000 psi (103 MPa) – 20,000 psi (138 MPa)
Ultra HP	>20,000 psi (138 MPa)

Table 2.2 Classification system for high pressure, high-temperature wells (Halliburton) [32]

The Society of Petroleum Engineers (SPE) is the largest individual-member organisation in the upstream segment of the oil and gas industry. It has more than 153,000 members and aims to collect, distribute, and exchange technical knowledge regarding the exploration, development and production of oil and gas resources [33].

The SPE Exploration & Production Glossary [34] defines a HPHT well as a well that fulfils the following criteria:

- The well has a stable bottomhole temperature, or temperature at a prospective depth, that exceeds 300°F (150°C)
- The maximum anticipated pore pressure of any porous formation to be drilled through in the well exceeds a hydrostatic gradient of 0.8 psi/ft, or the well requires pressure control equipment which is rated to at least 10,000 psi (69 MPa).

2.2.1 Conclusions

This chapter has disclosed quantitative boundaries which define high-pressure and high-temperature wells, and those boundaries have been accepted by leading organisations in the oil and gas industry. High-temperature wells have a temperature in the range of 150 to 200°C, while ultra high-temperature wells exceed a 200°C. Likewise, high-pressure wells, have a pressure in the range of approximately 69 to 138 MPa. Wells exceeding the extreme pressure of 241 MPa are unlikely to be drilled in the near future.

2.3 Modes of pipe failure under compressive stress

When a composite pipe is subjected to a compressive load, distinct structural pipe states and failure events can be recognised at scales ranging from the pipe bowing at the macroscale, down to nanoscale shear failure at interfaces. Hence, this section of the thesis discusses those modes of pipe failure at various scales. Those modes being global buckling, local buckling, microbuckling and interface failure.

Global buckling mode of failure in pipes

Upon applying a compressive load to a pipe in parallel to the pipe direction, the pipe will initially bend without permanent deformation inside its elastic range. Global buckling may occur horizontally (e.g. lateral buckling on the seabed), downwards (e.g. at a riser sagbend), or upwards (e.g. upheaval buckling of a buried pipe or a pipe on an uneven seabed) (see Figures 2.5 and 2.6). Furthermore, the temperature of a pipe can fluctuate considerably during startup and shutdown operations. That may lead to the pipe buckling laterally due to pipe walking. Pipe walking is a phenomenon that typically occurs when startup and shutdown cycles cause a pipe to undergo axial ratcheting (cyclic creep) [35].

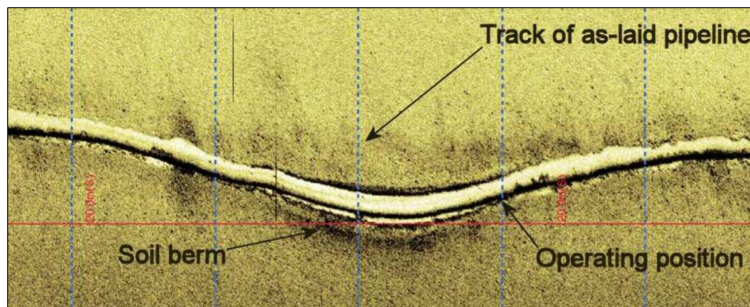


Figure 2.5 Sonar image of a lateral buckle in a pipe

[36]



Figure 2.6 Upheaval buckling of a pipe

[37]

Local buckling mode of failure in pipes

When a pipe is placed under a load that is strong enough to cause the pipe to bend and exceed its elastic limit, the pipe will cease to return to its initial shape after the load is removed. Continued loading will cause the pipe to bend further, leading to the commencement of local buckling within its structure.

Local buckling is seen as a local buckle or wrinkling on the compressed portion of the pipe cross-section. It takes place most frequently during pipelay, because of excessive bending at a sagbend in combination with external pressure [38]. As the load applied to the pipe is increased, its global deformation becomes more severe, while an increasing proportion of the deformation occurs in the local buckle until the maximum bending resistance of the pipe is reached. If the curvature of the pipe is increased beyond that point, it will undergo geometrical collapse. During that process, the material that the pipe is made out of will soften and the cross-sectional area of the pipe will diminish due to ovalisation, until opposing sides of its inner wall make contact [39]. That progression of geometrical collapse is illustrated in Figures 2.7 and 2.8.

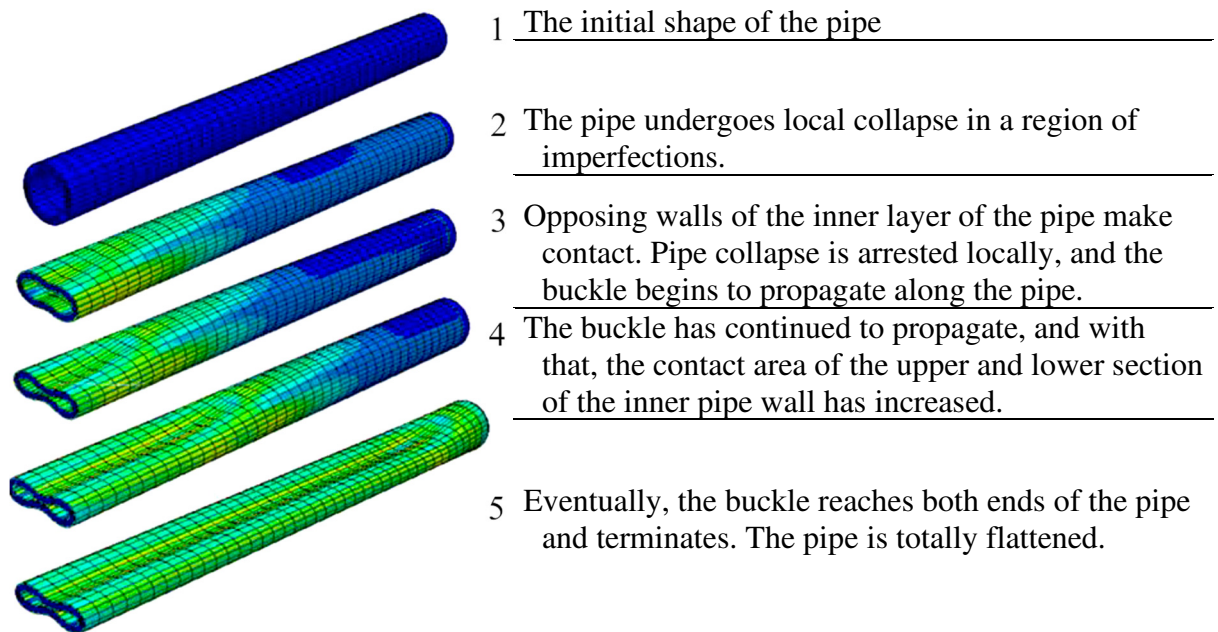


Figure 2.7 Illustration of buckle propagation during pipe collapse [40]



Figure 2.8 Pipe exhibiting buckle propagation after a collapse test in a hyperbaric chamber

[26]

Shear mode failure in composite pipes

Figure 2.9 is a stress contour map of a modelled pipe cross-section that is undergoing compression due to a load applied by a prismatic indenter. The map shows that stress has built up in the pipe wall and is inhomogeneously distributed within it. Consequently, regions of high shear stress have developed within the pipe wall. That is similar to how stress is distributed within the composite layers of a flexible pipe wall. However, because flexible pipes consist of composite layers, not only the pipe wall as a whole but also the fibres within the pipe wall can buckle and fail into kink bands due to compression and shear stress, as illustrated in Figures 2.10 to 2.13.

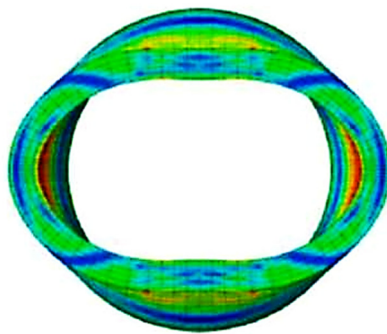


Figure 2.9 Stress contour map of a pipe cross-section undergoing compression [26]

In 1965 Rosen [41] produced one of the first and most quoted studies addressing fibre microbuckling and the failure of composite materials. In that study, Rosen [41] proposed that when a unidirectional composite is under overwhelming compressive stress, the fibres within it will microbuckle via an extension mode or a shear mode.

Extension mode – The composite does not deform with a relative horizontal shift in its structure during this mode of deformation. Instead, adjacent fibres align into sinusoidal deformation patterns which are 180 degrees out of phase with each other. In this mode, the interface alternates between being in a state of transverse tension and compression (see Figure 2.10)

Shear mode – The composite deforms with a band of localised horizontal shift and unidirectional fibres are likely to break into kink bands, as illustrated in Figures 2.11 to 2.14.

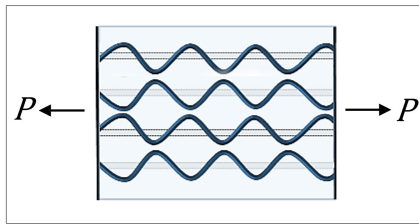


Figure 2.10 Diagram of compressive failure in the extension mode

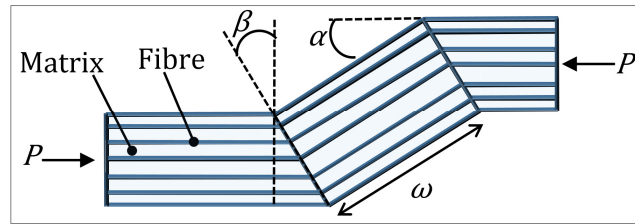


Figure 2.11 Diagram of compressive failure in the shear mode

Where P is the applied load, α is the kink band orientation angle, β is the kink band angle, and ω is the width of the kink band width.

Zhang and Latour [42] used finite element analysis to study fibre microbuckling and predicted that the shear mode is always the preferred buckling mode except in the case of composites that contain a very low volume fraction, V_f , of fibres. For example, $V_f < 5\%$, in their trials of a modelled composite. They predicted that in that situation, the fibres would act individually and with no interaction between each other.

Another mode of compressive failure is fibre crushing, which can occur when the matrix is stronger and stiffer than the fibres embedded within it. Conversely, matrix splitting may occur in a matrix of low toughness. Interestingly, Lee et al. [43] found that glass/epoxy composites failed under compressive loading by splitting at low fibre volume fractions of 10

to 30% or through a mixed-mode of splitting and kinking at fibre volume fractions of 40 to 60%. That highlights the imminent need to test a wide range of real composites.

The process of kink band formation can be realised by considering a unidirectional composite which contains vertically aligned fibres that are loaded in the fibre direction. For example, initially, a flexible pipe is under hydrostatic pressure, which causes a composite layer within it to be under an elastic load. As the hydrostatic pressure increases, the shear stress acting on the matrix between misaligned fibres in the composite increases. Eventually, the matrix yields, which initiates an incipient stage of kinking in the composite layer. During that stage, misaligned fibres within the area local to the buckle rotate away from their vertical orientation. As those fibres rotate, the material softens and that triggers nearby fibres to buckle as well, which causes a kink band to form and propagate through the composite [44]. Figures 2.11 to 2.14 illustrate that process.

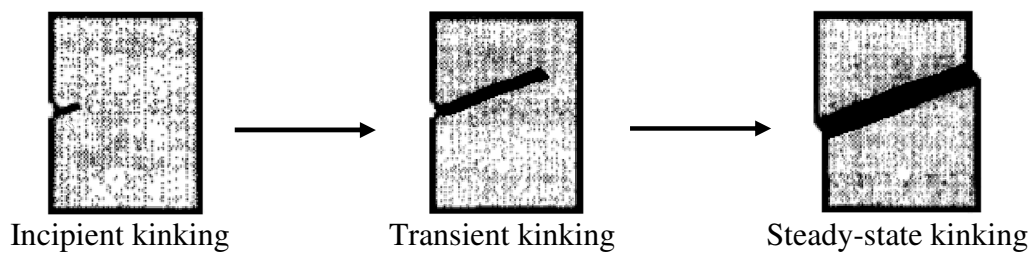


Figure 2.12 Stages of kink band growth in a composite under compressive stress [44]

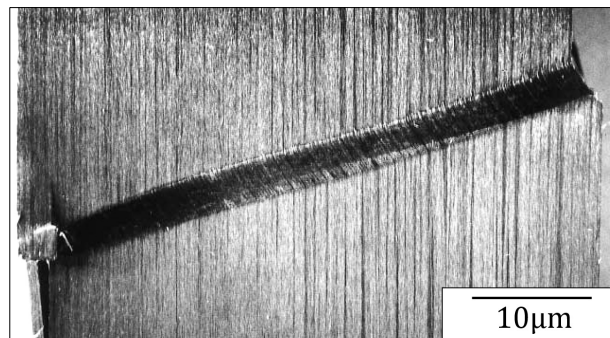


Figure 2.13 Kink band in a composite plate [45]

Figures 2.14 and 2.15 originate from Gutkin et al. [46]. Their research involved using a jig to compress carbon/epoxy laminates under longitudinal compression until the laminates failed, while observing the failure processes in-situ. Observing interface failure in-situ, rather than in post-mortem, was an important technological development because the form of buckled fibres

and fracture surfaces in a composite under an applied load may be unintentionally altered after that load is removed.

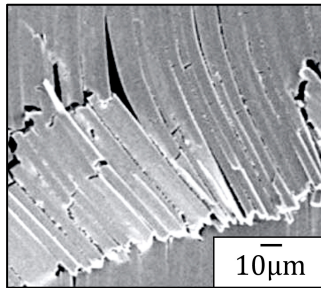


Figure 2.14 Microbuckling and kinking in a CFRP composite [46]

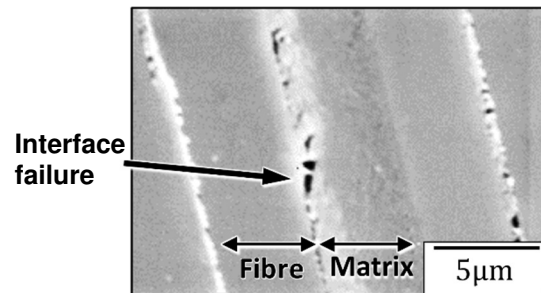


Figure 2.15 Interface failure in a CFRP composite [46]

Gutkin et al. [46] went on to propose that “matrix failure takes place in a region close to the fibre/matrix interface... microcracks accumulate, coalesce and finally separate from the fibre”. In line with those findings, Zhou et al. [47] used a two-dimensional model that was based on micromechanics to track the longitudinal compressive failure of unidirectional carbon fibre-reinforced polymers. They found that compressive failure of the composite was governed by matrix damage rather than fibre fracture, and they saw that interface cracks triggered matrix damage. Hence, it is clear that the integrity of fibre-matrix interfaces is critical for the strength of composite materials.

2.3.2 Conclusions

There is an increasing global demand for energy, and the availability of conventional sources of oil and gas is in decline. In response, operators in the oil and gas industry have been motivated to utilise underdeveloped and unexplored deepwater fields. However, high pressures and temperatures are more common in those fields, which presents complex challenges to achieving that goal.

A sought-after solution is to use flexible composite pipes and risers for service in high-pressure, high-temperature wells. However, pipes that are based on polymer composite materials tend to be more susceptible to high temperatures and moisture absorption than metallic pipes. Consequently, there is concern that if a flexible pipe is exposed to production fluids such as water or oil for prolonged periods, especially during service at high temperature, the pipe will age at an accelerated rate, causing it to lose strength and become prone to fail. For

example, that failure could occur due to compressive stress, which has been induced by hydrostatic pressure.

The mechanism through which metallic pipelines undergo geometrical collapse under high external pressure is fairly well understood. However, when using composite materials, another mode of failure can occur at high external pressure, namely failure through the shear mode of deformation. In that mode, fibre-matrix interfaces fail, and embedded unidirectional fibres break into kink bands. Kink bands may propagate through flexible composite pipes, causing the pipe to weaken.

Overall, the interface is a common point of failure in composite materials that are under high external pressure. Therefore, detailed research on the shear failure of interfaces in composites at elevated temperatures, and composites that have aged in offshore production fluids, can provide insight into ways of optimising the design and long term use of flexible pipes in challenging oil and gas production environments.

2.4 Properties of polymer composites and solvents

It is useful to first have an understanding of the constituent materials that make up composites, to support later analysis of how composites fail. A composite is a material that is made from chemically or physically distinct substances. When those substances are bonded together, they produce a unified material that has characteristics which differ from its components. Composites have two or more phases which remain separate with a distinct interface between each phase. The mechanical behaviour of a composite arises from the properties of its matrix, reinforcements and the interface between them. Engineered composites can have more desirable aesthetic, physical and chemical properties than the individual components from which they are made [48]. It is worth noting that in this thesis, the term ‘composite materials’ (or composites) refers to continuous fibre reinforced polymer composites, except where noted otherwise.

2.4.1 Properties of polymer matrices, polypropylene and polyamide 12

The matrix is the continuous phase in a composite. It is relatively soft and reinforced by stiff constituents which are embedded within it, such as engineered fibres, natural fibres, or particulates (e.g. mica). The matrix provides a barrier which protects the reinforcements within it from chemical and physical damage. Moreover, it governs the durability of the composite as

well as its resistance to temperatures and chemicals. It also transfers stress that is applied to the composite, to multiple embedded reinforcements, which reduces the stress that would be exerted upon an individual reinforcement unit. That action raises the strength of the composite.

Examples of natural composites are bone, skin, and wood. Engineered composites are usually based on polymeric, ceramic, metallic, or carbonaceous matrices. Polymers have low strength and stiffness, ceramics have high strength and stiffness but are brittle, metals have intermediate strength, intermediate stiffness, and high ductility [49].

Ceramic and metal composites have much higher thermal stability than polymer composites, but they are normally more expensive as well. They are used in very high-temperature environments, such as jet engines and automobile carbon-ceramic brake discs. Carbon fibre-reinforced carbon (CFRC) composites, also known as carbon/carbon (C/C) composites, consist of a carbonaceous matrix that is reinforced by carbon fibres. Although C/C composites are less brittle than many ceramics, they lack impact resistance. Still, C/C composites have outstanding thermal stability, excellent resistance to thermal shock, low thermal expansion, high resistance to creep and high resistance to corrosion [50]. Because of those characteristics, C/C composites are used in high-temperature applications such as nozzles for rocket engines, as well as the nose cone and wing leading edges of space shuttles [51]. Most commercially available composites are based on polymer matrices. That is because polymers are light weight, low cost and can wet fibre reinforcements at temperatures and pressures which are far lower than that needed for other materials such as metals. Some of the polymers which are most frequently used to make flexible pipelines are; nylons (also known as polyamides, e.g. PA11 and PA12), polyethene (PE), high-density polyethene (HDPE), Polyurethane (PU), and polyether ether ketone (PEEK).

Plastics are synthetic polymers, two categories of which are thermoplastics and thermosetting plastics. Polymers consist of macromolecules, which are characteristically made up of many shorter molecular chains, called monomers. Polymer matrices in composite materials are often made from thermosetting plastics. Thermosetting plastics represent about two-thirds of the composites market and approximately the same fraction of the total market value [27].

Common thermosetting plastics are epoxy, unsaturated polyester, and vinyl ester. Epoxy is the most widespread engineered matrix material, largely because it has high strength and low viscosity, which enhances the wetting of embedded fibres [52].

Thermosetting plastics are typically amorphous (non-crystalline) because they contain crosslinks between molecular chains. The crosslinks are irreversible chemical bonds that form as the liquid epoxy resin cures and transforms into a hard solid due to irreversible exothermic chemical reactions. After thermosetting resins cure, they do not melt and flow upon heating. Nor can they be returned to their uncured state. As a result, recycling is not a practical option for thermosetting plastics, at least not at commercially viable scales [53]. The higher the crosslink density of a thermosetting polymer, the higher its mechanical strength, hardness, and resistance to degradation from heat and chemicals [54].

In contrast to thermosetting resins, monomers in thermoplastics do not crosslink together. That allows thermoplastics to soften and flow once heated past their melting point, then become hard again when cooled. Because of that, thermoplastics are recyclable. Some of the most common thermoplastics are polypropylene, polyethylene, polyvinyl chloride, polystyrene, and polyether ether ketone (PEEK).

Semicrystalline thermoplastics contain regions of order (crystalline regions) and regions which do not have long-range order (amorphous regions). Figure 2.16 illustrates how molecular chains are organised within a semicrystalline polymer.

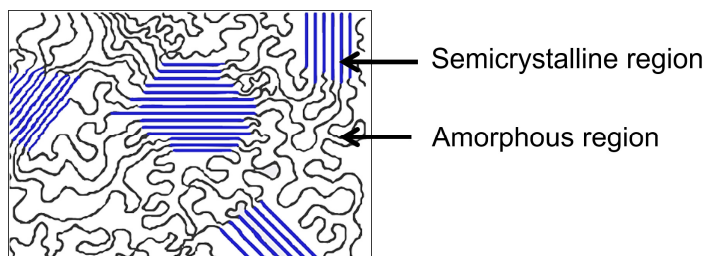


Figure 2.16 Illustration of a semicrystalline polymer [55]

2.4.2 Properties of polypropylene

Polypropylene (PP) was first polymerised in 1951 by petroleum chemists J. Paul Hogan and Robert L. Banks [56]. Polypropylene is a widely produced commodity plastic. It is used for packaging and labelling commodities such as chocolate bars and soft drink bottles. Moreover, it is used for fabricating carpet yarns, polymer banknotes, as well as flexible pipelines. It is one of the most widespread thermoplastic polymers because of its easy processability, ability to be recycled, and low production costs. Polypropylene is a low-cost plastic because it can be produced by a simple synthesis of the low-cost petrochemical gas, propylene, by polymerisation of the gas in the presence of a catalyst. Polypropylene is hydrophobic and non-

polar. Thus it is commonly used to prevent water from penetrating through pipeline walls [57]. It also has excellent resistance to many polar liquids, salts, acids and alkalis, alcohols, esters, and ketones. Those attributes make it an attractive material for use in flexible pipes for the transport of water.

Polypropylene would not typically be used in a pipeline that transports high concentrations of oil because it is an oil sorbent. Nonetheless, polypropylene specimens were aged in oil during the present work to provide a fundamental benchmark which can be employed to compare the behaviour of those materials to other polymers and composites which are used to construct flexible pipelines. Figure 2.17 illustrates the molecular structure of polypropylene.

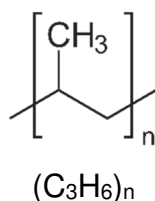


Figure 2.17 Molecular structure of polypropylene

Polypropylene has a density of 0.91 g/cm³; thus, it floats on water [58]. The maximum operating temperature of polypropylene is in the range of 100 to 130°C [59, 60], and in theory, some grades may be suitable for brief use at 140°C. The cited maximum operating temperature of 100°C is based upon the Underwriters' Laboratories rating for continuous long-term use. (100,000 hours, approximately 11.4 years). That value was determined from the ageing temperature that the material could endure for 100,000 hours and retain at least half of the original property being measured. It is worth noting that dissimilar material properties decay at different rates.

Polypropylene		
Density	0.91 g/cm ³	
Melting point	160 to 166°C	(Isotactic PP)
Modulus of elasticity	1300 MPa	
Coefficient of linear expansion	0.16 mm/m°C	
Maximum operating temperature	100 to 130°C	
Minimum operating temperature	-10°C	

Table 2.3 Physical and thermal properties of polypropylene [61, 62]

Tacticity is the relative stereochemistry of adjacent chiral centres in a macromolecule. In other words, it describes the way that pendant groups are arranged along the molecular chain of a polymer. Tacticity can have a pronounced effect on the physical properties of the polymer. For example, isotactic polypropylene is highly crystalline, syndiotactic polypropylene is less crystalline, and atactic polypropylene is amorphous (not crystalline).

Crawford et al. [63] stated that commercial polypropylene is typically 25 to 75% isotactic, and 25% atactic. Similarly, Domininghaus [64] reported that isotactic polypropylene, which is produced by standard industrial processes, shows degrees of crystallinity that range between 30% and 60%. Likewise, the melting point of commercial isotactic polypropylene ranges from 160 to 166°C, depending on crystallinity and atactic content [64]. Syndiotactic polypropylene, with a crystallinity of 30% has a melting point of approximately 130°C [65]. For polypropylene, tacticity is based on how the methyl group is oriented in the polymer chain, and Table 2.4 describes how that is the case.

Isotactic polypropylene (crystalline)	$\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 \\ & & & & & & & & & & & \\ \sim & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & \sim \\ & & & & & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \end{array}$	The methyl groups are located on one side of the polymer chain
Syndiotactic polypropylene (semicrystalline)	$\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & \text{H} & & \text{H} & & \text{H} & & \text{CH}_3 \\ & & & & & & & & & & & \\ \sim & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & \sim \\ & & & & & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{CH}_3 & & \text{H} & & \text{H} \end{array}$	The methyl groups alternate between each side of the polymer chain
Atactic polypropylene (amorphous)	$\begin{array}{ccccccc} & \text{H} & & \text{CH}_3 & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & & & \\ \sim & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & \sim \\ & & & & & & & & & & & \\ & \text{H} & & \text{H} & & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 \end{array}$	The methyl groups are positioned irregularly and on both sides of the polymer chain

Table 2.4 Molecular structure of isotactic, syndiotactic and atactic polypropylene [66]

2.4.3 Properties of polyamide 12

Polyamides are polymers which contain an amide bond between monomer units. Nylons are a subset of polyamides. High molecular weight polyamides are commonly known as nylon. In line with that, polyamide 12 is sometimes called nylon 12 because nylon is a well-recognised name. It is also referred to by its IUPAC name, poly(dodecano-12-lactam), or simply as polylauro lactam because lauro lactam is often used as a monomer for the synthesis of polyamide 12 (although it can also be produced through polycondensation of ω -aminolauric acid).

Polyamide 12 is frequently used in oil and gas piping applications, such as jumpers, risers, gas pipes, flowlines as well as liners and coatings for steel pipes. Two key reasons for that are

because it has excellent resistance to hydrocarbons and, according to Salazar et al. [67], outstanding fatigue resistance compared to other thermoplastics, even when compared to other polyamides. Furthermore, polyamide 12 has a maximum continuous operating temperature of 90°C, and its melting point lies in the range of 170 to 195°C [22, 23]. Polyamide 12 is also used as a pipe liner layer for the management of sour gas due to its exceptional resistance to corrosion [68]. It serves as an outstanding barrier to hydrocarbons found in gas condensates (such as benzene, toluene, and xylene (BTX)). Additionally, it is a favourable pipe material for use in situations where gasoline spills or other chemicals have contaminated soil [23]. As such, polyamide 12 is used to protect both the exterior and interior of onshore and offshore pipelines.

The properties of semicrystalline polyamides are governed by the concentration of amide groups in the polymer chains. Polyamide 12 has the lowest concentration of amide groups compared to all commercially available polyamides, and that property promotes its exceptional characteristics [69]. Figure 2.18 illustrates the molecular structure of polyamide 12.

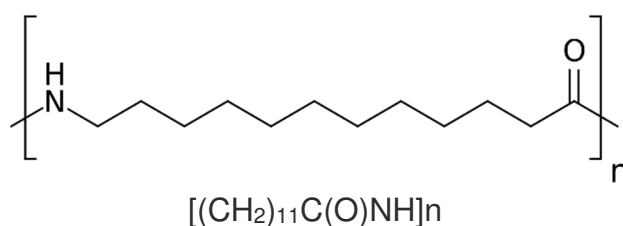


Figure 2.18 Molecular structure of polyamide 12

The amide groups in polyamide 12 chains are polar and can hydrogen bond with each other. Thus, polyamides are often crystalline and have outstanding resistance to oils, greases, hydraulic fluids, salt solutions, and natural gas [70]. They are also resistant to non-polar solvents such as toluene and pentane. However, they are sensitive to polar solvents, such as water, which can affect amide-amide hydrogen bonding within their structure. The polar amide groups form hydrogen bonds with water, reducing attractions between polyamide chains. As such, the absorbed water acts as a plasticiser. A plasticiser is a substance that is added to a polymer to lower its glass transition temperature; doing so will make it softer and more flexible. Plasticisation occurs when chemically benign molecules migrate between the molecular chains of a polymer, causing it to lose its stiffness. Plasticisation is a reversible process as the original properties of the material can be recovered when the plasticiser is removed (e.g. by evaporation) [71]. Touris et al. [72] provided evidence for that as they hydrated PA12 in water

for one day at 48% relative humidity and then left the specimens to dry out overnight, either at room temperature or at 60°C for 16 hours (15% relative humidity). The specimens dried out and returned back to their initial stiff state under both conditions, thus they concluded that the plasticisation effect of water on PA12 was not permanent.

Nonetheless, interaction with water also causes polyamides to undergo hydrolytic degradation [73]. The mechanism through which hydrolytic degradation takes place is described in Chapter 2.5.3. Nonetheless, PA12 has the lowest affinity for water among all polyamides due to its relatively long hydrocarbon chain [72].

Furthermore, polyamide 12 has outstanding resistance to abrasion, mechanical fatigue, impact, and stress cracking. Stress cracking is one of the most common causes of unanticipated brittle failure of thermoplastic polymers. It particularly affects amorphous polymers (polyamide 12 is semicrystalline). Stress cracking is defined as “internal or external cracking of the material caused by tensile stresses less than the short time mechanical strength of the material” [74]. Those properties make polyamide 12 an attractive material of choice for use in flexible composite risers that are designed to operate in dynamic subsea environments.

Polyamide 12

Melting point	170°C to 195°C
Glass transition temperature	35°C to 36°C (approximately)
Maximum operating pressure	1.6 MPa
Maximum continuous operating temperature	70°C to 90°C
Linear expansion	12 ($^{\circ}\text{C} \times 10^{-5}$)
Density	1.03 (g cm^{-3})

Table 2.5 Physical and thermal properties of polyamide 12 [22, 23, 75]

2.4.4 Structure and properties of fibre-matrix interfaces

In 1972 Sharpe [76] became the first researcher to provide a detailed description of the concept of a fibre-matrix “interphase” [77]. Sharpe [76] gave evidence for its existence, explained how it influences the mechanical behaviour of composite materials and provided details regarding how its properties can be controlled.

Depending on the scale considered, the area through which stress is transferred between the fibre and matrix may be thought of as [50]:

- 1) a two-dimensional ‘interface’ in which there is a clear division of physically dissimilar and separable phases/entities.
- 2) a three-dimensional ‘interphase’ region in which the gradually progressively change to chemically distinct bulk phases on each side. Chemical reactions, as well as changes in residual stresses and volumes, can take place in that region [78].

The tensile strength, compressive strength, strain to failure, impact properties, fracture toughness, and fatigue life of composites are variables which are all sensitive to the strength of interfaces [79]. Therefore, interfaces must stay intact for the performance of composites to be maintained. That can be difficult to achieve for composites which are used in subsea pipes because those pipes may be continuously exposed to harsh chemicals, solvents, wide temperature fluctuations and pressures during service. Nonetheless, manufacturers have used a range of methods to create high-performance composites with tailored interfaces, that enhance the suitability of the composite for use in demanding operating conditions. For example, the chemical composition of the matrix, as well as the surface chemistry and structure of fibres, has been engineered to produce advanced composites. Also, fibres have been covered in chemical agents (sizing) to promote optimal bonding at the interface between the fibres and matrix.

2.4.5 Chemical composition of interfaces in polymer composites

Coupling between the fibre and matrix in a composite can occur through a range of mechanisms such as mechanical interlocking [80], electrostatic attraction [81], van der Waals attraction [82], or chemical bonding [83]. Coupling may occur directly between the fibre and matrix or via a chemical agent called 'size'. An interface can also form due to the migration of additives or a low molecular weight contamination layer through the composite [84]. Tiwari and Bijwe [85] published a report which details surface treatments that have been used to enhance fibre bonding within matrices, such as gamma irradiation, rare earth treatments, plasma treatments, and acid oxidation. Manufacturers may also oxidise fibres by using electrolysis, or by using gas or liquid chemicals to produce functional groups on the surface of fibres that will enhance the subsequent adhesion of a size to the fibres [86]. Jones [87] emphasised the importance of oxidative treatments and sizing by stating that at least one of those processes needs to be carried out during the manufacture of carbon or glass fibre-reinforced plastics. Knowledge of ideal procedures which can be used to improve the performance of interfaces in composites is valuable, so manufacturers tend to keep the specific fibre treatment processes and size formulations that they use undisclosed. However, some details can be found in patent documents, and Thomason [88] has published a book that details more than five hundred patented size formulations for glass fibres. Figure 2.19 illustrates the relative proportion, by weight percent, of constituents in a typical size that is used on glass fibre-reinforced thermosetting resins.

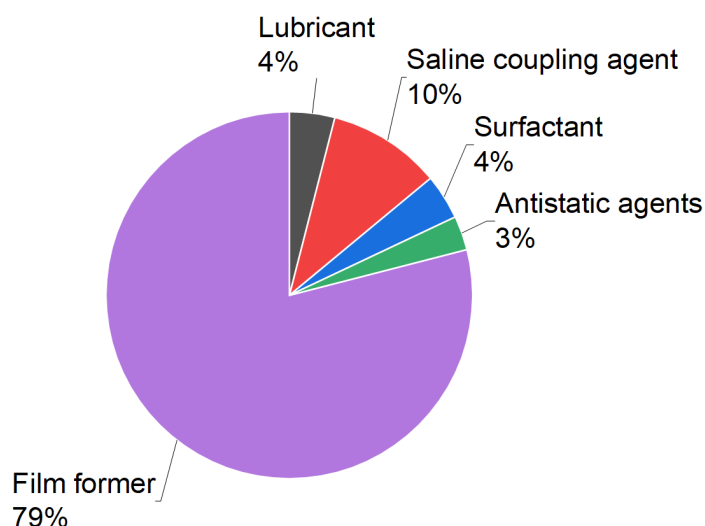


Figure 2.19 Relative proportion of typical dry components in a GFRP size formulation

[89]

Sizing is a blend of several chemicals; those chemicals can include [88]:

- Film formers. Film formers coat fibres for protection during manufacture. That is useful because fibres can fracture or break at several stages of a production process, for instance, when they are chopped, wound, weaved, dried, or packaged.
- Lubricants. Lubricants improve the dispersion of additives on fibres, provide fibres with protection against abrasion, and promote the distribution of sizing.
- Coupling agents. Coupling agents establish strong bonds between the fibre and matrix.
- Emulsifiers. Emulsifiers stabilise insoluble substances that are added to the sizing suspension.
- Anti-foaming agents. Anti-foaming agents reduce the formation of foam in the sizing.
- Acids or alkalis. Acids and alkalis adjust the pH of the size to enable hydrolysis of size formulations.
- Antistatic agents. Anti-static agents dissipate static charge that accumulates on fibres due to friction.

2.4.6 Thickness of interfaces in polymer composites

Researchers have found that the thickness of the interface in polymer composites is not necessarily uniform, and it can gradually change in width due to the climate in which the host composite is situated, or the degree to which the matrix cures during composite manufacture.

For example, Hodzic et al. [90] measured the width of the interphase in two composites which have a similar chemical structure, namely glass/phenolic CL1880 and glass/phenolic CL1916. After those composites were immersed in water for ten weeks at room temperature, they saw that the width of the interface did not change in the phenolic CL1916/glass specimen, whereas it increased by a factor of 6.3 in the phenolic CL1880/glass specimen.

Cross et al. [91] used a glass fibre-optic evanescent wave Fourier-transform infrared spectroscopy (FTIR) sensing system to study the effect of interface curing on interface properties and formation in an epoxy and a polyester matrix composite. The unsaturated polyester system did not show an interface between the fibre and the matrix, whereas the interface in the epoxy system was approximately 2.5 μm thick. The polyester composite exhibited essentially complete curing both near the fibre and in the bulk composite, whereas the epoxy composite had incomplete curing in the region near the fibre, but essentially complete curing in the bulk. Those results imply that incomplete curing of the matrix in the vicinity of the fibre caused the interface in the epoxy composite to form.

Atomic force microscopy (AFM) is a high-resolution type of scanning probe microscopy. It can be used to detect variations in the elasticity and adhesion of specimens and provide atomic and subnanometer resolutions in ambient conditions [92]. Scanning probe microscopy (SPM) works in a comparable way to AFM, although a key difference is that it uses an alternative sensing method. Li et al. [93] used scanning probe microscopy combined with modulus mapping to determine that the thickness of the interface in a carbon/epoxy composite ranged from 80 to 270 nm depending on whether the carbon fibres were desized or sized, respectively. Those results suggested that the sizing agent strongly controlled the interface thickness. Similarly, nanoscratch tests indicated that the interface was 70 to 150 nm thick in the sized composite. Following that, Gu et al. [94] used nanoscale dynamic mechanical analysis (nanoDMA) on a carbon/epoxy composite to examine how the storage modulus of the epoxy resin varied nearby the carbon fibre reinforcements. With that, the interface thickness was determined to be irregular and approximately 100 nm wide (118 nm in a T300 carbon fibre/epoxy composite and 163 nm in a T700 carbon fibre/bismaleimide composite). Like Li et al. [93] and Gu et al. [94], Qing et al. [95] also investigated the thickness of interfaces in a carbon/epoxy composite. In that work, Qing et al. [95] used transmission electron microscopy to inspect a carbon/epoxy composite, which revealed that interfaces within it were about 200 nm thick. That thickness is similar to the aforementioned interface measurements completed by Li et al. [93] and Gu et al. [94], even though each group of researchers utilised a different interface measurement technique, and the fibres in each of their experiments may have been treated with a different sizing formulation.

Gao and Mäder [96] characterised interface hardness in glass/PPm (modified polypropylene) composites and γ -APS/PU-epoxy composites. The fibres were sized using a saline coupling agent, γ -APS (γ -aminopropyltriethoxysilane), in conjunction with PP or PU (polyurethane) film formers. The interface with γ -APS/PU sizing was much softer than the PPm matrix, whereas the interface with the γ -APS/PP sizing was slightly harder than the matrix.

Molazemhosseini et al. [97] studied carbon/PEEK (Polyether ether ketone) composites reinforced with short carbon fibres and nano-silica by using nanoindentation and nanoscratch tests. The addition of short carbon fibres into PEEK resulted in a remarkable improvement in the reduced elastic modulus and hardness of the polymer (143% increase in reduced elastic modulus). Moreover, the addition of 2 wt.% nano-SiO₂ particles to the carbon/PEEK composite improved the reduced elastic modulus and hardness even further (i.e. additional 44% increase in the reduced elastic modulus, and 21% increase in hardness). Those results were supported

by past research on the mechanical properties of hybrid composites reinforced with carbon fibres and nanoparticles [98, 99]. After the nanoindentation and nanoscratch tests were completed, Molazemhosseini et al. [97] concluded that interfaces were stiffer at locations close to the fibres. Also, the hard interface formed by inter-diffusion and chemical bonding between fibre surfaces and the matrix. Moreover, Molazemhosseini et al. [97] estimated that the average thickness of the interface in the carbon/PEEK composite, reinforced with short carbon fibres and nanoparticles, was $1.7\ \mu\text{m}$.

Wu et al. [100] used transmission electron microscopy (TEM) to observe that the fibre cortex of a carbon-epoxy composite contained well-aligned graphite crystallites and fibrils along the fibre axis. The microstructure exhibited a gradual variation from an essentially amorphous structure to nanocrystalline from the matrix to the fibre. Likewise, electron energy loss spectroscopy revealed that the microstructure also had a chemistry gradient. Specifically, a gradual decrease in the ratio of oxygen to carbon from the matrix to the fibre was observed. Furthermore, phase-contrast in bright-field transmission electron microscopy imaging was used to observe and estimate the thickness of the interface. With consideration of the roughness of the fibres, incomplete uniform distribution of the sizing agent (the sizing agent was essentially glycerol ether epoxy), and mutual diffusion between the components, the thickness of the interphase was estimated to be 200 nm.

Nonetheless, the thickness and chemical composition of an interface can change over time due to a range of factors. For example, the rate at which the matrix or size cures. Or the depletion/introduction of chemical substances such as sizing or plasticisers to the interface. That could occur due to the environmental conditions to which the composite is subjected.

Figure 2.20 presents an interpretation of both of those concepts of interface morphology, as well as the descriptions of interfaces that were provided in this chapter, in a single diagram.

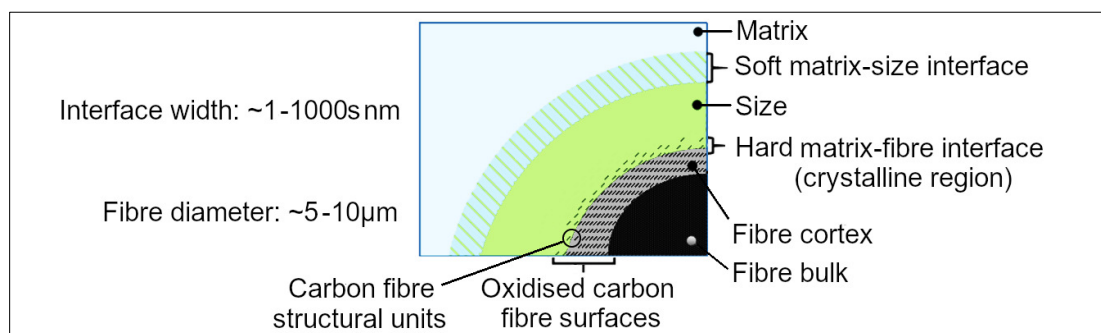


Figure 2.20 Diagram of components in a carbon fibre-reinforced polymer composite

2.4.7 Viscoelastic behaviour of interfaces

Viscoelasticity is the property of materials that demonstrate both elastic and viscous behaviour when undergoing deformation. When stress is applied to a viscoelastic material, it will undergo an immediate elastic strain followed by a time-dependent, viscous strain. Accordingly, viscoelastic materials have characteristics of both the solid phase and the liquid phase [101].

Therefore, consideration of the viscoelastic behaviour of interfaces is valuable for the design of experimental tests in which interfaces are subjected to an applied load. For example, during fibre push-out tests, an indenter is used to apply a load at a given rate to a fibre in a composite, so that the interface surrounding that fibre will fail under shear stress. Table 2.6 states indenter displacement rates that various research groups have used to conduct fibre push-out tests on glass/epoxy and carbon/epoxy composites.

Research group	Composite type	Indenter displacement rate
Li et al. [102]	Carbon/epoxy	0.05 $\mu\text{m/s}$
Ma et al. [103]	Carbon/epoxy	0.20 $\mu\text{m/s}$
Rodríguez et al. [104]	Carbon/epoxy	0.01 $\mu\text{m/s}$
Medina et al. [11]	Glass/epoxy	0.05 $\mu\text{m/s}$
Möder et al. [105]	Glass/epoxy	0.70 $\mu\text{m/s}$ (approximately)

Table 2.6 Indenter displacement rates which external research groups have used when analysing polymer composites through push-out tests

As discussed in Chapter 2.4.1 of this thesis, thermoplastic and thermosetting plastics have considerably different thermal, chemical, and mechanical characteristics. However, although information regarding the behaviour of interfaces in thermoplastic composites was sought after during the writing of this literature review, most of the scientific reports that were found focused on thermoset composites. Reports on the behaviour of interfaces in thermoset composites, and especially epoxy-based thermoset composites, were relatively widespread. No reports about the viscoelastic behaviour of interfaces in thermoplastic composites under different strain rates were found. That is even though there is an increasing demand for thermoplastic composite pipes in the oil and gas industry.

A pipe will deform at an increasing rate as it collapses under hydrostatic pressure [40]. Also, immediately before it collapses, the materials that it is made from will soften [39]. Those phenomena are thought to affect the viscoelasticity of interfaces in thermoplastic flexible pipes; however, literature regarding the viscoelasticity of interfaces in thermoplastic composites is scarce at best. Therefore, the completion of research into those matters has considerable potential to support the advancement of polymer composite materials and flexible pipe infrastructure, which is an objective of the present work.

2.4.8 Properties of engineered fibres

Almost all high-strength and high-stiffness materials fail under overwhelming stress because of the propagation of flaws through their structure [106]. A fibre of a material is stronger than the same material in bulk form because the narrow diameter of the fibre limits the size of its flaws. Glass, carbon, and aramid fibres are some of the most widely utilised fibres in the composite layer of flexible pipes. Aramid fibres are sometimes used to reinforce risers, but their low compressive strength and high susceptibility to moisture, in comparison with carbon fibres and glass fibres, limits their applications for that purpose [107]. Aramid fibres have remarkable impact resistance. For example, Kevlar® is an aramid fibre that is well renowned for being used to make ballistic armour, such as bulletproof vests [108]. Along with safety requirements, the ideal type of fibre for use in a flexible pipe is often contingent on the strength, stiffness, corrosion resistance, and cost of the fibre [109]. Glass fibres are the least expensive type of advanced fibre, followed by aramid fibres, carbon fibres are more expensive than both glass and aramid fibres [110]. Over 90% of engineered composites are reinforced with glass fibres. Carbon fibres only make up about 0.6% of the market, yet they account for around 12% of the composites market value [27]. Those metrics highlight the importance of evaluating composites that are based on carbon fibres and glass fibres.

Structure and characteristics of carbon fibres

Carbon fibres out-perform the strength and stiffness of glass fibres. They are often preferred for use in flexible pipes that are destined for deepwater oil and gas operations because they possess outstanding strength, plus excellent resistance to high temperatures, solvents, and fluids. Also, carbon fibre reinforced polymer composites are used to construct high-performance marine infrastructure such as hulls for ultralight and luxury yachts, as well as steering wheels for sailing teams.

Carbon fibres are at least 92% carbon and can be amorphous, crystalline, or partly crystalline [111]. The carbon atoms in carbon fibre are bonded together in crystals that are aligned in parallel to the longitudinal axis of the fibre. That crystal alignment gives carbon fibre an exceptionally high strength-to-weight ratio [112].

Highly graphitic fibres are known as graphite fibres. Most commercially produced carbon fibres are manufactured from polyacrylonitrile (PAN), others are made from rayon or petroleum pitch. Pitch based carbon fibres can attain a higher modulus than PAN based carbon fibres because pitch is more graphitisable than PAN [113]. Pitch is a viscoelastic substance that is produced by the distillation of carbon-based materials such as crude oil, coal and plants. Carbon fibre consists of wrinkled and distorted sheets of graphite, as illustrated in Figure 2.21. Graphene consists of carbon atoms that are arranged like a honeycomb lattice. Thus, graphite can be thought of as a stack of graphene layers, as shown in Figure 2.22.

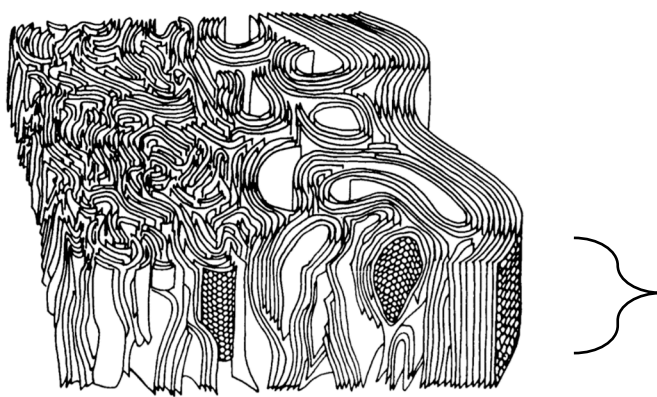


Figure 2.21 Illustration of a cross-section of carbon fibre

[114]

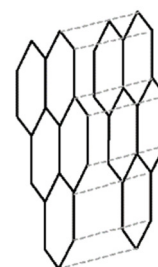


Figure 2.22

Illustration of graphite

There are several grades of carbon fibres, and those grades are usually categorised according to the fibre modulus. Pitch-based carbon fibres that have ultrahigh modulus (exceeding 900 GPa) and ultrahigh strength (exceeding 6 GPa) are commercially available [115]. The strongest carbon fibres are ten times stronger than steel and five times lighter [116]. Table 2.7 states the mechanical properties and density of representative high strength and high modulus carbon fibres.

Carbon fibre type	Density (g/cm ³)	Tensile strength (GPa)	Modulus of elasticity (GPa)	Ductility (%)
High strength	1.5	5.7	280	2.0
High modulus	1.5	1.9	530	0.36

Table 2.7 Representative physical properties of two grades of carbon fibre [113]

Carbon fibre costs more than glass fibre, and flexible risers are rising in size and weight to meet increasing demands for subsea production from deepwater wells. Risers frequently experience large top tensions due to the long length of pipe supported. Thus, the option to convert from using glass fibres to carbon fibres in flexible risers is attractive because of the light weight and high tensile strength of carbon fibres, despite the higher capital cost of carbon fibre.

Structure and characteristics of glass fibres

Glass fibres are the most common type of fibre used to reinforce plastics [117]. Glass fibres are made by extruding molten glass through metal dies that have narrow diameter holes and then drawing the fibres into filaments which have a diameter in the range of 3 μm to 30 μm .

E-glass (also called electrical glass) is an alumino-borosilicate based glass that has low electrical conductivity [118]. It is a very popular reinforcement for plastics due to its low cost compared to carbon fibres, and its superior electrical insulation properties (carbon fibres are electrically conductive) [119]. However, glass fibres are denser than carbon fibres. Consequently, glass fibre-reinforced plastic pipes are less expensive but heavier than similar pipes which are based on carbon fibre-reinforced plastic.

Glass fibres are based on silica (SiO_2) and typically contain added oxides of calcium, sodium, boron, iron and aluminium. In general, E-glass consists of, by weight percent; 54% SiO_2 , 14% Al_2O_3 , 22% $\text{CaO} + \text{MgO}$, 10% B_2O_3 and less than 2% $\text{Na}_2\text{O} + \text{K}_2\text{O}$ [120] although other compositions are available.

S-glass (S for 'silica') fibres are made from the same constituents as E-glass, but with a difference in the weight percent of the constituents [121]. For instance, S-glass has a greater percentage by weight of silica oxide, aluminium oxide and magnesium oxide than E-glass. Accordingly, the letter S in S-glass is regarded as being representative of its higher silica content [52]. S-glass is more expensive than E-glass, but it is also 40 to 70% stronger than E-glass [122]. Additionally, S-glass has a higher fatigue strength and keeps its strength at greater temperatures compared to E-glass. S-glass is used when high modulus and tensile strength are important requirements; accordingly, it is typically used to fabricate composites that are required for use as infrastructure in buildings and aircraft. Both grades of glass fibre are used to construct flexible pipes.

Glass fibre	Density (g/cm^3)	Tensile strength (GPa)	Young's Modulus (GPa)	Ductility (%)	Melting point ($^{\circ}\text{C}$)
E -glass	2.55	3.4	72.4	4.7	<1725
S-Glass	2.50	4.5	86.9	5.2	<1725

Table 2.8 Representative physical and thermal properties of E-glass and S-glass

Carbon fibres are used to reinforce plastics in flexible pipes when strength and stiffness are critical requirements, such as in extreme pressure applications. Although glass fibres are not as rigid as carbon fibres, glass fibres are less brittle when used in composites and far less expensive. Nonetheless, if pipe flexibility and resistance to high pressures are both necessary, carbon and glass fibres can be combined to fabricate a glass-carbon hybrid composite pipe [123, 124]. As another example, glass fibres are susceptible to corrosion and stress corrosion cracking in high-temperature water [125, 126]. In contrast, carbon fibres are inert to water and dilute acids. However, carbon-glass hybrid composites can be combined to fabricate a pipeline that has more resistance to stress corrosion than a similar pipeline that is made from a glass fibre-reinforced plastic alone [127].

2.4.9 Influence of fibre arrangements in matrices

The way that fibres are arranged in a composite can affect the amount of external load that the composite can withstand before failure and its failure mechanism under that load. For instance, the composite may fail through fibre kinking, matrix splitting, or matrix crushing.

Composites that are reinforced with particulates or short fibres of a discontinuous random orientation are typically used in situations where cost is a foremost concern. Discontinuous aligned and continuous fibre composites are used where greater strength and stiffness are required despite the higher cost of those fibres [49]. Figure 2.23 illustrates those fibre arrangements.

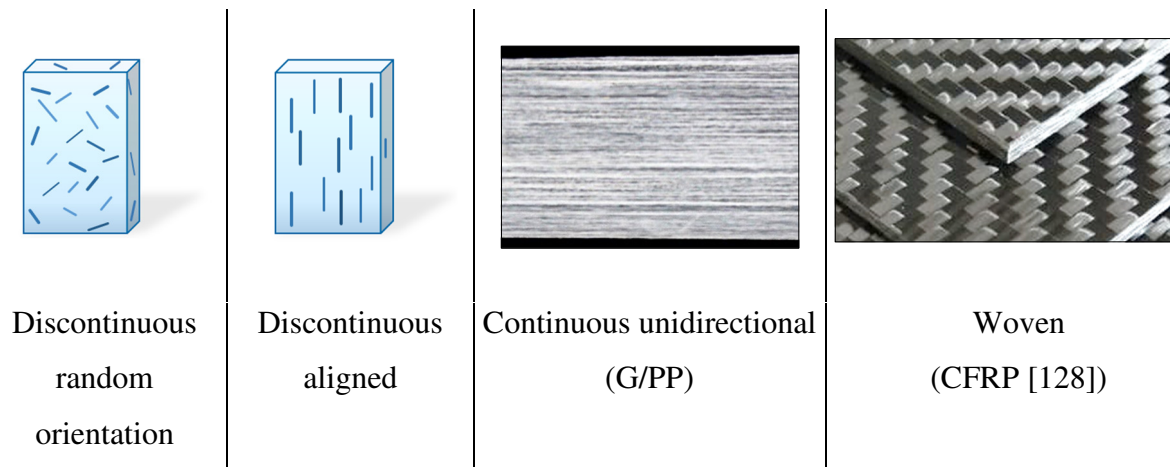


Figure 2.23 Common fibre arrangements used in engineered composites

A material is isotropic if its mechanical properties are identical in every direction. Accordingly, the strength, stress, strain, hardness, and Young's modulus characteristics of an isotropic material will be the same when a given load is applied to the material at any point in its x, y or z-axis. Most metals, glasses, and polymers are isotropic materials. In contrast, the properties of anisotropic materials differ in alternative directions. For example, unidirectional composites, such as those used in flexible pipes, have anisotropic mechanical properties due to the orientation of the embedded fibres. Because of that, a load that is applied to a flexible pipeline at an off-axis angle can lead to significant reductions in its stiffness and strength, such that its strength perpendicular to the fibre direction is several times lower than its strength parallel to the fibre direction [129].

Orthotropic materials are a subcategory of anisotropic materials. Orthotropic materials have at least two orthogonal (perpendicular) planes of symmetry. When a load is applied to an orthotropic composite laminate, each ply within it will experience a different magnitude of

stress depending on its geometry and composition [130]. Most composite materials that are used to reinforce flexible pipes are in the form of quasi-isotropic laminates. The laminate is made up of a number of composite tapes (lamina) which are stacked on top of each other at various angles, typically 0° , 90° , $+45^\circ$, and -45° . The orientation of the plies is balanced so that the stiffness of the laminate, i.e. the reinforcement layer of the pipeline, is identical in each in-plane direction. Figures 2.23 and 2.24 illustrate composite laminates which contain continuous unidirectional fibres in lamina that are oriented in specific directions to enhance the strength of the composite in the primary load directions.

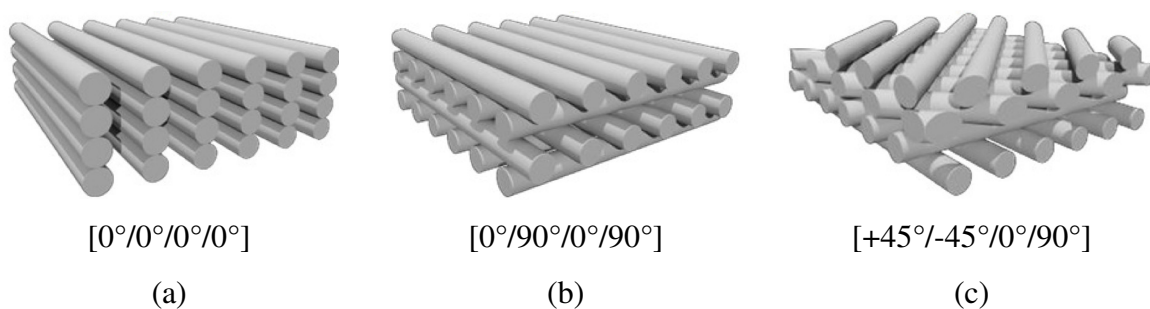


Figure 2.24 Continuous unidirectional fibres in laminates, oriented in various directions [131]

Where (a) = Unidirectional lamina layup

(b) = Orthotropic lamina layup

(c) = Quasi-isotropic lamina layup

Composites are frequently cited as being stronger than steel; for instance, graphite/epoxy composites are approximately five times stronger than steel on a weight-for-weight basis [52]. However, the strength and stiffness of an anisotropic or quasi-isotropic composite can differ depending on the direction from which load is applied to it. For example, the in-plane modulus of a quasi-isotropic GFRP composite can be an order of magnitude lower than steel [132]. Quasi-isotropic laminates demonstrate isotropic properties under in-plane extension at the laminate level, but only in-plane. Advantageously, fibre-reinforced composites can be tailored so that their strength and modulus coincides with the direction of an applied load. The majority of unidirectional composites fail under hydrostatic compression in the shear mode [41, 42]. Therefore, it is crucial to understand how the interface within those materials behaves under shear stress.

2.4.10 Properties of solvents, pentane and toluene

In this work, a 50/50 pentane/toluene solution was selected to represent oil and used to age specimens for several reasons. Firstly, pentane and toluene are found naturally in crude oil and natural gas. Additionally, they are a significant component of many fuels [133]. Because flexible composite pipes carry those fluids, it is vital to recognise their impact on the composite materials from which the pipes are made. Secondly, polyamide 12 is resistant to pentane and toluene, whereas polypropylene is susceptible to those solvents. Those polymers have notably different susceptibilities to pentane/toluene solutions. Therefore, it is beneficial to compare how the micromechanical strength of composites that are based on those polymers changes as they are aged in pentane/toluene. Hence, primary experimental research on that topic was completed in the present work, with G/PP and C/PA12 selected as the composite materials of investigation. Lastly, toluene and pentane are inexpensive and common organic solvents [134] that have been used as laboratory solvents in a broad range of experiments on polymers [135-137]. Thus, they are readily available for use in experiments by a wide array of researchers. The next two sections of this chapter focus on the thermal and chemical properties of toluene and pentane, respectively.

Thermal and chemical properties of toluene

Toluene is also known as toluol, methylbenzene, methyl benzol and phenyl methane. It is a toxic, highly-flammable, colourless, non-polar aromatic hydrocarbon that is a derivative of benzene, and it has a benzene-like odour (sweet and pungent odour).

Hydrocarbons are either aliphatic or aromatic compounds. The molecular structure of an aromatic hydrocarbon is characterised by one or more planar rings of atoms that are connected by covalent bonds of two distinct kinds. Accordingly, toluene is an aromatic hydrocarbon. In contrast, pentane is an aliphatic compound. An aliphatic compound is a hydrocarbon which contains carbon and hydrogen atoms that are bound together in straight chains, branched chains, or non-aromatic rings.

Toluene is a liquid at room temperature, insoluble in water, and naturally present at low levels in crude oil. In line with that, it is a product of oil-refining processes. Its molecular structure consists of a CH_3 group which is attached to a phenyl group (see Figure 2.25). Accordingly, its systematic IUPAC name is methylbenzene. Toluene is used in the synthesis of trinitrotoluene (TNT), benzoic acid, dyes, and saccharin. It is also used in aviation and automotive fuels, as a solvent and as an industrial feedstock. As an industrial feedstock, toluene

is used as an additive during the production of gasoline to improve fuel octane ratings, also to synthesize other fuels from crude oil. Octane ratings are measures of fuel stability. The higher the octane number of a fuel, the more compression it can withstand before undergoing spontaneous combustion (auto-ignition). The use of gasoline with a low octane number may lead to the problem of uncontrolled secondary combustion in an engine, which can reduce fuel efficiency and damage the engine over time [138].

As a solvent, toluene is used for the manufacture of various compounds, including paint thinners, adhesives (glues) and printing ink [139]. Polyamides are either not affected or slightly affected by toluene at room temperature [140]. In line with that, polyamide 12 is resistant to toluene at 25°C [141].

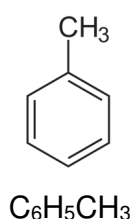


Figure 2.25 Molecular structure of toluene

Chemical formula	$\text{C}_6\text{H}_5\text{CH}_3$	
Molecular weight	92.138 g/mol	
Melting point	-94.9°C	
Boiling point	110.6°C	
Vapour pressure	0.0038 MPa	(at 25°C)
Solubility in water,	0.526 mg/ml	(at 25°C)
Specific Gravity (liquid)	0.87	(relative to water)

Table 2.9 Thermal and chemical properties of toluene [142]

Thermal and chemical properties of pentane

Pentane is a constituent of natural gas and crude oil [143]. It has a mild gasoline-like odour, is a colourless liquid at room temperature, and is miscible with toluene. Pentane is also an aliphatic hydrocarbon with three structural isomers. N-pentane is the unbranched isomer, whereas isopentane (2-methylbutane) and neopentane (2,2-dimethylpropane) are branched isomers. The branched isomers are more stable than n-pentane, as they have a lower heat of formation and heat of combustion.

Alkanes have the general formula C_nH_{2n+2} . Accordingly, pentane has the formula C_5H_{12} [144]. Pentane can be burnt for use as a fuel, and it is used as a speciality non-polar solvent in some laboratories. For instance, it is utilised as a solvent for wax and high-molecular-weight organic compounds such as greases [145]. As a solvent, pentane can be conveniently evaporated at a very high rate because it has one of the lowest boiling points among hydrocarbon liquids (36.06°C). Additionally, pentane is frequently used as a blowing agent for the production of polystyrene and polyurethane foams, as reaction media for polymerisation processes, and as an aerosol propellant.

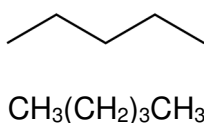


Figure 2.26 Molecular structure of n-pentane

Chemical formula	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	
Molecular Weight	72.151 g/mol	
Melting point	-129.7°C	
Boiling point	36.06°C	
Solubility in water	0.038 mg/ml	(at 25°C)
Vapour pressure	0.0685 MPa	(at 25°C)
Specific Gravity (liquid)	0.63	(relative to water)

Table 2.10 Thermal and chemical properties of pentane [146, 147]

2.4.11 Conclusions

Composite manufacturers use a range of methods to engineer tailored fibre-matrix interfaces in composites so that the end product has enhanced mechanical properties. Those interfaces can be produced through various mechanisms, including mechanical interlocking, electrostatic attraction and van der Waals forces [81-83]. Interfaces may also form by a chemical reaction directly between the matrix and fibres, or by chemical bonding between a fibre, size and matrix [88, 89, 148]. It is common for composite manufacturers to add sizing to fibres to protect the fibres against abrasion and fracture as they are processed, wet the fibres well, produce composites that contain a low volume of voids, and provide optimum stress transfer through

interfaces [148]. Those methods of composite fabrication, as well as the environmental climate that a composite is exposed to, can influence the thickness of fibre-matrix interfaces. The thickness of interfaces in polymer composites is commonly in the range of one to thousands of nanometres. Commercially produced glass fibre and carbon fibre reinforced polymer composites are widespread, whereas carbonaceous, ceramic and metal matrix composites tend to be used for relatively niche applications.

For example, G/PP and C/PA12 composites are commonly used to reinforce flexible pipes. Also, pentane and toluene are naturally present in crude oil and natural gas. Therefore, fundamental properties of those materials and fluids were detailed in this chapter, and they were used to conduct experiments in the present work.

2.5 Ageing processes that affect polymer composites

It is particularly challenging to inspect pipes which are located in deepwater, yet the intense hydrostatic pressures present at those depths make pipe failures more likely. Forecasting how the strength and condition of a flexible pipe will change decades in advance is often complicated as well. That is because the polymers on which the pipes are based can gradually age and degrade due to their interaction with production fluids, elevated temperatures, fatigue, and plasticisation (due to moisture absorption). The rate at which polymers age can be accelerated by a wide variety of variables, including elevated temperatures, alternating stresses, harsh chemicals, and ultraviolet rays. The consequences of ageing can include strength reduction, embrittlement, softening, and colour change of the material.

In general, the variables which cause polymers to degrade at an accelerated rate can be divided into categories. In this chapter, those variables are categorised as thermal, mechanical and chemical. Nonetheless, there is considerable overlap between the categories because they can have a synergistic impact on the ageing process. For instance, researchers have investigated the condition of polymeric materials which have aged due to thermomechanical degradation [149], thermochemical degradation [150], and mechanochemistry [125]. Likewise, flexible pipelines are often used in HPHT environments wherein they are constantly subjected to a combination of elevated temperatures, high hydrostatic pressures, alternating stresses, and contact with production fluids. Therefore, it is useful to acknowledge how those variables act in cooperation as they damage composite materials

2.5.1 Thermal ageing processes

Thermal stress, thermal cycling and annealing

Thermal stress can age a composite, potentially causing it to crack or even break [71]. In general, the greater the temperature change of a material, the higher the level of thermal stress that it will experience. Thermal expansion describes the fractional change in the size of a material in response to a change in temperature. That includes a change in its length, area, and volume.

The linear coefficient of thermal expansion, α_L , of a material is equivalent to the relative expansion of that material, ΔL , divided by its change in temperature, ΔT . Also, it varies with temperature [151] (Equation 2.1).

$$\alpha_L = \frac{1}{L_0} \left(\frac{\Delta L}{\Delta T} \right) \quad 2.1$$

Where α_L is the linear coefficient of thermal expansion, L_0 is the initial specimen length, ΔL is the relative expansion of the material, and ΔT is the change in temperature of the material.

Thermal cycling can induce micro-cracks in laminates, and crack growth may be accelerated in oxidative environments. For example, Lafarie-Frenot and Rouquie [152] completed thermal cycling tests on carbon/epoxy laminates in an oxidative atmosphere and saw a coupling effect between oxidation and matrix cracking which accelerated the rate of degradation. Thermal stress is highly dependent on the thermal expansion coefficient of a material. Singh and Wang [153] investigated the response of monolithic ceramics and ceramic composites to thermal shock by using a water quench technique.

Ceramics have a high degree of brittleness, high Young's modulus of elasticity, and low thermal conductivity. That renders them highly susceptible to failure under severe thermal transient conditions of decreasing temperature (e.g. during a quench test)

Singh and Wang [153] found that the ceramic composites had better resistance to thermal shock damage than the monolithic ceramics. Catastrophic failure due to severe thermal stresses was avoided in the composites, and a substantial portion of their initial strength was retained. Significant reasons for those outcomes are that; dissimilar properties of fibres and matrices introduced additional thermal stresses during thermal transients, the fibre-matrix

interfaces influenced how stress was transferred, and the fibre reinforcements changed fracture initiation and crack propagation behaviour [153].

Pipelines that are used for chemical or oil and gas production can experience thermal cycling during operation startup or shutdown. That may cause microcracks to form and accumulate in flexible pipes due to residual stresses [74, 154, 155]. However, there is a lack of detailed information regarding how thermal transients or thermal cycling affects the shear strength and shear failure behaviour of interfaces in thermoplastic composites. Therefore, this thesis reports the outcomes of original experiments in which the shear strength of interfaces in thermoplastic composites, G/PP and C/PA12, was tested over a range of elevated temperatures.

Effects of annealing on the crystallinity and mechanical properties of polyamides

In 1942, Brill [156] reported that nylon-66 (Polyamide 66) shows a reversible polymorphic phase transition, from the triclinic α phase structure to a pseudohexagonal crystal structure, at 162°C. That type of crystal-crystal transition became known as a Brill transition. Even though the transition is sharp, it follows gradual crystallographic changes, which take place over a relatively broad temperature range [129]. The transition can be monitored by using wide-angle X-ray diffraction (WAXD) performed as a function of temperature because changes in the diffraction pattern occur as the Brill transition progresses.

Pepin et al. [157] studied the thermal stability of crystal polymorphs in polyamide 11 by using in-situ wide-angle x-ray scattering (WAXS) and differential scanning calorimetry analysis (DSC). Specifically, they studied PA11- α , PA11- α' , and PA11- δ' . Those phases are attained from different preparation methods: the α phase is produced from solution casting using m-cresol, the α' form is attained from slow cooling the melt or annealing quenched samples, and the smectic phase, δ' , is produced by quenching the melt. The α' and δ' forms of PA11 undergo a Brill transition at approximately 100°C, which is far below the melting point of PA11 (180°C to 189°C, depending on the grade).

Hence, if PA11 is exposed to an elevated temperature, even a temperature well below its melting point, that heat can permanently affect its crystallinity and mechanical behaviour. Nonetheless, it is unclear how long-term exposure to elevated temperatures will affect the interfacial shear strength of polyamide-based composites, which is a key motivation of the present work.

2.5.2 Mechanical ageing processes

Mechanical ageing is irreversible and typically exhibited by matrix cracking, delamination, or fibre breakage in polymer composites. It can be caused by stresses including compression, tension, bending, torsion, or by a combination of physical and chemical means (such as stress-corrosion cracking). Stress-corrosion cracking is initiated at a flaw in a glass fibre; the crack grows under stress which can eventually cause the fibre to break. Khennane and Melchers [71] noted that stress-corrosion cracking can be exacerbated by matrix swelling, which occurs when a composite absorbs moisture.

Risers that are connected to an offshore vessel or a rig must resist fatigue damage and stresses caused by motions of the sea-level facility. Such as heave motions (linear vertical motions), sway (linear horizontal motions), offset which causes high bending moments, plus wave and current forces that will cause tension variations and alternating stresses [158]. Fatigue can also be caused by operation startup, shutdown, and vortex-induced vibrations that are triggered by vortex shedding [159]. In fluid dynamics, vortex shedding is an oscillating flow that occurs when a fluid or gas flows past a bluff (in contrast to a streamlined body) at specific velocities, depending on the size and shape of the body.

Moisture absorption under hydrostatic pressure

Several authors have provided suggestions regarding what happens to the strength of fibre-matrix interfaces in polymer composites that are subjected to a high hydrostatic pressure [160, 161]. Common propositions are that the pressure will drive moisture into the composite (damaging interfaces) or reduce the volume of microvoids within the composite (improving interfaces).

Avena and Bunsell [162] immersed glass/epoxy composites in water at hydrostatic pressures ranging from atmospheric pressure up to 20 MPa. Those materials showed no change in stiffness as a function of pressure, although their failure stress upon bending lowered. Conversely, Tucker and Brown [161] studied graphite fibre-reinforced vinyl ester composites by immersing them in seawater, which was pressurised to a depth equivalent to 610 m of seawater (approximately 6.3 MPa). The samples that were subjected to that pressure had a 15% reduction in flexure strength and stiffness. Avena and Bunsell [162] predicted that high pressures would, if anything, benefit the integrity of composites by closing defects at interfaces. In contrast, Tucker and Brown [161] predicted that higher pressures would promote damage at interfaces by driving capillary flow along the interfaces.

Humeau et al. [163] hydrothermally aged glass/epoxy composites for 50 days in an oven at 60°C with and without 25 MPa of hydrostatic pressure. Like Avena and Bunsell [162], Humeau et al. [163] found that the added pressure did not affect the flexure strength of the composites. Noting that bend tests are “quite sensitive” to interface properties [163]. Humeau et al. [163] also postulated that ageing at the higher pressure did not affect the strength of interfaces in their specimens either. However, that is not in line with the prediction that higher pressures will tend to drive capillary flow along interfaces, through cracks and into voids, which will promote damage [161]. It also differs from the findings of Shin and Pae [164]. Shin and Pae [164] analysed the shear stress-strain behaviour of graphite/epoxy composites and epoxy under torsional loading. That was done at pressures ranging from atmospheric pressure, up to 600 MPa of hydrostatic pressure, in 100 MPa increments. They concluded that the interfacial strength and, the interlaminar strength of the composite increased as the pressure was raised. They also saw that as the hydrostatic pressure was raised, the fracture surfaces of the samples which were tested a high pressure (500 MPa) featured more resin adhered to the surface of exposed fibres. Also, more plastic deformation occurred in the matrix of the epoxy resin. which indicated that the shear strength of the interface increased.

In short, some of the available literature suggests that when a composite is immersed in a liquid, such as water, high hydrostatic pressures may enhance moisture sorption by driving moisture into the composite, which will damage interfaces [161]. In contrast, other publications suggest that high pressures will strengthen interfaces by closing defects at interfaces [160]. Humeau et al. [163] found that 25 MPa of hydrostatic pressure did not affect the flexure strength of aged glass/epoxy composites. Whereas Shin and Pae [164] examined graphite/epoxy composites at pressures that reached up to 600 MPa of hydrostatic pressure and concluded that interfacial strength between the fibres and the resin increases as hydrostatic pressure is raised. Overall, there have been contrasting conclusions drawn regarding what happens to the volume voids and the integrity of interfaces in polymer composites that are under high hydrostatic pressure.

2.5.3 Chemical ageing processes

Chemical ageing in polymers regards the irreversible modification of polymer chains through mechanisms such as hydrolysis, oxidation, molecular chain splitting, and the crosslinking of molecular chains. Thermal stress, chemicals, and ionising radiation (such as ultraviolet radiation or gamma radiation) can break long polymer chains. The resultant shorter chains may,

or may not, react with each other causing the molecular weight of the polymer to change [165]. That can affect the thermal, chemical, and mechanical characteristics of polymers. Some of the ways that can manifest are through a change in the ductility, resistance to fatigue, and temperature resistance of the polymer. Also, corrosion and cracking can occur in the fibre [71, 166]. Wright [167] wrote a book entitled 'Failure of Plastics and Rubber Products', which includes a case study about chemical ageing. In that case study, a water bottle failed catastrophically after about three months of use. Traces of copper were present in the water that was used to fill the bottle. Copper is known to be a catalyst for the oxidative degradation of natural rubber [168]. Also, natural rubber is commonly used to make hot water bottles. Thus, it was concluded that the failure was caused by copper, causing the water bottle to age at an accelerated rate.

H₂S (hydrogen sulfide) combines with water to form sulfuric acid (H₂SO₄), a strongly corrosive acid that can damage steel pipelines. Corrosion due to H₂SO₄ is often referred to as sour corrosion. Similarly, high concentrations of CO₂ and H₂O in production fluids can cause corrosion of metals in pipes. The intensity and rate of corrosion are dependent on the temperature of the aggressive compounds, their type and concentration (pressure), flow regime, and velocity [169]. Extra precautions in terms of the design and operation of the facility, as well as the safety of staff, are required to develop sour wells due to corrosion, H₂S toxicity and the enhanced sulphur content of the produced oil [170]. As a solution, thermoplastic composite pipes are currently being used in sour service conditions due to their outstanding resistance to corrosion. Using thermoplastic composite pipes as a replacement for steel pipes can eliminate the requirement to store and pump corrosion inhibitors. That can lead to reduced energy requirements, higher production uptimes and reduced operating costs.

Oxidation mechanism

Most polymers are vulnerable to thermo-oxidative ageing [171]. That can occur at elevated temperatures through free radical reactions. The vast majority of polymers contain free radicals due to their history of polymerisation and curing [172]. Bolland [173] proposed an autooxidation mechanism in 1946, which has not been fundamentally revised since that time. Equations 2.2 to 2.6 summarise the mechanism.

Initially, polymer radicals, $P^\bullet$, are formed by scission of the polymer chain. Scott [174] acknowledged that the nature of the initiation process, particularly in commercial polymers, is not well understood. Nonetheless, it is known to be caused by factors such as high temperatures and chemical reactions.

For example, when a polymer is exposed to solar radiation, C-H bonds in the polymer chains can dissociate, leading to the formation of free radicals [110].

Initiation



A polymer radical, $P^\bullet$, reacts with oxygen, O_2 . Producing a polymer-derived peroxy radical, $POO^\bullet$.

Propagation



Once formed, $POO^\bullet$ radicals oxidise polymers by removing hydrogen from another polymer chain, PH. That event produces a hydroperoxide $POOH$ along with another polymer radical $P^\bullet$.

Propagation



Hydroperoxides can dissociate to form various decomposition products such as ketones and aldehydes. The presence of those carbonyl groups can be used as a chemical index for polymer degradation [110]. The $P^\bullet$ radical may interact with oxygen again. Consequently, the chain reaction repeats until termination. For example, by the recombination of two radicals, such as peroxy radicals, producing a non-radical product, $POOP$, and oxygen.

Termination

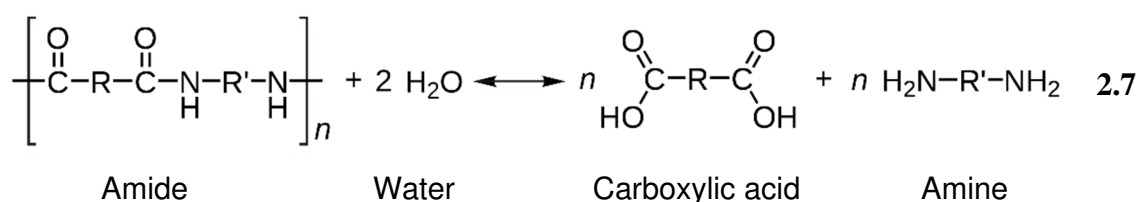


Free radicals cause chain scission reactions to occur in the polymer, reducing its molecular weight. Additionally, each polymer chain produced due to chain scission is a free radical and capable of causing further chain scissions. That continues until the chain reaction terminates when two free radical species react with each other to form a stable, non-radical product. Still, termination reactions are rare events due to the low concentration of radical species and the low probability of free radicals colliding with one another.

Hydrolytic degradation mechanism that affects polymers

Condensation polymers, such as polyamides, are formed by polycondensation [175]. A condensation reaction is a chemical reaction in which two molecules or moieties (functional groups) unite to form a single molecule, with the loss of water or another small molecule, it is the reverse of hydrolysis [176].

Hydrolysis is the reverse of the condensation reaction, and it is the primary ageing mechanism for polyamides in water. Hydrolysable chemical groups include Si-O bonds in silicones [177] and amide groups in polyamides [178]. When polyamides are immersed in water, a chemical equilibrium takes place. In the forward direction, H⁺ or OH⁻ ions in the water break amide bonds within polyamide molecular chains. That produces one monomer with carboxylic acid groups (-COOH) and one with amide groups (-NH₂). It also reduces the molecular weight of the polymer and if enough hydrolysis occurs the molecular weight of the polymer will be reduced to the extent that it dissolves. Equation 2.7 describes that equilibrium:



In the past, researchers have investigated the hydrolytic degradation of polyamides in water [179], oilfield water [180], saltwater [181], natural seawater [182], substitute ocean water [183], under sour and neutral conditions [177], and in acid/water solutions [184], under high hydrostatic pressure (50 MPa) and in deionised water-supercritical CO₂ phase equilibrium [177].

Acidic conditions can accelerate amide hydrolysis. Though, the rate at which hydrolysis accelerates is dependant on the acid concentration. O'Connor [185] explained that in acid

catalysed polyamide reactions, most reactions are accelerated, some acceleration rates reach a maximum, whereas others pass through a maximum before decreasing. Subsequently, Hocker et al. [184] studied acetic, propanoic, and butanoic acids which were mixed with deionised water at a concentration of 1.05×10^{-2} M and saw that those weak small organic acids at low concentrations hydrolysed a polyamide at approximately twice the rate of a water hydrochloric acid solution of the same pH (hydrochloric acid is a strong acid). With that research, Hocker et al. [184] proposed that the rate of hydrolysis was governed by solubility rather than the pH of the water environment.

Meyer et al. [73] studied polyamide 11 (PA11) specimens of different molecular weights ($M_w \approx 15,000$ to $78,000$ g/mol). PA11 at each molecular weight was artificially aged at one of four temperatures, either 90, 105, 120, or 135°C , in a controlled pH 7 water environment. The PA11 specimen of low molecular weight, gained molecular weight with time. Whereas the PA11 specimen of high molecular weight, lost molecular weight with time. Those results suggest that competing recombination and hydrolysis reactions led to the formation of an equilibrium molecular weight. The degradation process approached an equilibrium between molecular chain scission due to hydrolysis and recombination due to polymerisation.

During the writing of this literature review, a far greater proportion of relevant publications regarding polyamide 11 was found compared to relevant publications which focus on polyamide 12. That was even though literature about polyamide 12 was sought after with greater intensity, and both types of polymer are used to construct flexible pipes. Therefore, because of the present information gap concerning the chemical and mechanical characteristics of polyamide 12. It is of interest to study how prolonged exposure to water and oil can alter the interfacial shear strength of polyamide 12 based composites.

Dissolution mechanism that affects polymers

A solvent is usually a liquid, but it can also be a solid, a gas, or a supercritical fluid. The dissolved substance is called the solute. Solvents can dissolve solutes to form a homogenous mixture called a solution. Solubility describes the ability of one compound to be dissolved in another. Miscible substances are capable of mixing in any ratio to form a homogeneous solution. In general, polar solvents dissolve polar compounds well, whereas non-polar solvents dissolve non-polar compounds well. For example, pentane and toluene are non-polar liquids and miscible with each other.

A solubility equilibrium is a type of dynamic equilibrium that results from the opposing and simultaneous processes of dissolution and phase combination (e.g. precipitation). The solubility of a solid or liquid can increase or decrease with a rising temperature, depending on whether the dissolution reaction is exothermic or endothermic. Solids and liquids consist of particles which are held together by inter-particulate bonds, energy is required to break the bonds in the solvent and the solute so that they will combine to form a solution. Hence those processes are endothermic. Conversely, heat energy is released when solute molecules form bonds with the solvent molecules, and that is an exothermic process. Overall, the reaction can be exothermic or endothermic. Whether the reaction is exothermic or endothermic depends on the amount of energy that is used to break bonds within the solute and the solvent, as well as the amount of energy that is released when new bonds are formed between the solute and solvent.

Typically, the solubility of a solid or liquid will not change substantially in response to a change in pressure. However, the solubility of a gas is far more dependent on the pressure of the system. In general, increasing the temperature of a system will accelerate the rate at which dissolution takes place within it by providing energy to break bonds in the solvent. Conversely, nearly all gases become less soluble with the addition of heat, which is a phenomenon that can be rationalised by considering Le Chatlier's principle [186]. Le Chatlier's principle is also called 'The Equilibrium Law', and it states that if one of the variables that describe a dynamic equilibrium is changed (e.g. heat, pressure, or the concentration of a reactant), the equilibrium will shift to counteract the effect of that change.

2.5.4 Conclusions

In contrast to steel pipes, flexible composite pipes have a high strength to weight ratio, low susceptibility to fatigue, plus resistance to corrosion and sour well fluids. Those properties provide flexible pipes with performance and cost-saving advantages. However, elevated temperatures, repetitive stress, and production fluids can gradually degrade polymers. Notorious mechanical and chemical degradation mechanisms have been described in this chapter, although there is little published literature regarding their effects on the shear strength of interfaces in polymer composites. Consequently, there is considerable apprehension to the use of thermoplastic composite pipes in some high-pressure, high-temperature fields. Hence there is a need for scientific research to clarify those matters and enhance the development and adoption of flexible pipes.

2.6 Techniques used to determine interfacial shear strength

Interface shear strength is the standard figure of merit for the characterisation of the mechanical properties of interfaces in flexible pipes [11]. There are several ways that the strength of interfaces in composites can be assessed. In this chapter, five of the most widely used practical methods for characterising the interface surrounding individual fibres are discussed. Subsequently, those methods are evaluated to confirm their suitability for fulfilling the aims and objectives of the present work. Those methods being the push-out test, push-in test, fragmentation test, pull-out test, and microbond test (see Figure 2.27).

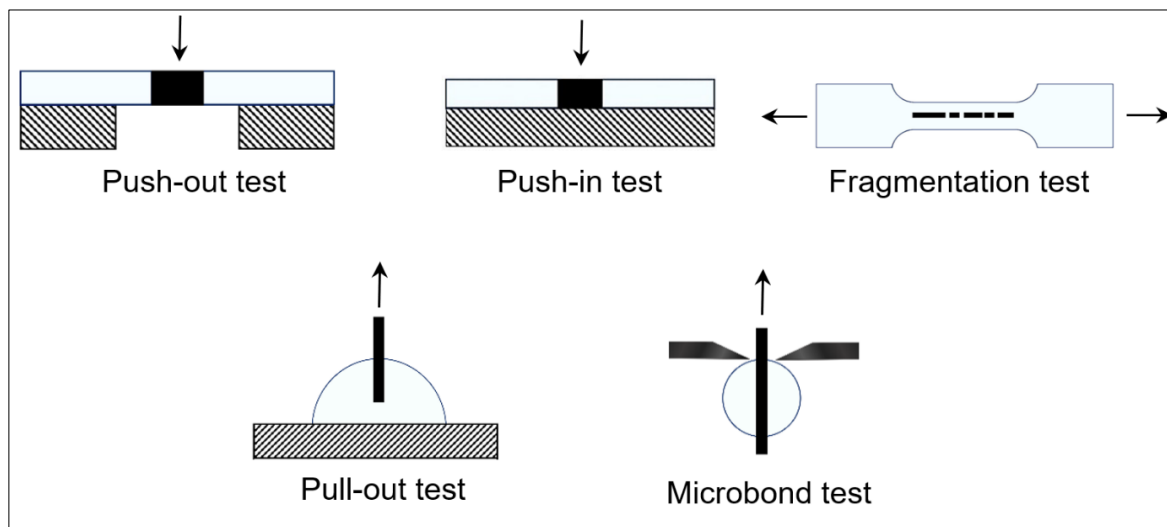


Figure 2.27 Single fibre interface shear strength test methods

In addition to the single fibre interface shear strength test methods illustrated in Figure 2.27, there are others such as the Broutman test, push-through test, nanoscratch test, and the atomic force microscopy (AFM) technique. Those methods have not been reviewed extensively in this chapter because they are less commonly used for investigations which have similar objectives to those of the present work. For example, the Broutman test is more suited to understanding how interfaces debond under transverse tensile stress rather than shear stress. Polymer composites that are subjected to high hydrostatic pressure, such as those present in flexible subsea pipelines, are more likely to fail through the shear mode than the transverse tensile mode. Thus, alternative single fibre interface shear strength tests can provide a stress situation in composites that is more comparable to that typically encountered by flexible pipes in deepwater. Secondly, some alternative methods, such as those based on nanoscratch tests or

AFM, cannot be used to measure the ultimate shear strength of interfaces directly because the interface remains intact during those tests.

2.6.1 Single fibre fragmentation test method

The single fibre fragmentation test is one of the most popular methods used to evaluate the shear strength of fibre-matrix interfaces [2]. This test was developed from pioneering research conducted by Kelly and Tyson [187]. They used the test to investigate the tensile properties of fibre-reinforced metals, copper/tungsten and copper/molybdenum.

To conduct a fragmentation test, a polymer that has a single fibre embedded within it is shaped into a flat dumbbell (see Figure 2.28). Next, the specimen is subjected to a tensile load which is transferred to the fibre through shear forces at the fibre-matrix interface. That causes the fibre to fracture into decreasingly short lengths because the maximum strain of the fibre is lower than that of the matrix. Eventually, the tensile stress applied is not enough to cause the fibre to fracture further [188]. The critical fibre length, l_c , is the shortest length of fibre that will break when stress is applied. If the matrix is transparent fibre breaks can be observed under a light microscope. Alternatively, if the matrix is opaque, it can be ground down and polished, dissolved away or burned off to expose fibre fragments [189].

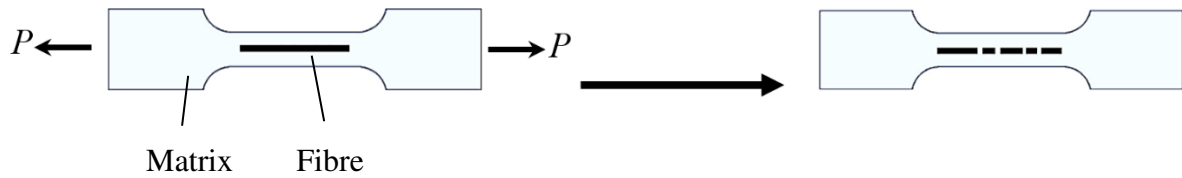


Figure 2.28 Diagram illustrating the single fibre fragmentation test

The average shear stress at the interface, τ_i , can be estimated from the Kelly-Tyson equation (see Equation 2.8) [187, 190].

$$\tau_i = \frac{3}{8} \frac{\sigma_f(l_{sat})d_f}{l_{sat}} \quad 2.8$$

Where τ_i is the shear stress at the interface, $\sigma_f(l_{sat})$ is the strength of a fibre segment which has a length equal to the saturation length, and d_f is the fibre diameter. The saturation length, l_{sat} , is reached when fibre breaks cease during the fragmentation test.

It is worth mentioning that the strength of the fibre was assumed to be deterministic, constant, and absent of fibre length effects in the original Kelly-Tyson [187] model. However, to determine the fibre saturation length, l_{sat} , the fragmentation test must be monitored with the fibre strength measured at progressively decreasing average fragment lengths, followed by extrapolation to the saturation length. Alternatively, the test must be performed on several fibres of different lengths. Both methods would typically need to be followed by extrapolation to the saturation length because that length is often too short to be tested directly.

Schutte et al. [191] studied glass-epoxy composites by using single fibre fragmentation tests. They investigated the influence of thermal and hydrothermal exposure on the average critical length/diameter (l_c/d) ratio of fibre fragments. The l_c/d for the thermally treated samples showed no change, whereas it increased for the hydrothermally treated samples, which indicated that degradation of the interface strength was dominant.

Evaluation of the single fibre fragmentation test method

An advantage of the fragmentation test is that fibres that are embedded within a composite matrix can be observed as they fragment and fail under a tensile load, if the matrix is transparent. That allows further study of composite failure mechanisms. However, a drawback is that Poisson effects can cause misleading interfacial shear strength measurements. Poisson effect is the phenomenon in which a material tends to expand in directions perpendicular to the direction of compression. Thus, during single fibre fragmentation tests, the matrix will contract due to Poisson effects which will increase transverse normal forces on the fibre, which can result in erroneously high interface shear strength measurements [192].

Another drawback is that there must be a significant elastic mismatch between the matrix and the fibre for practical single fibre fragmentation tests. As such, the failure strain of the matrix must be considerably higher (i.e. ideally at least three times higher) than that of the fibre to avoid early failure of the sample [193].

2.6.2 Single fibre pull-out and microbond test methods

Single fibre pull-out tests involve embedding a single fibre in a matrix bead, block or disk. A tensile load is applied to the fibre, and the distance to which it is displaced is recorded as it is pulled in order to determine the load at which it slips. Figure 2.29 illustrates popular ways of conducting single fibre pull-out tests, namely the conventional pull-out test and the microbond test. The microbond test is a type of pull-out test in which a small droplet of resin is cured onto a fibre then one end is pulled to free the fibre. The droplet is restrained by opposing knife-edges while the fibre is pulled through the gap between the knife edges, which causes the matrix to be stripped off [194]. The main difference between the conventional pull-out test and the microbond test methods is that the matrix is in compression in the microbond test (at the knife edges), whereas it is in tension during the pull-out test.

In single fibre pull-out tests, the ultimate tensile load applied to the fibre before interface failure, divided by the embedded area of the fibre, is equal to the interfacial shear strength of the fibre (see Equation 2.11).

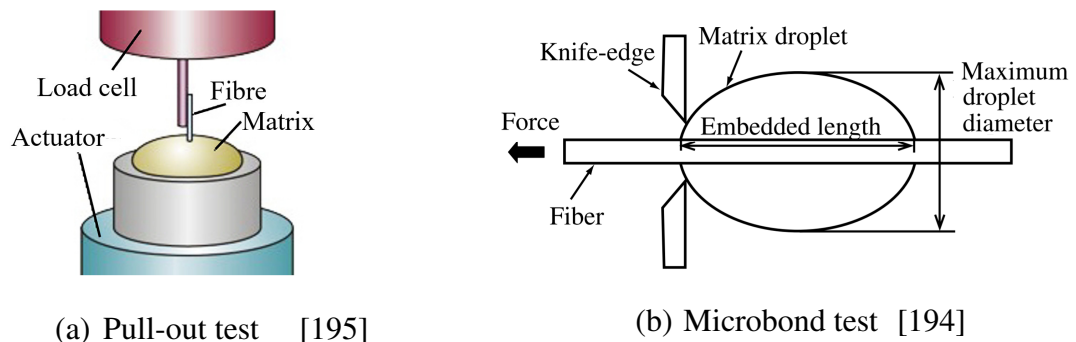


Figure 2.29 Illustrations of single fibre (a) pull-out and (b) microbond test methods

Evaluation of the single fibre pull-out and microbond test methods

In the past, researchers have found that interface shear strength measurements attained from single fibre pull-out tests can differ from measurements attained through other methods. That can be due to how the specimens were prepared for the tests.

For example, Rao et al. [196] made direct comparisons of the fragmentation test and the microbond test for determining interfacial shear strength in a carbon fibre-reinforced diglycidyl ether of bisphenol A (DGEBA) thermoset composite. They noticed that smaller droplets of DGEBA incompletely cured during sample preparation. Because of that, diffusion of the relatively volatile m-PDA curing agent from the droplet at the early stages of cure led to

low values of interfacial shear strength measured from microbond tests when compared with results obtained from fragmentation tests performed on the same composite system.

Still, an advantage of the microbond test is that the embedded fibre length can be determined quickly and accurately. However, past researchers have found it difficult or have been unable to control the exact position of the knife-edge from the embedded fibre during microbond tests [194]. The knife-edge position tends to influence fibre debonding, and matrix cracking which can reach the interface, during the fibre pull-out process and affect the test results. Fortunately, Nishikawa et al. [194] developed a numerical technique which can be used to extract interface properties while excluding the influence of matrix plasticity and cracking during microbond tests.

Nonetheless, other researchers have found that conventional pull-out tests are difficult to perform on narrow and brittle fibres. That is due to the problem of gripping the fibre and pulling it out without premature breakage of the fibre itself, or the matrix in which it is embedded. For example, Rathod [197] found that it was challenging to perform the test on a cementitious composite that used 30 μm diameter polyester fibres as the reinforcement phase.

In contrast, the composites examined in the present work were G/PP which had an average fibre diameter of around 16 μm , as well as C/PA12, which had an average fibre diameter of around 6 μm (see Chapter 3.1.1). Consequently, there are some reasons why analysing those specimens via fibre pull-out and microbond tests would have hindered the fulfilment of the aims and objectives of this present work.

Firstly, the composites studied in this work contained even narrower fibres than those tested by Rathod et al. [197]. That would have made them especially difficult to grip and pull out of the matrix without breaking. Secondly, pull-out and microbond tests typically require composite specimens which have been explicitly fabricated for those tests rather than for commercial use. In this work, composite specimens were extracted from commercially produced flexible pipes, making it infeasible to test them using pull-out and microbond tests. It would have been remarkably complicated, time-consuming, and costly to machine or chemically etch the composites into the form required for pull-out or microbond tests.

Furthermore, single fibre pull-out and microbond tests cannot account for how local fibre density affects the mechanical characteristics of interfaces. That is a drawback because, during the compressive failure of composites under hydrostatic pressure, embedded fibres interact with each other as they break and rotate into a kink band formation (see Chapter 2.3).

2.6.3 Single fibre push-out and push-in test methods

Single fibre push-in test method

The principle of the push-in test is to use an indenter to put axial pressure on a fibre which is embedded in a matrix until interface failure occurs. Figure 2.30 shows how the test is conducted.

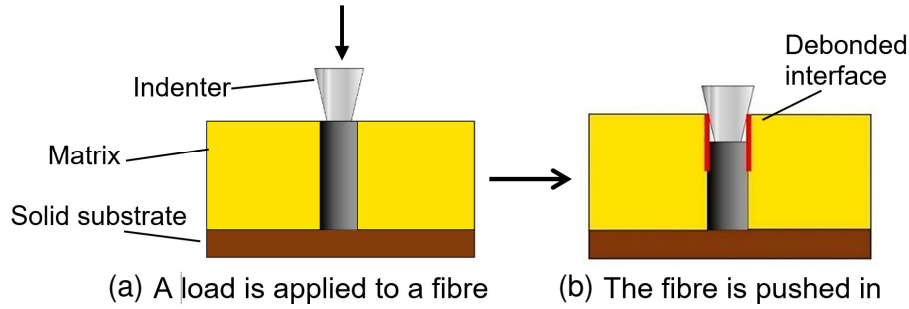


Figure 2.30 Illustration of the push-in test

Thin samples, typically less than 300 μm thick, are mounted upon a flat surface for push-in tests. That can be easier than mounting the small, delicate samples upon a grooved or perforated surface as required for push-out tests.

During the push-in test, interface shear strength can be determined from the shear-lag model [11, 104] (see Equation 2.9).

$$\tau_c^{SL} = \frac{nP_c}{2\pi r^2} \quad 2.9$$

Where τ_c^{SL} is the interfacial shear strength determined from the push-in test, P_c is the critical load applied to the fibre at the onset of interface decohesion, r is the fibre radius, and n is a parameter that depends on the elastic properties of the matrix and the fibre, as well as the local constraint imposed by neighbouring fibres.

n can be ascertained from the stiffness of the elastic region in the load-displacement curve, as described by Equation 2.10 [104].

$$n = \frac{S_0}{\pi r E_f} \quad 2.10$$

Where S_0 is the slope of the load-displacement curve in the linear region, and E_f is the longitudinal elastic fibre modulus.

Single fibre push-out test method

The single fibre push-out test requires a sample of composite material, with the fibres embedded within it orientated vertically such that the faces of the composite are perpendicular to the axis of the fibres. The composite is aligned over a hole to allow the embedded fibres to be pushed out without obstruction. Then an indenter is used to push the centre of a fibre of interest until it debonds from the matrix, as depicted in Figure 2.31. The load applied by the indenter tip and its penetration depth are continuously monitored. That data is used to produce a load-displacement curve. Figure 2.32 provides an idealised example of the curve [11, 79].

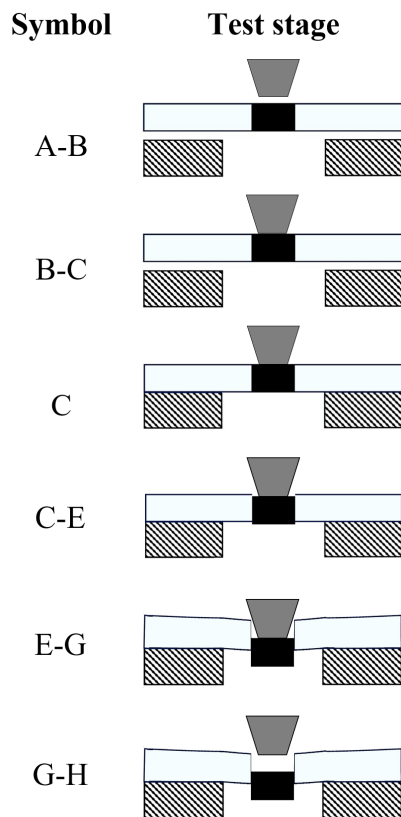


Figure 2.31 The position of a flat punch at successive stages of the push-out test

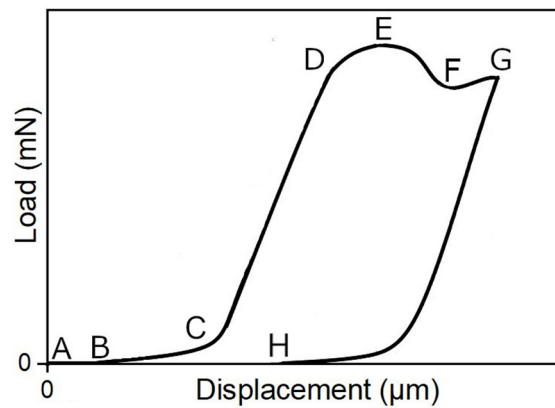


Figure 2.32 Typical load-displacement plot of a push-out test

In Figures 2.31 and 2.32 at section A-B, the indenter is not in contact with the composite. Accordingly, the composite is not under an applied load. From B-C the load-displacement trend is due to the sample being pushed down with the indenter until it makes full contact with the substrate at C. From C-D the load applied by the indenter increases rapidly because the composite is resistant to strain. Eventually, fibre debonding starts to occur at the interface (D-E), and with that, the applied load increases at a slower rate because the fibre is being displaced. That leads to a maximum in the applied load (E) because after that point, the fibre slides out from the matrix under friction (E-F). Soon after that, the load rises again because the indenter starts to contact the matrix (F-G). Finally, because the fibre cannot be pushed any further without the indenter pressing into the matrix surrounding the fibre, it is retracted back to its initial position, and the applied load decreases to zero (G-H).

Load-displacement data recorded from a push-out test can be used to produce a shear stress-displacement curve by applying Equation 2.11. The equation states that the load applied to a fibre, P_f divided by its surface area (curved surface only) is equal to the average shear stress at the interface [198].

$$\tau = \frac{P_f}{\pi dh} \quad 2.11$$

Where τ is the shear stress at the interface, P_f is the load applied to the fibre, d is the fibre diameter, and h is the specimen thickness. After interface failure has occurred τ is representative of the frictional shear stress at the interface τ_f .

Evaluation of push-out and push-in test methods

Push-in tests and push-out tests are convenient techniques that can be carried out on commercially produced composites, unlike single fibre fragmentation tests, microbond tests, and pull-out tests. Additionally, push-out and push-in tests are often easier to conduct than pull-out tests on narrow or brittle fibres because gripping a fibre is not an issue. Also, because samples that are prepared for push-out and push-in tests can be extracted from commercially produced products, composites examined using push-out and push-in tests can have an identical manufacturing and ageing history to commercial composites.

Fibres are subjected to stronger axial stress during push-in tests than during push-out tests. That is because fibres are pushed into a gap without obstruction throughout push-out tests. Whereas, fibres are in contact with a rigid substrate and pushed into it as push-in tests are conducted. That can cause the fibre in contact with the flat punch to become indented significantly and undergo Poisson expansion as it is pushed against the rigid substrate, influencing shear stress values calculated from the test [199]. As a result, additional knowledge about the properties of the composite, such as the longitudinal elastic modulus of the fibres, is required for a thorough analysis of load-displacement data produced from push-in tests. That increases the difficulty of analysing data from push-in tests and restricts its applications, especially for composites in which the longitudinal elastic modulus of the embedded fibres is unknown.

That deduction is supported by Medina et al. [11], who authored a paper that compared data produced from push-in and push-out tests which were used to measure the shear strength of interfaces in glass/epoxy composites. They recognised that an advantage of the push-out test method is that it can be conducted on bespoke laboratory specimens as well as commercially produced composites. It can also be used as a quality control check for interfacial strength independent of fibre tensile strength, which is not feasible for single fibre pull-out, microbond and fragmentation tests. They performed push-in and push-out tests on a composite and saw that both experimental methodologies provided equivalent values of interface shear strength for each material. However, data had to be post-processed after the push-in tests were completed to subtract the elastic deformation of the specimen from measured interfacial shear stress values. In contrast, during push-out tests, interface shear stress values were obtained directly from the thickness of the composite, and the maximum load applied.

Another advantage that the push-out test has over the push-in test is that fibres can be pushed through the matrix during push-out tests. That allows frictional shear stress at the interface to be measured (e.g. by using Equation 2.11). That information can be useful for the development of models which forecast how strong infrastructure that is made from composite materials will be after that infrastructure undergoes compressive failure.

2.6.4 Influence of local fibre density on interface shear strength

In the past, researchers have found that the volume fraction of fibres present in a composite can affect how it will fail under compressive stress [42, 43, 200]. One reason for that is because if the volume fraction of fibres is too low, a load applied to the composite may break the embedded fibres. The region of broken fibres can then be regarded as a hole that carries no load [200]. Consequently, there is a fibre volume fraction below which the failure of a composite under compressive stress is governed by the matrix. Below that volume fraction, the embedded fibres weaken the composite instead of strengthening it.

Furthermore, as detailed in Chapter 2.3 of this thesis, Zhang and Latour [42] predicted that the shear mode is always the preferred buckling mode, except in the case of composites that contain a very low fibre volume fraction, such that the fibres will fail without interaction between each other. Likewise, as detailed in that chapter, Lee et al. [43] saw that glass/epoxy composites failed under compressive loading through different modes, depending upon the volume fraction of fibres in the matrix. Moreover, as detailed in Chapter 2.4.6 of this thesis, researchers have measured the thickness of fibre-matrix interfaces in polymer composites and observed specimens in which the thickness of the interface was in the range of microns. For example, Molazemhosseini et al. [97] estimated the thickness of the interface in a carbon/PEEK composite to be 1.7 μm . Likewise, Cross et al. [91] determined the thickness of the interface in a glass/epoxy composite to be 2.5 μm thick.

Devireddy and Biswas [201] explained that, for simplicity, most micromechanical models assume that a periodic arrangement of fibres is present within a modelled composite, for which a representative volume element or unit cell can be isolated. The periodic sequences that are commonly used for models are a square array and a hexagonal array (see Figure 2.33). Figure 2.33 illustrates two composites in which the embedded fibres are orientated vertically, and the composites are observed from a top-down view. Specifically, in Figure 2.33a, the fibres are packed in a square array. Whereas in Figure 2.33b, the fibres are arranged in a hexagonal array. Fibre packing determines the maximum fibre volume fraction that a continuous unidirectional fibre-reinforced composite can contain. Devireddy and Biswas [201] provided details regarding the maximum fibre volume that is theoretically achievable in composites with a square or hexagonal packing geometry. Accordingly, in Figure 2.33a, the fibres are packed in a square arrangement, thus in that composite, the maximum theoretically achievable fibre volume fraction is 78.54% [201]. Also, in Figure 2.33b, the fibres within the matrix are packed in a hexagonal arrangement. Therefore the maximum theoretically achievable fibre volume fraction in that composite is 90.69% [201].

Figure 2.33a depicts a composite in which the interface surrounding fibres is relatively thin, and the composite has a low fibre volume fraction compared to that of the composite shown in Figure 2.33b. Because the composite in Figure 2.33a has that composition, interfaces within it do not merge with each other, also the interfaces are relatively distant from each other when compared to those in Figure 2.33b. In that figure, the interfaces are thicker than those surrounding the fibres depicted in Figure 2.33a. Also, the fibres are organised in a hexagonal arrangement and tightly packed together. Thus, the interface surrounding each fibre in Figure 2.33b is partially merged with the interface surrounding its neighbouring fibre. That is more likely to occur when the interface is thick, the composite has a high fibre density, and the fibres within the matrix are tightly packed, as illustrated in Figure 2.33.

Thus, it is thought that if the interface surrounding a single fibre in a composite of that structure, or similar, were to fail under shear stress. That may also damage the interface surrounding its neighbouring fibre. Because of that, literature regarding how the failure of one fibre in a composite affects the shear strength of its neighbouring fibres in thermoplastic composites was sought after during the writing of this literature review. However, no information that was relevant and detailed on that topic was found. Hence, original experiments were designed and conducted in the present work, with an intention to gather that information. (Chapters 3.4.3 and 4.5).

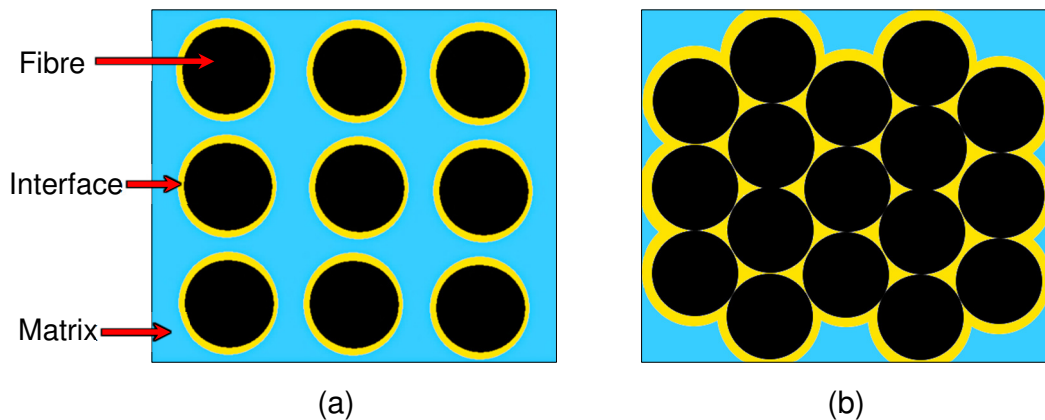


Figure 2.33 Square (a) and (b) hexagonal fibre packing in unidirectional composites

Almost all commercially produced composites contain regions of high fibre density, wherein there are many fibres, and low fibre density, where the presence of fibres is seldom. Because of that inhomogeneous fibre distribution, three distinct approaches to performing single fibre based tests of interface shear strength can be made. The fibres can be selected at random; alternatively, only those which are found in regions of high fibre density or those found in regions of low fibre density can be selected. Some researchers, such as Naya et al. [202], performed push-in tests on polymer composites, solely in regions of high fibre density. In each test, the central fibre of a hexagonal fibre cluster was pushed, which was beneficial because that target fibre was always subjected to the same constraint from its nearest neighbouring fibres.

Conversely, other researchers have performed push-out tests on composites, solely in regions of low fibre density. For instance, You et al. [203] fabricated a bespoke copper matrix composite in which the distance between fibres was always more than 160 μm . That composite was push-out tested, and the fibres that were pushed were distant enough from each other to exclude the influence of neighbouring fibres from the test results.

In contrast to Naya et al. [202], who consistently push-out tested fibres that were close to each other, and You et al. [203] who consistently push-out tested fibres that were distant from each other, Mueller et al. [198] push-out tested fibres randomly and irrespective of the local fibre density when studying a SiC/PyC/SiC composite (silicon carbide fibre-reinforced silicon carbide matrix composite). An advantage of their approach is that it is a method which has the potential to avoid statistical bias. However, a drawback is that several tests must be conducted to gain a representative sample of results. That is considerably time-consuming and can be challenging given the diverse range of surroundings in which a single fibre within a composite may be located. For example, the fibre which is selected to be pushed-out may be surrounded by zero, a couple, or many neighbouring fibres, and those fibres can be located at different distances from the selected fibre.

2.6.5 Conclusions

Popular single fibre interface shear strength test methods were described and evaluated in this chapter. Those tests include the push-out test, push-in test, fibre fragmentation test, pull-out test, and microbond test. The push-out test was identified as being the most promising method for achieving the aims and objectives of the present work. That was because push-out tests can be performed on composites that have been commercially manufactured, and this present research involves the use of composite specimens that have been extracted from flexible pipes. The push-out test was also deemed to be the most promising because some details about the properties of the composite specimen, such as the longitudinal elastic modulus of the embedded fibres, was not well known. That information is essential for detailed analysis of data generated from push-in tests [11, 104]. However, in general, those details are not necessary for the analysis of data produced from push-out tests.

In the past, researchers have used different methods to target individual fibres for push-out tests. Frequently, the fibres that are selected to be pushed out are either located in regions of high fibre density, regions of low fibre density, or the fibres are randomly selected irrespective of the local fibre density. Also, past researchers have determined the average thickness of the interface in some fibre reinforced polymer composites to be in the range of microns [91, 97]. Thus, it is thought that the interface surrounding a fibre may merge with the interface surrounding close neighbouring fibres. Consequently, the failure of a single fibre in a composite under shear stress may damage the shear strength of its neighbouring fibres. However, no relevant and detailed information on that topic was found during the writing of this literature review.

Hence, it would be beneficial if investigations were conducted to find the effects of local fibre density on the outcomes of push-out tests. Understanding how local fibre density affects the failure behaviour of interfaces would assist the development of flexible pipelines, in which the shear strength of interfaces has been optimised, not only by chemical or physical treatment processes. But also, by ideal fibre placement and fibre volume fraction within the composite layer of the pipe. Therefore, the effects of local fibre density on the mechanical behaviour of interfaces was studied through experiments in the present work (see Chapter 4.2).

2.7 High-temperature nanoindentation

Composite materials are often used at high temperatures and in a wide variety of applications. Such as in high-performance automotive vehicles, aircraft and spacecraft vehicles, also in the walls of furnaces, and as fire barriers. That requires knowledge of how well different types of composites resist high temperatures.

Wheeler et al. [204] authored a paper that explains technological advancements and future challenges in the field of high-temperature nanoindentation. In the document, they stated that nanoindentation is currently one of the most popular techniques for mechanical characterisation.

Poisl et al. [205] conducted early research work into the relationship between the indentation and uniaxial creep of selenium at elevated temperatures. At that time, high-temperature microprobes were not readily available, so amorphous selenium was selected as the test specimen. It has a glass transition temperature that is close to room temperature. The nanoindenter was placed into a room which was heated from 32.1 to 34.3°C. Since that pioneering work, other materials and physical phenomena have been investigated through nanoindentation at elevated temperatures, which shows that it is a highly versatile and sought-after technique.

For example, Phani and Oliver [206] performed high-temperature nanoindentation creep tests on aluminium. Volinsky et al. [207] used high-temperature nanoindentation to measure the elastic modulus and hardness of aluminium and copper thin films as a function of temperature. Recently, researchers have used the tip of indenters to study distinct events which occur at elevated temperatures. For example, Ruffell et al. [208] used nanoindentation at elevated temperatures to induce phase transformations in silicon. Eldridge [209] compared how fibre-reinforced composites with thermal expansion mismatches of opposite sign, responded to elevated temperatures. Specifically, silicon carbide fibre-reinforced titanium alloy, SCS-6/Ti-24-11 ($\alpha_m > \alpha_f$) and silicon carbide fibre-reinforced reaction bonded silicon nitride, SCS-6/RBSN ($\alpha_m < \alpha_f$). The interfacial shear strength of SCS-6/RBSN increased with raised temperatures, which was consistent with a decrease of residual radial tension, whereas the interfacial shear strength of SCS-6/Ti-24-11 regressed, which was consistent with a reduction of radial compression. Due to those findings, it became known that elevated temperatures can both strengthen or weaken bonding between the fibre and matrix in a composite, depending upon the thermal expansion coefficient of each phase.

As an example of a nanoindentation system used at high-temperatures, in 2016 Harris et al. [210] used a nanoindentation system to indent polycrystalline tungsten at 950°C. Polycrystalline tungsten has excellent potential for use in nuclear fusion applications. In fact, it has been proposed for use in the diverter of future fusion devices such as tokamaks. A tokamak is a device that uses a strong magnetic field to confine a hot plasma, and it is as of 2016, it is a leading design for a fusion reactor [211]. A divertor is used within a tokamak to remove waste material from plasma while the reactor is still operating. As such, the divertor is subjected to extremely high heat fluctuations. Fittingly, among metals, tungsten has the highest melting point (3410°C) [212].

In 2020 Minnert et al. [213] provided a report on a new ultra-high temperature Prometheus (UHT) nanoindentation system that can be used in-situ with scanning electron microscopy at testing temperatures of up to 1100°C. The system facilitated the determination of reliable Young's modulus and hardness data at temperatures up to 1100°C for the first time. Minnert et al. [213] demonstrated the system on fused silica, molybdenum, and single-crystalline nickel.

Overall, nanoindentation is a valuable and versatile technique that can be used to analyse the micromechanical characteristics of materials at a wide range of elevated temperatures. There is a strong demand for flexible pipes to be used in high-pressure, high-temperature wells. Fittingly, thermoplastics have exceptional flexibility when compared to other conventional pipe materials, such as steel and thermoset composites. However, thermoplastics are prone to soften at lower temperatures than steel and thermoset plastics. Because of that, it would be beneficial if research which focuses on understanding the thermomechanical characteristics of thermoplastic composites of the type used in flexible pipes was completed. Advantageously, nanoindentation systems can be used to analyse the shear strength of interfaces, as well as the micromechanical characteristics of the fibres and matrix in composites, at elevated temperatures. That versatility is valuable for research regarding the use of thermoplastic composite materials in flexible pipes that operate in high-pressure, high-temperature production conditions.

2.8 Tensile testing

Tensile testing is a method of mechanical analysis wherein a sample is pulled under a controlled tension until failure. The force applied to the sample and its corresponding change in length are recorded during the test. When that data is plotted on a graph, it produces a stress-strain curve that can be used to identify the tensile properties of the material. Such as its modulus of elasticity, yield strength, yield elongation, Young's modulus, ultimate tensile strength, and strain-hardening characteristics.

Figure 2.34 is an illustration of a typical tensile testing machine, and it is the same design as the one that was used for the present research. Plastics that are evaluated using this apparatus are typically cut or moulded into a dumbbell shape. That shape consists of two shoulders with a gauge section in between those shoulders. The shoulders have a large surface area so that they can be gripped easily, whereas the gauge section has a smaller cross-sectional area so that deformation and failure will occur in that region. Figures 3.26 and 3.27 illustrate a dumbbell-shaped thermoplastic polymer specimen. Figure 2.35a presents a typical stress-strain curve which is representative of the tensile behaviour of a thermoplastic polymer.

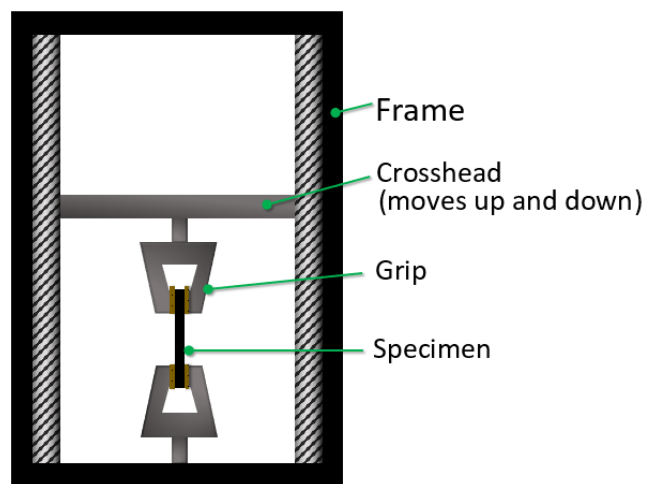


Figure 2.34 Illustration of a tensile testing machine

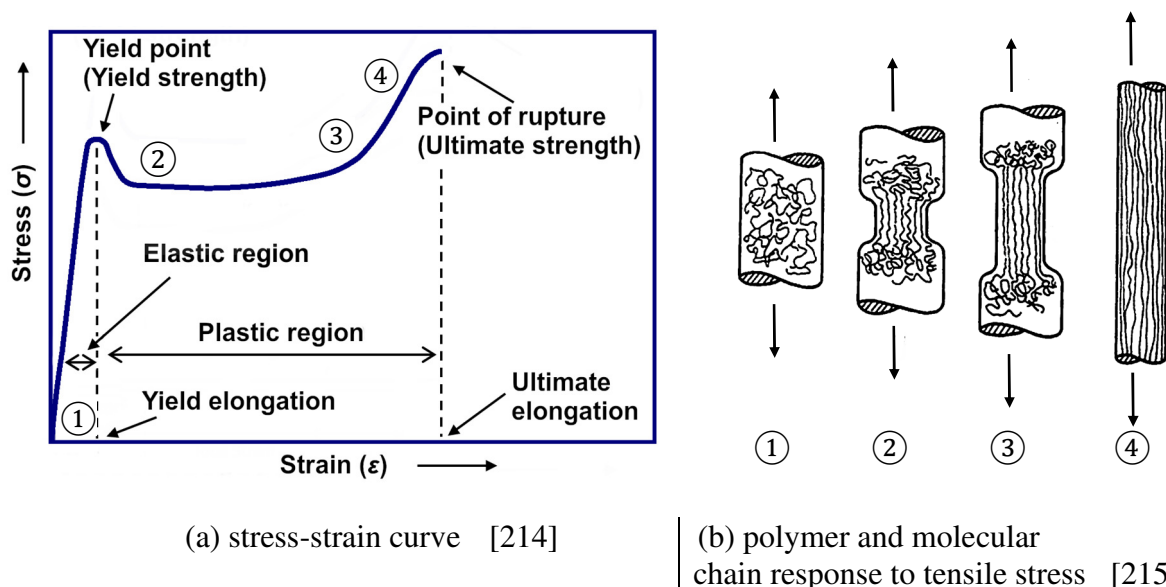


Figure 2.35 Typical stress-strain response of a semicrystalline thermoplastic polymer

Figures 2.35a and 2.35b show that four distinct changes in the mechanical behaviour and morphology of a semicrystalline thermoplastic polymer can be observed as the polymer is pulled under a tensile load until failure. Those phases are described in further detail below:

- ① The initial slope of the stress-strain curve shown in Figure 2.35a can be used to determine the Young's modulus of the polymer (also known as the tensile modulus of elasticity). The Young's modulus is determined from the ratio of stress to strain below the elastic limit. That elastic limit is the greatest stress which a material can sustain without any measurable permanent strain remaining after the applied stress has been released. The yield point is the first point on the stress-strain curve at which strain rises without an increase in stress. The yield strength is the stress at which a material exhibits a specified deviation from constant stress to strain proportionality. Brittle fractures occur with no apparent yield or zero yield before fracture.
- ②-③ A fall in stress occurs after the yield point because polymer chains stretch, slide, rotate and disentangle under load. That results in the polymer undergoing permanent plastic deformation. The polymer chains straighten under sufficient load, which allows the chains to slide past each other under less stress, and necking occurs. When necking occurs, the chains in the polymer straighten, causing the polymer to become more crystalline. That

strengthens the polymer at the neck, and therefore it begins to withstand deformation in that region. The remainder of the polymer continues to deform.

- ④ Eventually, the chains become tightly packed and align in parallel with each other, which increases van der Waals bonding between them. Consequently, more stress is required to cause the polymer to deform further until it fractures.

Gauge length is the length of the portion of the specimen over which strain occurs. The increase in the length of the gauge section of a material at a given load, divided by the initial (stress-free) length of the gauge section is equal to the engineering strain (ϵ). That produces a dimensionless number for engineering strain, although it is often noted in a non-simplified form such as meters per meter or inches per inch (see Equation 2.12 [216]).

$$\text{Engineering strain } (\epsilon) = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \quad \mathbf{2.12}$$

Where ΔL is the change in gauge length, L_0 is the initial gauge length and L is the final gauge length.

Engineering stress is the applied load, P , divided by the original (before any load is applied) cross-sectional area of the material, A (Equation 2.13 [216]).

$$\text{Engineering stress } (\sigma) = \frac{P}{A} \quad \mathbf{2.13}$$

2.9 Literature review conclusions

This literature review has detailed prominent benefits and concerns regarding the use of flexible thermoplastic composite pipes in high-pressure, high-temperature oil and gas production environments. With that, information gaps in associated literature and discrepancies between the viewpoints held by different researchers were discussed. That information was used to set the objectives for the present work. Even though information from scientific articles regarding the use of thermoplastic composites in pipes was sought after during the writing of this literature review, the majority of the literature found focused on thermoset composites. Thermosetting and thermoplastic polymer composites have notably different thermal, chemical, and mechanical characteristics. Hence, new research which focuses on the characteristics of thermoplastic composites at elevated temperatures and pressures is particularly valuable.

3. EXPERIMENTAL METHODS

3.1 Materials of investigation

The materials of this investigation were glass fibre-reinforced polypropylene (G/PP) and carbon fibre-reinforced polyamide 12 (C/PA12), as well as the non-reinforced matrices of those materials. The composite specimens were extracted from sections of fully bonded thermoplastic flexible pipes (G/PP and C/PA12) and tapes of composite material (G/PP and C/PA12) (see Figures 3.1 to 3.6 and Figure 3.19). Also, the non-reinforced polymers were obtained from the pipe sections and neat polymer standard sheets.

Distilled water and oil (represented by a 50/50 pentane/toluene solution) was used to artificially age specimens at temperatures ranging from 25 to 140°C for up to 51 days. Specific details regarding the ageing procedures are provided in Chapter 3.2.

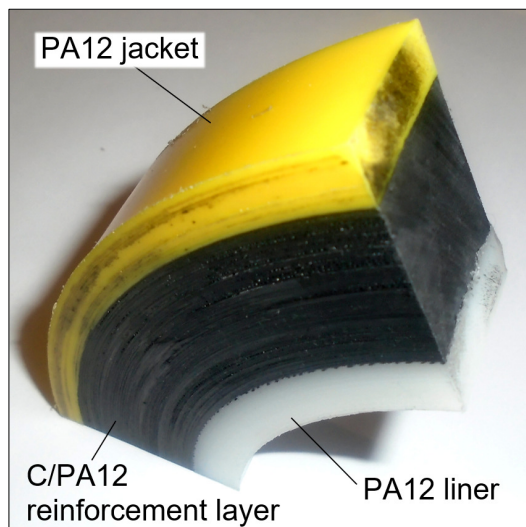


Figure 3.1 Cross-section of C/PA12 flexible pipe specimen

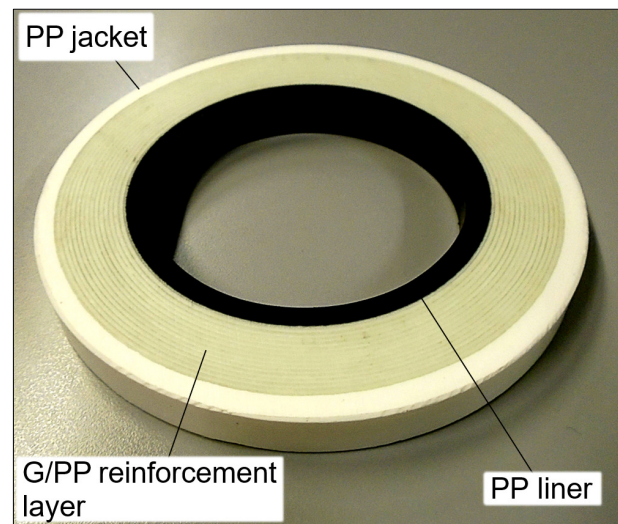


Figure 3.2 Cross-section of G/PP flexible pipe specimen



Figure 3.3 Photograph of G/PP tape specimen



Figure 3.4 Photograph of C/PA12 tape specimen

The liner and jacket of the pipes were made of the same polymer matrix material as the rest of the respective pipe. The original function of each layer in the pipes was as follows:

Liner – The liner was designed to prevent production fluids and materials which are transported through the pipe from being absorbed into the reinforcement layer, where they might cause damage. It was also constructed to prevent production fluids from escaping into the external environment.

Nonetheless, thermoplastic liners have also been used to rehabilitate existing pipes. As such, thermoplastic liners have been used to mitigate corrosion, reduce wear, eliminate the use of toxic corrosion inhibitors, reduce pumping costs, and reduce heat loss (which also lessens pipe buckling risks) [217, 218].

Reinforcement layer – The reinforcement layer was designed to absorb loads applied to the pipe during installation and service. This layer was made up of composite tapes which were melt-fused together. The reinforcement layer was extracted from each pipe specimen and mechanically tested in this work. Micrographs of this layer are shown in Figures 3.5 and 3.6.

Jacket – The jacket was designed to prevent water ingress into the composite reinforcement layer of the pipe, wherein the water could degrade the melt-fused composite tapes. This layer also protected the reinforcement layer from impact damage and abrasion.

3.1.1 Distribution, diameter, and volume fraction of fibres in specimens

Micrographs of the G/PP and C/PA12 specimens are shown in Figures 3.5 and 3.6 (Some debris is on the surface of the G/PP specimen shown in Figure 3.5a). The images were taken using an Olympus BX51 optical microscope. The images show that the reinforcement layer in each of the pipes was comprised of composite tapes. The fibre orientation angle in the tapes alternated between $+\theta$ and $-\theta$. The figures also show that the spatial distribution of the fibres in each composite was not uniform. Accordingly, there were regions of high and low fibre density in each specimen.

This ply was cut at an angle to the 0° direction.
Thus, the embedded fibres appear oval shaped

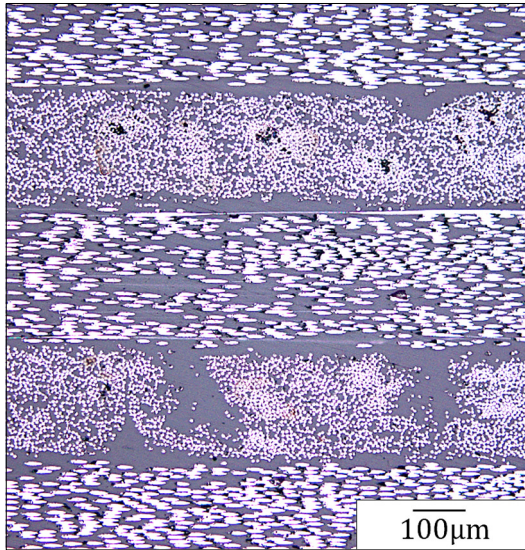


Figure 3.5 Cross-section of the C/PA12 layer in the C/PA12 pipe specimen

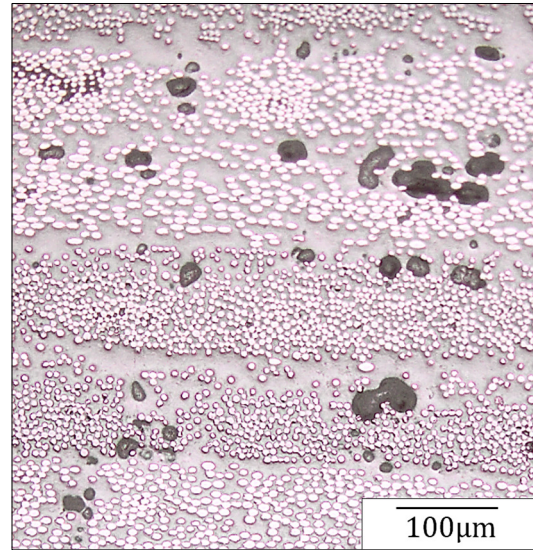


Figure 3.6 Cross-section of the G/PP layer in the G/PP pipe specimen

Each composite specimen contained continuous unidirectionally aligned fibres, which allowed the fibre volume fraction (V_f) of a single-ply to be quantified by means of Equation 3.1.

$$V_f (\%) = \frac{\sum \text{Fibre cross-sectional area}}{\text{Matrix cross-sectional area}} \times 100 \quad 3.1$$

To determine the volume fraction of fibres, V_f , in the plies that were vertically orientated (and subsequently assessed to find their interfacial shear strength). An Olympus BX51 optical microscope was used to produce three micrographs of the cross-section of each specimen. Each image showed a different region in the cross-section of its respective composite. Next, Adobe Photoshop software was used to; crop the images so that they only showed a vertically orientated ply, digitally remove debris from the images so that the fibres were well defined, and adjust the images so that the fibres had a high contrast to the matrix. Next, ImageJ software was employed to convert the images to black and white, then calculate the fibre volume fraction within each ply. That was done for each of the micrographs. The resultant values of fibre volume fraction, which were calculated using ImageJ, were averaged to determine the average fibre volume fraction in a given ply.

Figures 3.4 to 3.6 show that fibres were clustered near the centre of each ply, leaving the edges with a high proportion of matrix material. That makes sense because the primary purposes of the matrix include to; hold embedded fibres in place, protect the fibres from abrasion, and to protect the fibres from exposure to destructive environmental conditions.

Thus, the average fibre volume fraction in each specimen was assessed twice. The first assessment of fibre volume fraction (V_f) took the full cross-section of each sampled ply into account, including the edges. The second assessment of fibre volume fraction (V_{f2}) excluded the edges of each ply to focus on the regions of relatively high local fibre density (e.g. such as inside the blue box in Figure 3.7b). Figure 3.7a shows an image of a G/PP specimen and the final modified image of that specimen which was subsequently assessed using ImageJ analysis software (Figure 3.7b, excluding the blue box annotation). Table 3.1 states the volume fraction of fibres, V_f , range of fibre diameters, and average fibre diameter that was present in each composite specimen.

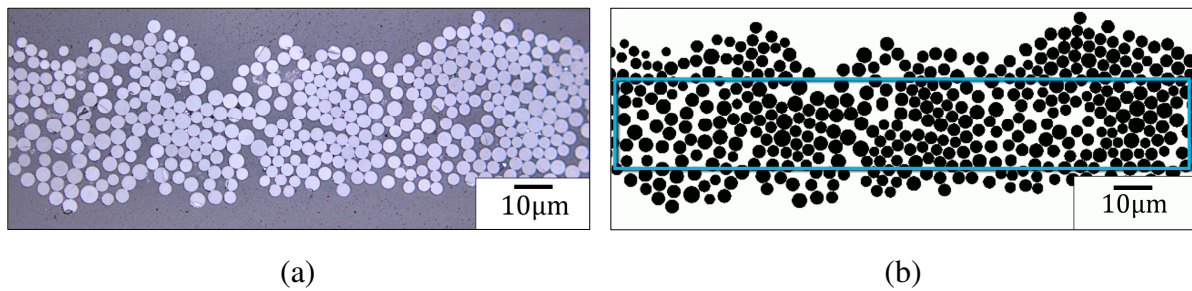


Figure 3.7 Original (a) and modified (b) image of a G/PP sample surface

Material of investigation	Fibre volume fraction (V_f) (including edges)	Fibre volume fraction (V_{f2}) (excluding edges)	Fibre diameter range (μm)	Average fibre diameter (μm)
G/PP from G/PP tape	42%	58%	9-22	15.7
G/PP from G/PP pipeline	45%	57%	13-24	16.5
C/PA12 from PA12 pipeline	45%	50%	6-8	6.0

Table 3.1 Volume fraction of fibres in the composite specimen

Engineered composites normally consist of 50 to 65% fibre content by volume fraction. That is consistent with the volume fraction of fibres observed in the composite specimens that were examined during this investigation (see Table 3.1). It should be noted that the G/PP tape and the G/PP pipe specimens were produced by different manufacturers. Thus, it is not out of the ordinary that the range of glass fibre diameters in each of those composite specimens slightly differed.

Generally, carbon fibres have a diameter of 5 to 10 μm [112], and glass fibre diameters stay in the range of 3 to 20 μm [219]. That is consistent with the fibre diameters that were measured using ImageJ software in the present work. Moreover, during subsequent experiments, a scanning electron microscope was used to measure the diameter of each fibre that was mechanically tested using a nanoindenter. That further confirmed the fibre dimensions and matched the analysis conducted using ImageJ software. Overall, the average fibre diameter that was measured in the-glass fibre and carbon fibre composites was typical.

3.2 **Procedures used to age polymer and composite specimens**

Flexible pipes are often specified to have a service life that exceeds 20 years [220, 221]. Because of that, specimens were aged at accelerated rates in this work to enable the findings gathered to be used at the earliest opportunity. That was achieved by immersing samples in water and oil at elevated temperatures. Distinct types of polymers and composites were investigated in this work, so with consideration of their unique characteristics, they were aged under different environmental conditions.

Specifically, coupons and thin samples of G/PP, C/PA12, PP, and PA12 were artificially aged in distilled water and a 50/50 pentane/toluene solution. During that process, the weight of each coupon was monitored. Also, the specimens were held in their respective immersion fluid at a selected constant temperature in the range of 25 to 130°C. The 130°C temperature that was used is within the bounds of the temperatures present in many oil and gas wells (see Chapter 2.2). Furthermore, those temperatures did not induce any extraneous phase or chemical changes. Historically, researchers have aged polyamides at higher temperatures without encountering those issues. For example, Hochstetler and Dang [222] artificially aged polyamide 11 in water at 140°C for up to 60 days and found that the ageing protocol was representative of field conditions. Likewise, Jacques et al. [181] successfully tracked the molecular weight evolution of polyamide 11 as it was artificially aged in water and oil at 140°C for 1000 hours (42 days).

Furthermore, the maximum operating temperature of polypropylene is in the range of 100 to 130°C [59, 223], and in theory, some grades of polypropylene may be suitable for very short term use at 140°C [60]. The highest temperature that polypropylene specimens were aged in the present work was 100°C, which is considerably below those operating temperatures. That is additional evidence that the temperatures which were used to age specimens in the present work, was reasonable. Table 3.2 states the ageing conditions that were used in this present work. Further details about the sample dimensions are provided in Figures 3.8 and 3.26.

Material	Dimensions	Solvent	Solvent temperature (°C)	Duration aged (days)
Carbon fibre / polyamide 12	Thin sample	Pentane/toluene	100 & 130	51
		Water	130	3
Glass fibre / polypropylene	Thin sample	Pentane/toluene	25, 85 & 100	51
		Water	80	35
	Coupon	Pentane/toluene	25, 85 & 100	51
		Water	50, 80	7 (50°C) 12.6 & 13 (80°C)
Polyamide 12	Dumbbell	Water	100	0, 0.1, 0.3, 1 & 3
	Coupon	Water	50, 80 & 85	4.5 (50°C), 16 (80 & 85°C)
	Thin sample	Water	130°C	3
	Coupon	Pentane/toluene	100 & 130	51
Polypropylene	Coupon	Water	50 & 80	7 (50°C) 22.5 & 35 (80°C)
	Coupon	Pentane/toluene	25, 85, 100	51

Table 3.2 Environmental conditions that specimens were aged under

Distilled water and oil (a 50/50 pentane/toluene solution) was used to age the polymer and composite specimens at specific constant temperatures ranging from 25 to 130°C for up to 51 days (see Table 3.2). To achieve that, the materials were sealed within individual 45 ml autoclaves, then placed into a preheated climactic chamber. A closed oil bath was used as the climactic chamber for the samples that were aged in oil, whereas a laboratory oven was used for the samples that were aged in water. Samples were periodically removed from their respective autoclave, wiped dry using a lint-free towel, and then weighed on a Mettler Toledo analytical balance to a precision of 0.1 mg. Finally, the solvent inside each autoclave was renewed to mimic subsea conditions before the samples were returned to continue ageing. The period that each sample remained outside of a climactic chamber was kept to a minimum and never more than thirty minutes. Likewise, the surface of each sample was moisture free for no more than five minutes per weighing session to minimise moisture evaporation.

The percentage weight change of the samples, $W_{\%}$, was calculated using Equation 3.2.

$$W_{\%} = \frac{W_t - W_i}{W_i} \times 100 \quad 3.2$$

Where $W_{\%}$ is the percentage change in sample weight, W_t is the weight of the sample at a given immersion time, and W_i is the initial sample weight.

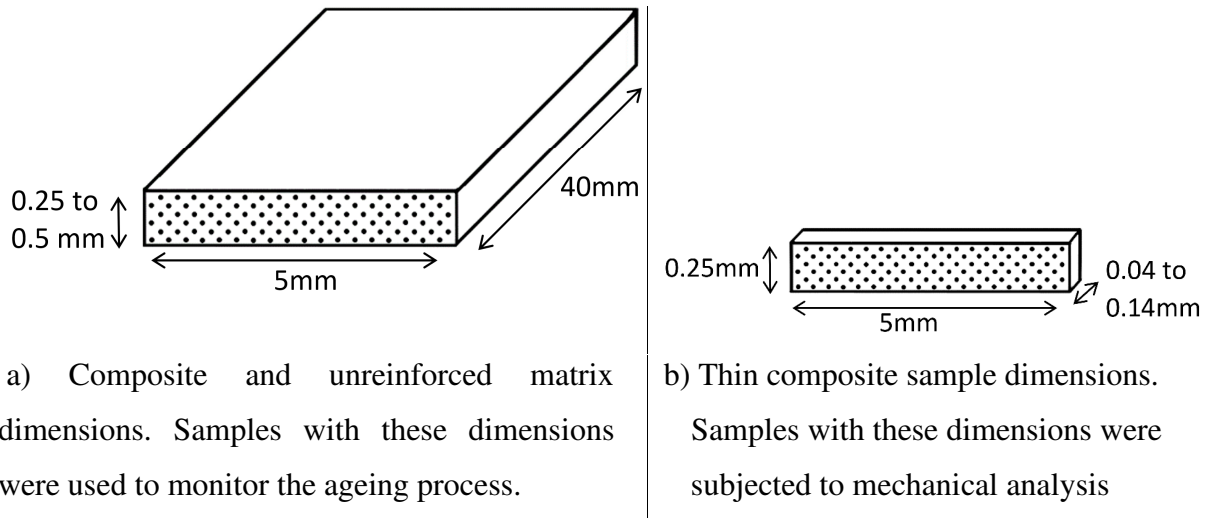


Figure 3.8 Dimensions the samples used in (a) ageing and (b) micromechanical tests

Fick's law states that the rate of moisture diffusion through a membrane is inversely proportional to the thickness of the membrane, whereas it is proportional to the surface area and concentration difference (see Equation 3.3).

$$\text{Rate of diffusion} \propto \frac{\text{concentration difference} \times \text{surface area}}{\text{membrane thickness}} \quad 3.3$$

Thin composite samples were examined using nanoindentation based experiments. Those samples had dimensions of approximately 5 mm × 0.25 mm × 0.07 mm (length × width × depth, Figure 3.8b). Because of that, it was not feasible to weigh them on a standard laboratory scale like the coupons, due to the limited precision of the scale and because the samples were tiny, very lightweight, and delicate. According to Fick's law, if the thickness of a sample is halved, the rate of diffusion is doubled. Thus, it was assumed that due to their greater thickness,

once the coupons became saturated with moisture, it was also true that their thin counterpart samples (which were aged under the same environmental conditions) were saturated as well.

3.2.1 Vapour pressure within climactic chambers

The vapour pressure, P_{vp} , of a liquid is the pressure exerted by the molecules which escape from the liquid to form a vapour phase above the liquid surface. Also, vapour pressure increases as the temperature of the liquid increases. In this work, polymer and composite specimen were aged by being heated in climactic chambers (sealed autoclaves), which were filled with either distilled water or a 50/50 pentane toluene solution

The vapour pressure of water at 130°C is 0.3 MPa [224].

Therefore, the maximum vapour pressure of water in each autoclave at 130°C was 0.3 MPa. (130°C was the highest temperature used to hygrothermally age specimens.)

Equation 3.4, as well as the corresponding coefficients and temperature data provided in Tables 3.3 and 3.4 were provided by the Korea Thermophysical Properties Databank (KDB) [225].

$$\ln(P_{vp}) = A \ln(T) + \frac{B}{T} + C + DT^2 \quad 3.4$$

Where vapour pressure, P_{vp} , is in kPa, T is in K, and A, B, C, and D are coefficients (see Tables 3.3 and 3.4)

n-Pentane	
Temperature range	143.42 to 469.65K (-129.73 to 196°C)
Coefficient	
A	= -1.041840E+01
B	= -5.778024E+03
C	= 8.192460E+01
D	= 1.178208E-05

Table 3.3 N-pentane. Coefficients for vapour pressure in Equation 3.4

Toluene	
Temperature range	178.18 to 591.79K (-94.97 to 318.64°C)
Coefficient	
A	= -8.795480E+00
B	= -6.918798E+03
C	= 7.413580E+01
D	= 5.754912E-06

Table 3.4 Toluene. Coefficients for vapour pressure in Equation 3.4

Raoult's Law states that for fully liquid solutions, the equilibrium vapour pressure which each component in the liquid exerts is proportional to the mole fraction of that component in the liquid.

The mathematical definition of Raoult's law, for a single component in an ideal solution, is:

$$p_i = p_i^* x_i \quad 3.5$$

Where p_i is the vapour pressure of component i in the gaseous mixture, p_i^* is the equilibrium vapour pressure of the component i alone, and x_i is the mole fraction of component i in the gaseous mixture [226].

Dalton's law of partial pressures states that the total pressure, p_{total} , exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the individual gases. Dalton's law is expressed mathematically in Equation 3.6.

$$p_{total} = p_1 + p_2 + p_3 + \dots + p_n \quad 3.6$$

$p_1, p_2, p_3 \dots p_n$ represent the partial pressures of each component. Once the components in a gaseous mixture reach equilibrium, the total vapour pressure of the mixture can be determined by combining Dalton's law of partial pressures with Raoult's law to produce Equation 3.7.

$$p_{total} = p_1^* x_1 + p_2^* x_2 + p_3^* x_3 + \dots + p_n^* x_n \quad 3.7$$

The polymer and composite specimen which were investigated in the present work were immersed in a 50/50 pentane/toluene solution at a maximum temperature of 130°C. Thus, applying Equation 3.7 revealed that the theoretical maximum pressure that the samples were subjected to under the highest immersion temperature was 0.64 MPa (C/PA12) and 0.32 MPa (G/PP). The autoclaves were 10 cm deep; thus, the hydrostatic pressure which the immersion fluids exerted upon the samples was negligible. It is highly unlikely that the theoretical maximum 0.64 MPa of pressure that the samples were subjected to in this work had a significant effect on their mechanical properties for three key reasons.

Firstly, in the past, researchers have placed composites under far higher pressures without seeing a change in their mechanical properties. For example, Avena and Bunsell [162] and Humeau et al. [163] immersed glass/epoxy composites in water at hydrostatic pressures of 20 MPa (and 50 MPa in the case of Humeau et al. [163]). They saw that those pressures did not change the mechanical behaviour of the specimens. Secondly, the minimum shear stress that was needed to cause interface failure in the composites that were assessed in the present work was 40 MPa (C/PA12) and 12 MPa (G/PP). Thirdly, flexible composite pipes have been qualified for use at pressures of up to 68.9 MPa [16].

In each of those examples, the pressures which the composite materials encountered was far higher than the hydrostatic pressures experienced by the specimens which were hygrothermally aged in the present work. However, those pressures were not strong enough to significantly change the mechanical properties of the composite specimens that were assessed, nor were they strong enough to cause interface failure. Therefore, it is concluded that the total pressure that was present in each autoclave as composite specimens were aged had a negligible effect on their mechanical behaviour and interfacial shear strength.

Chapter 2.2 of this thesis explains that HPHT-hc wells have a high pressure, exceeding 241 MPa. Those wells are unlikely to be used for oil and gas production in the near future. Likewise, the definition of high-temperature wells lies in the range of 150 to 200°C, and above 200°C for ultra high-temperature wells. Considering those production conditions, the polymer and composite specimens of this present work were hygrothermally aged at temperatures up to 130°C, and mechanically tested at temperatures up to 120°C. Because of that, the specimens were aged and mechanically tested at temperatures and pressures which are comparable to those experienced by many in-service flexible pipes.

3.3 Fabrication of specimens for micromechanical tests

The materials that were subjected to hygrothermal ageing and mechanical tests in this work were continuous unidirectional fibre-reinforced G/PP and C/PA12 composites, as well as neat PP and PA12. Those materials originated from composite tapes, flexible pipes, and non-reinforced polymer sheets.

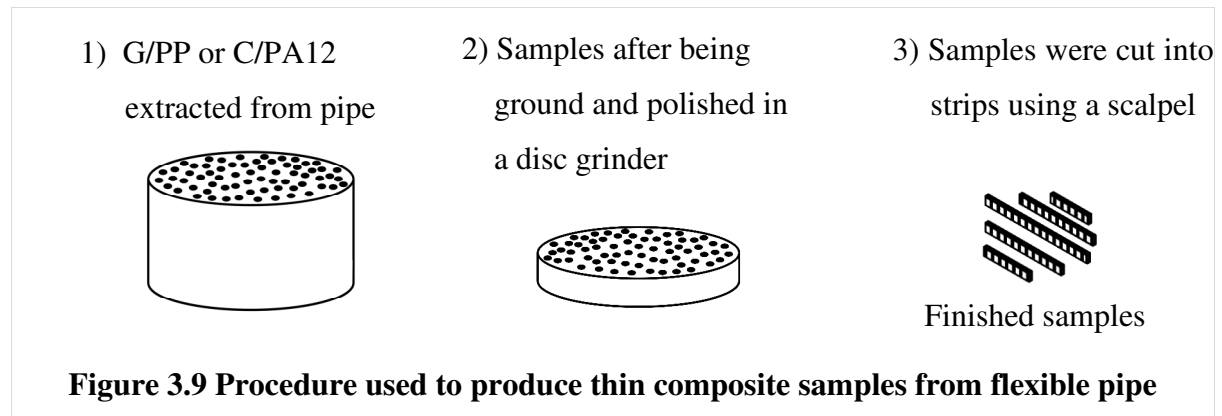
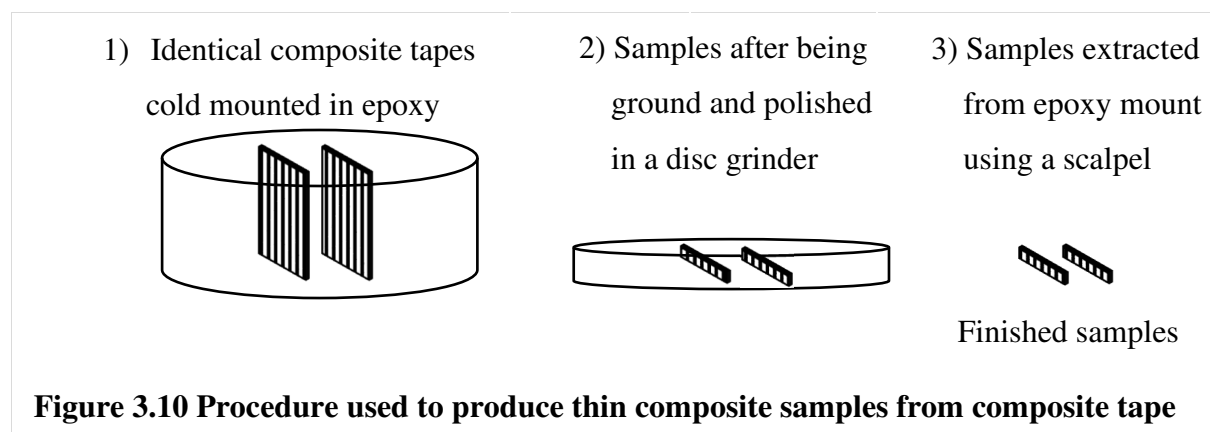
Samples were cut out from the bulk materials by using a Buehler AbrasiMet 250 bench top abrasive cutter, hacksaw, heavy-duty hand shears, and a scalpel. Those tools were used to cut the samples which originated from either a tape or neat polymer sheet, into coupons of approximate dimensions 5 mm (length) $\times$ 0.25 to 0.5 mm (width) $\times$ 40 mm (depth), as shown in Figure 3.8a. In addition, thin G/PP and C/PA12 composite samples were prepared from the pipe specimens by grinding, polishing, and cutting the composite layer in those specimens to dimensions of approximately 5 mm (length) $\times$ 0.25 mm (width) $\times$ 0.04 to 0.14 mm (depth), as shown in Figure 3.9. That was achieved by hand using a Gatan disc grinder (Model 623). The disc grinder was used in combination with silicon carbide abrasive papers of grit #180 to #4000 (supplied by Struers). The target thickness of the C/PA12 specimens that were destined to be tested in the nanoindenter was 50 μ m. Likewise, the target thickness of the G/PP specimens was 70 μ m. The G/PP and C/PA12 tapes were narrow (250 to 500 μ m wide) and prone to split as they were ground and polished down to that target thickness. To prevent that outcome, the samples that were cut from tapes were cold mounted in epoxy, with the fibres orientated vertically, before being ground and polished down to the target thickness (That process is illustrated in Figure 3.10). Transparent epoxy resin was used because it permitted visual confirmation that the samples remained identically orientated after they were encapsulated in the cured epoxy resin. Plus, its transparency facilitated viewing of the samples from the side so that their thickness could be measured as they were ground and polished down. Identical pairs of specimens from the tapes were ground and polished in the epoxy cold mount simultaneously. That was to ensure that the specimens in each pair had identical thickness and were subjected to the same processing conditions in terms of grinding speed, polishing duration, and the amount of force used to grind the samples. Additionally, those procedures enhanced the validity of interface shear strength comparisons between specimens that had been aged under different environmental conditions and mechanically tested at different temperatures. After the specimens reached the target thickness, a scalpel was used to cut them out of the epoxy cold mount. For the experiments wherein one of the specimens out of a pair had been hygrothermally aged, both specimens were mounted to the same SEM stub in

preparation for push-out tests. That allowed their mechanical properties to be compared under identical environmental and operating conditions (see Figure 3.12).

An Olympus BX51 optical microscope was used with Olympus Stream Essentials software to measure the final thickness of the thin composite specimens. Those composites were mounted on SEM sample stubs, using one of the methods outlined in Chapter 3.3.1. Then they were individually inserted into an Alemnis nanoindenter which was subsequently placed into a Quanta 650 FEG scanning electron microscope. It generated high-resolution images of the composites, which were used to confirm their thickness and condition in greater detail.

Each composite specimen that was selected to be tested in the nanoindenter was paired with a counterpart coupon of the same material. As explained in Chapter 3.2, the coupons were aged, and their weight was recorded during that process. Thus, they were used as proxy entities to monitor the ageing process in their counterpart, which was made from identical materials and aged under the same environmental conditions.

Lastly, various experiments, based on nanoindentation, push-out tests, and hybrid-push tests, were performed on the composites at a range of temperatures in-situ with scanning electron microscopy.



3.3.1 Procedures used to mount composites to substrates

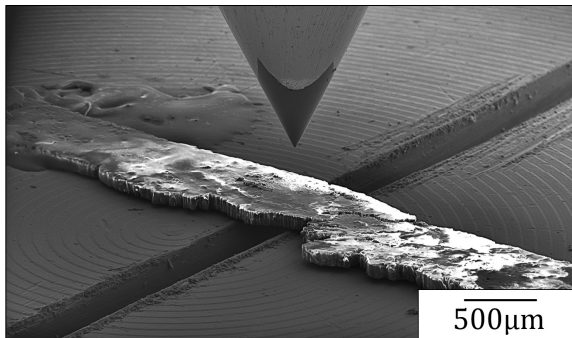
One of three different methods was used to mount each composite specimen to a SEM specimen stub in preparation for micromechanical tests. Either it was secured using a wax substrate, silver-epoxy paste combined with a TEM grid, or adhesive carbon tape combined with a TEM grid. The mounting method used was dependent on whether the experiment was due to be based on hybrid-push tests, push-out tests conducted at room temperature, or push-out tests conducted at elevated temperatures, respectively. Those materials would not outgas at higher temperatures nor while being held in the SEM chamber under vacuum pressure. That helped to prolong the life of the microscope and aided the generation of high-resolution images. Also, silver-epoxy paste and carbon tape are electrically conductive. That helped to ensure that the samples did not become excessively charged by the electron beam of the SEM microscope, which would have reduced the quality of the images it produced.

Samples mounted using adhesive carbon tape

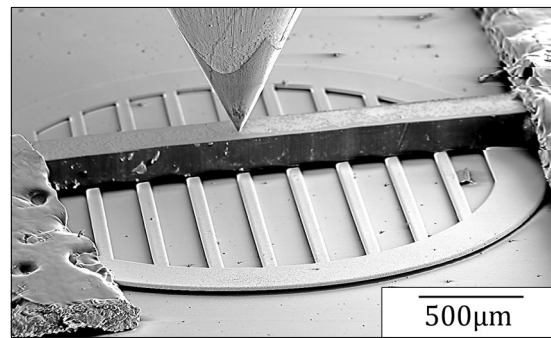
The conventional method that researchers use to mount composite specimen in preparation for push-out tests is to secure the composite over a flat surface which has a single groove [11, 227, 228]. The purpose of the groove is to provide space for each pushed fibre to protrude from the bottom surface without obstruction. In this work, composite samples were mounted to a surface with a single groove at first as per the conventional method. Then that method was improved by mounting the samples to a TEM grid (see Figures 3.11 and 3.12)

Mounting composite samples on a TEM grid, rather than over a surface with a single groove, provided several valuable advantages. For example, around four to eight times more fibres could be push-out tested per sample. That allowed more data about the shear strength of interfaces in each specimen to be gathered, which reduced the number of specimens that needed to be machined to fit the nanoindenter, and aged in some cases, in order to gather a sufficient volume of data from push-out tests. It also facilitated access to a greater number of fibres that were located in regions of high fibre density and low fibre density. That was useful for subsequent experiments in which the effects of fibre constraint on interfaces, and cumulative damage to the interface caused by the shear failure of neighbouring fibres, was assessed (see Chapters 4.2 and 4.5, respectfully). Furthermore, it was especially useful for experiments in which composites were push-out tested at elevated temperatures. That is because, during those tests, heat caused the samples to expand and bow upwards and away from the grooves (as

shown in Figures 5.1, 5.6 and 5.7). Usefully, because samples were fixed to the TEM grid at both ends, those ends were closest to the grooves. Hence push-out tests were conducted at those ends of the sample to minimise the influence of sample compliance on the stress-displacement curves produced from the tests. That solution could not have been carried out if the centre of the specimens were placed over a single groove, in accordance with the conventional method for mounting samples for subsequent push-out tests.



(a) Conventional method, single groove



(b) Improved method, multiple grooves

Figure 3.11 Composites mounted using the (a) conventional and (b) improved method

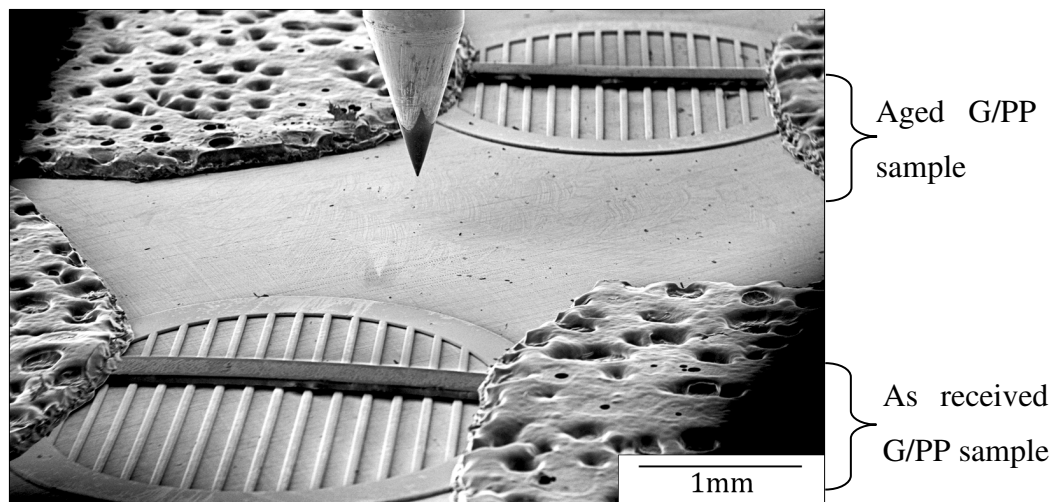


Figure 3.12 Aged and as-received G/PP samples, mounted using carbon tape

Samples mounted on wax

In this work, a hybrid-push test method was devised. This type of test regards pushing fibres into a soft substrate, such as wax or a different type of soft solid, rather than into air or a vacuum which is the conventional method. Subsequently, an experiment was conducted to investigate the hybrid-push method. That experiment was used to explore the advantages and drawbacks of the test method, ways to improve the test method, and potential unique use cases for the test.

A G/PP sample was push-out tested, then mounted upon wax and hybrid-push tested. After that, the interfacial shear strength values generated from both tests were compared. The wax used was QuickStick temporary mounting wax. It was softened at 50°C on a hot plate and then pressed onto a SEM sample stub. Next, the G/PP sample was pressed into the wax with the fibres orientated vertically. Figure 3.13 shows the G/PP sample after it was push-out tested and then mounted upon the wax so that it was ready for hybrid-push tests.

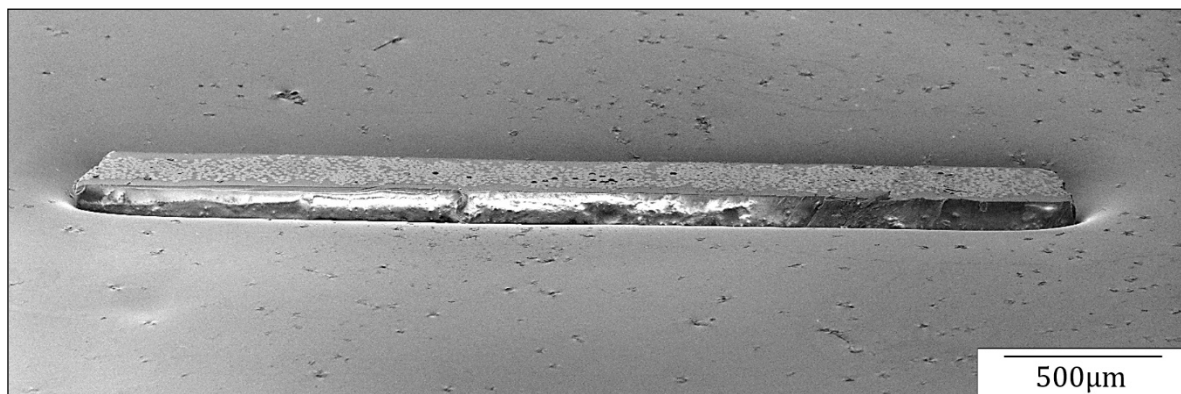


Figure 3.13 G/PP sample mounted on wax

This setup was used to investigate:

- How a soft substrate might reduce sample compliance during push-out tests
- The effects of soft substrates on load-displacement profiles

Samples mounted using silver-epoxy paste

Composites that were selected to be push-out tested at elevated temperatures were secured onto a grooved TEM grid by using a two-part silver conductive adhesive epoxy paste (see Figure 3.14). Once cured, the silver-epoxy paste would not soften or degrade when heated to 120°C, which was the highest temperature used during mechanical tests.

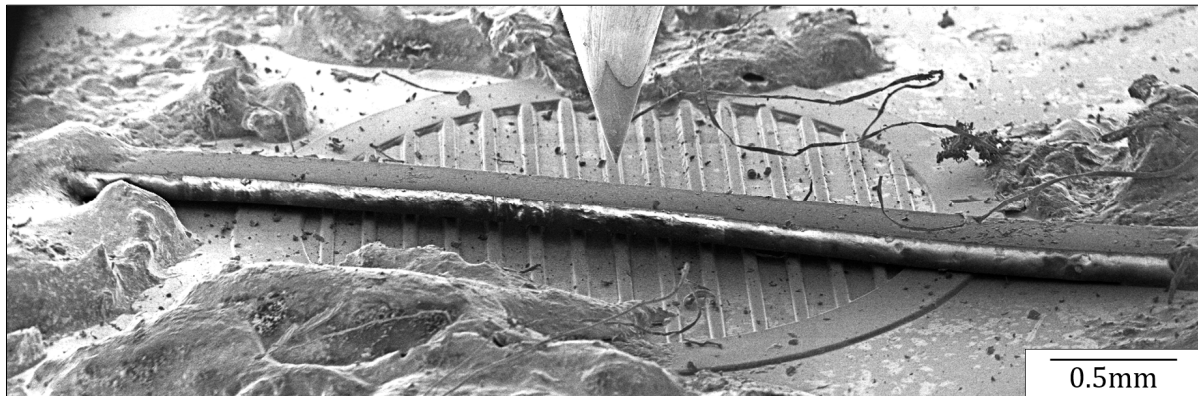


Figure 3.14 G/PP sample mounted using silver-epoxy paste

This setup was used to investigate:

- How the interfacial shear strength of G/PP is affected by long term ageing at elevated temperatures in water
- How far the interfacial shear strength of G/PP will recover after it is heated from 30°C to 70°C and then cooled back to 30°C.
- The effect of temperatures ranging from 30°C to 120°C on the shear strength and mechanical behaviour of interfaces in G/PP and C/PA12.

3.4 Interface test apparatus and experiment procedures

Interface shear strength tests were carried out using an Alemnis nanoindenter in-situ with a scanning electron microscope and controlled temperatures which reached a maximum of 120°C. Figures 3.14 and 3.15 show the apparatus setup. Each test was video recorded. The nanoindenter was used in conjunction with a 50 g calibrated load cell supplied by Honeywell. It was also equipped with a diamond flat-tipped punch which was used to probe samples. The distance between the sample and the flat punch was adjusted by a motorised stage. The sample stage in the SEM was used to move the sample in the x and y directions. A piezoelectric

actuator conducted subtle movements. Piezoelectric actuators are devices that can produce small movements with a high speed and strong force when a voltage is applied. The nanoindenter was operated under a displacement-controlled mode. In general, carbon fibres were pushed out at a displacement rate of $0.1 \mu\text{m/s}$, and glass fibres were pushed out at a displacement rate of $0.2 \mu\text{m/s}$. Following that, the flat punch was retracted at double the velocity of that which it was protracted. An exception is that during experiments regarding the viscoelastic behaviour of interfaces (Chapter 4.4), glass fibres were pushed out at displacement rates of 0.1, 5, and $10 \mu\text{m/s}$. In each experiment, after the target fibre was pushed out, the flat punch was retracted at double the velocity of which it was protracted.

Micromechanical tests were conducted in-situ with a Quanta 650 FEG scanning electron microscope (SEM). The microscope was operated with xT microscope server software, a 2 kV accelerating voltage, and a secondary electron detector. The nanoindenter was secured within the sample chamber of the SEM at a 30-degree angle. That allowed flat punch movements and the progress of fibre debonding to be observed without obstruction. Every test was viewed in real-time and video recorded, that allowed visual confirmation of how compliant each composite was during the test, where matrix deformation/cracks appeared during fibre debonding, and how that corresponded to quantitative load-displacement data.

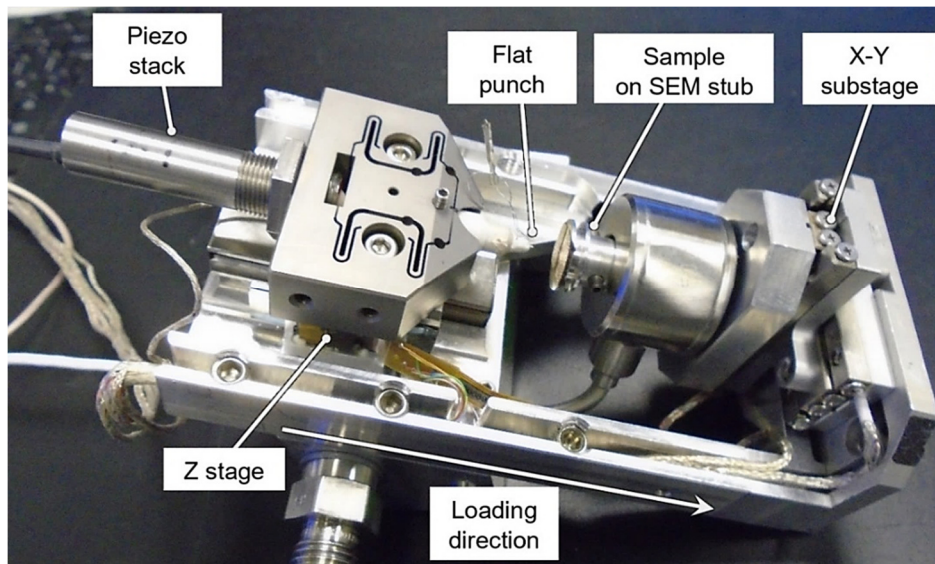


Figure 3.15 Alemnis nanoindentation instrument and details of its components

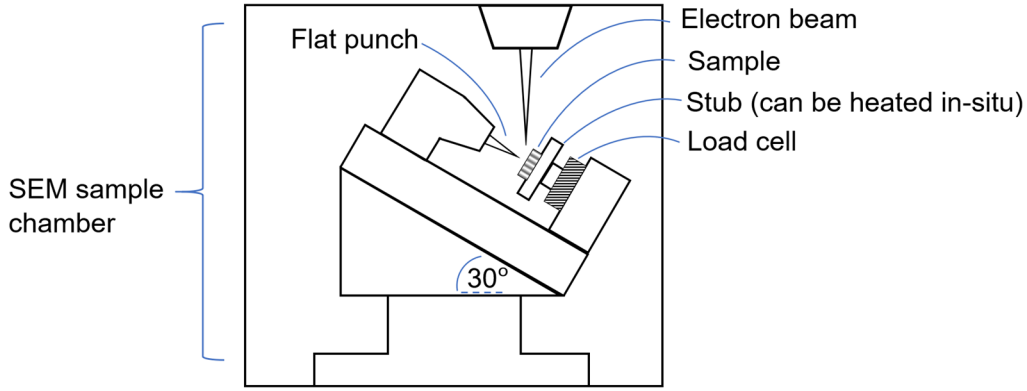


Figure 3.16 Schematic of the nanoindenter setup within the SEM

The nanoindenter was tilted by 30-degrees with respect to the horizontal plane. Also, the microscope provided a top-down view of the samples within it, as Figure 3.16 illustrates. Consequently, vertical measurements of the samples, when observed through the microscope, were shorter than in reality. To solve that issue, the xT microscope server software was set to account for the tilt. Additionally, its vertical measurements were manually checked using trigonometry via Equation 3.8.

$$\text{Actual vertical distance} = \frac{\text{Measured vertical distance}}{\cos(x)} \quad 3.8$$

Where x is the degree to which the specimen is tilted with respect to the horizontal plane (see Figure 3.6).

The average diameter of the glass and carbon fibres was dissimilar, being around 16 μm for the glass fibres and 6 μm for the carbon fibres. Because of that, flat punches of different dimensions were used in the nanoindenter. In most cases, a conical punch with a 3.5 μm diameter flat tip was used to push the carbon fibres, whereas a flat punch with a 10 μm diameter tip was used to push the glass fibres. An exception is that a cylindrical flat punch with a 3.5 μm tip was used to push the carbon fibres that were push-out tested during experiments in which the interface was mechanically damaged in increments (Chapter 4.5). The 10 μm flat punch was too wide to push-out the carbon fibres.

Flat punches were used to provide uniform loading of fibre ends which minimized indentation damage before fibre push-out. That may be considered as an improvement over Berkovich and pointed indenters which have been used for push-out and push-in tests in numerous other works [228-230]. The main advantage of using an indenter with a flat tip, instead of an indenter with a pointed tip, was that the flat tip spread the load applied to the

surface of a fibre, over a wider surface area of that fibre, which reduced the depth to which the fibre would have been indented before interface failure occurred. If a pointed indenter had been used instead, that would have increased the measurements of how much indenter displacement was required to cause interface failure. That difference would need to be corrected.

A cylindrical rather than conical flat-tipped indenter was used to carry out push-out tests on C/PA12 during the incremental mechanical damage experiments. That was because the carbon fibres were very narrow, and the conical indenter allowed the fibres to be pushed out to a greater distance before contacting the matrix. This indenter had to be used with exceptional care because it had lower lateral strength than the conical indenters. Another disadvantage was that debris from the matrix, dust and fragments of fibre quickly became trapped around the indenter near its base as it was used and handled. That had the potential to influence the outcome of push-out tests if left unremoved. Nevertheless, the debris was difficult to remove because the tip was narrow at $3.5\ \mu\text{m}$ and weak to bending stresses when compared to the other indenters. Those issues were avoided when the conical flat-tip indenters were used, so they were used for most micromechanical tests. Figure 3.17 illustrates the nanoindenter geometries that have been described in this chapter. The nanoindenter geometries shown in Figures 3.17b and 3.17c were used during the present work.

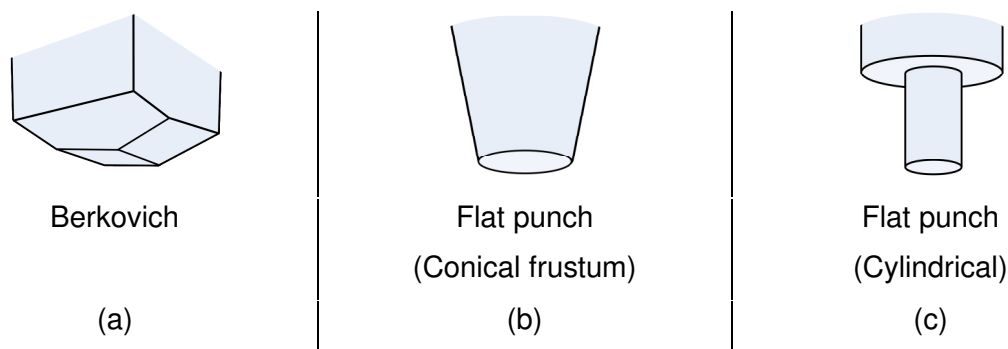


Figure 3.17 Common nanoindenter geometries

3.4.1 Interface shear strength tests conducted at elevated temperatures

Composite specimens were fixed to a TEM grid using silver-epoxy paste during push-out tests which were conducted at elevated temperatures. Further details regarding the mounting method are provided in Chapter 3.3.1. As shown in Figure 3.18, each TEM grid with a sample upon it was individually fixed upon a steel platform. Then the steel platform was attached to a ceramic SEM sample stub. The stub was fitted with a resistance heater and a thermocouple for temperature monitoring and temperature control with the aid of software. A braided copper

wire was wrapped around the base of the stub and fixed to the indentation rig. It dissipated excess heat generated by the heater to avoid that heat from interfering with the nanoindenter's electronics. It also helped to dissipate heat from the specimens which were warmed up to elevated temperatures and then allowed to cool back to room temperature. The heater was operated in open-loop control and in a fixed power mode whereby upon increasing the voltage sent to the heater, it increased in temperature. Before each push-out test began, the temperature measured by the thermocouple was left to stabilise within a range of $\pm 0.1^\circ\text{C}$ of the target temperature for at least 10 minutes. Also, the indenter was placed to rest upon the sample for at least 5 minutes before each push-out test commenced to help bring the flat punch and the specimen to identical temperatures, that mitigated thermal drift, which would otherwise shift load-displacement measurements due to the expansion/contraction of the sample and the indenter upon coming into contact with one another. C/PA12 composites were push-out tested at 30°C (room temperature), 80°C and then 120°C , whereas G/PP composites were push-out tested at 30°C , followed by 70°C and then 30°C again.

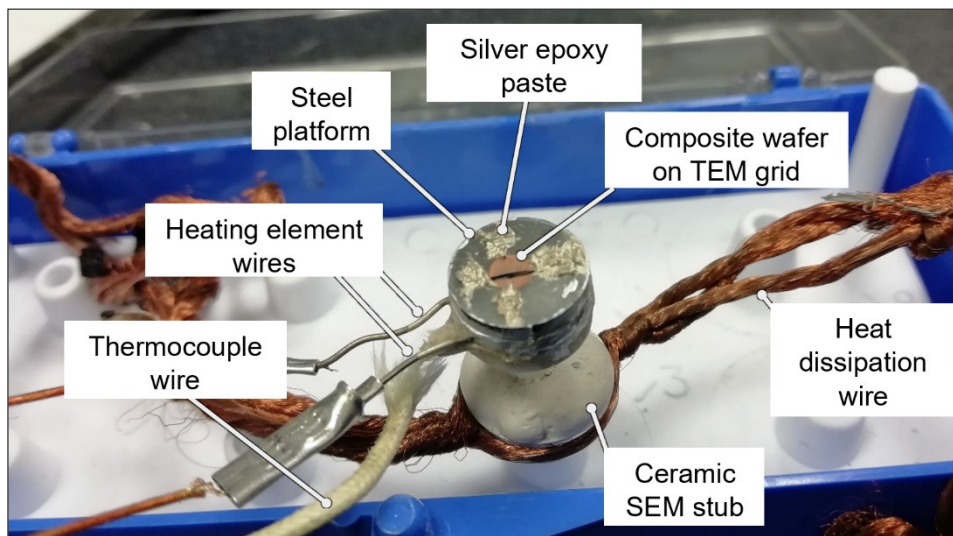


Figure 3.18 C/PA12 sample mounted for push-out tests at elevated temperatures

3.4.2 Fibre selection criteria for interface shear strength tests

For consistency, the fibres that were pushed using the nanoindenter had a similar diameter to each other and were located in regions of high fibre density. A region of high fibre density was defined as one in which fibres were hexagonally packed and located within a distance of $4\ \mu\text{m}$ from the perimeter of the fibre that was pushed by the nanoindenter. The fibres which were pushed by the nanoindenter were always surrounded by six neighbouring fibres (see Figures 3.18 and 3.19).

An exception to that method of selecting fibres was made when the experiment which was conducted to investigate the influence of fibre constraint on the mechanical behaviour of interfaces was performed (Chapter 4.4). In that experiment, fibres were also pushed out from regions of low fibre density. A region of low fibre density was defined as one in which local fibres were not hexagonally packed around the pushed fibre and were located at a distance of least $8\text{ }\mu\text{m}$ away from the perimeter of the pushed fibre (see Figure 3.19).

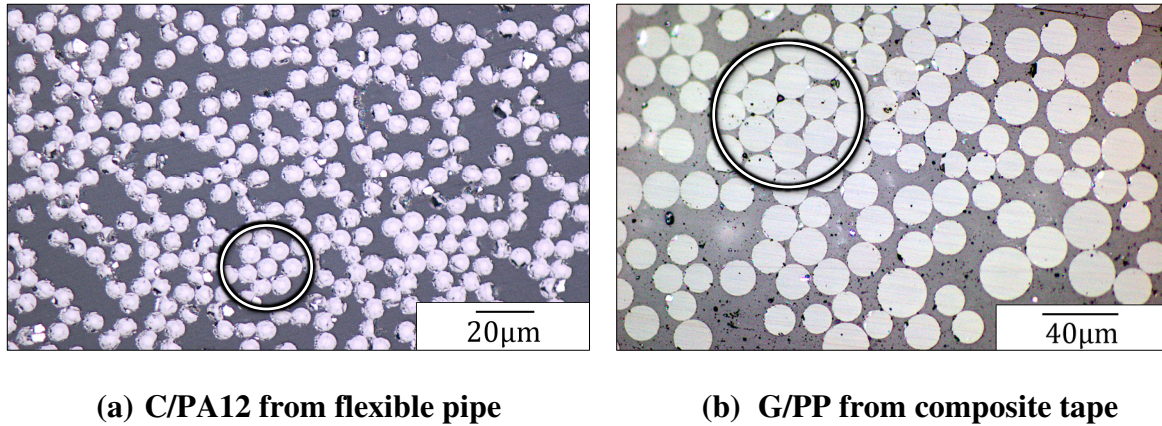


Figure 3.19 Fibre packing in (a) C/PA12 and (b) G/PP specimens

A region of high fibre density and hexagonal fibre packing is circled in Figure 3.19a and 3.19b

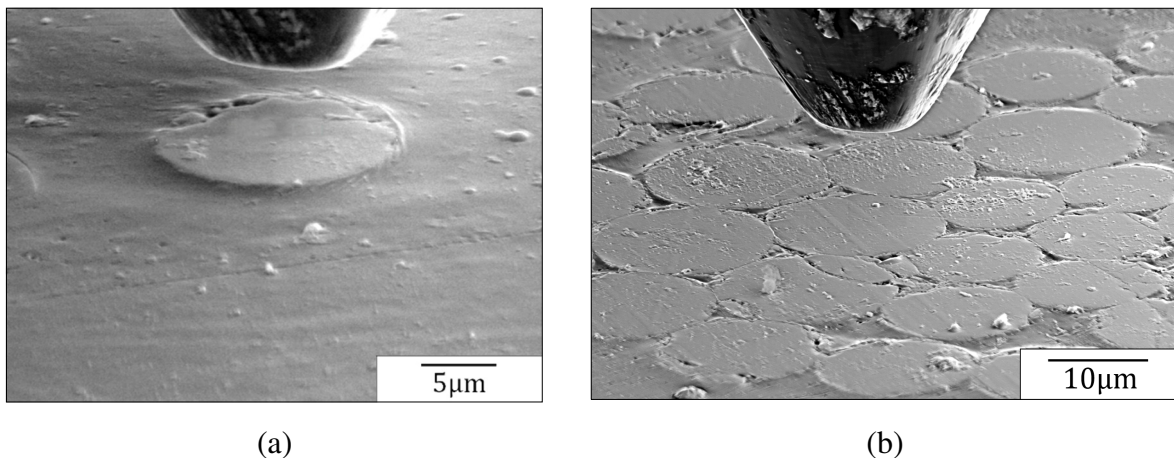


Figure 3.20 Regions of low (a) and high (b) fibre density in a G/PP composite

3.4.3 Induction and analysis of incremental interface damage

As explained in Chapter 2.5, flexible composite risers are often continuously exposed to a range of dynamic and alternating stresses that will gradually damage the pipe. That can occur due to mechanisms such as thermal cycling, vortex-induced vibrations, and pipe sway. Therefore, to investigate the effects of incremental mechanical damage on interfaces in composite materials, the following experimental procedure was conducted.

Neighbouring fibres in G/PP and G/PP specimen were push-out tested in groups, as shown in Figures 3.21 to 3.24. Fibres 1, 2, and 3 were pushed out first. That was done so that they damaged the interface surrounding their neighbouring fibres, 4, 5, 6, and 7. Next, fibres 4, 5, and 6 which were located in-between failed fibres 1, 2, and 3, were pushed out, so that they caused further damage to the interface surrounding the central fibre, fibre 7. That fibre, being located within the centre of failed fibres 1 to 6, was pushed out last. Load-displacement data was recorded during each push-out test and used to produce stress-displacement curves, with the employment of Equation 2.11.

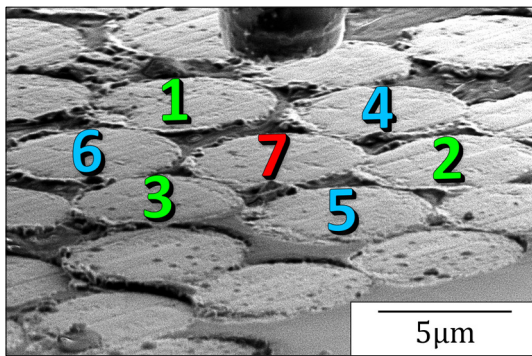


Figure 3.21 C/PA12 before fibres were pushed-out in numerical order 1 to 7

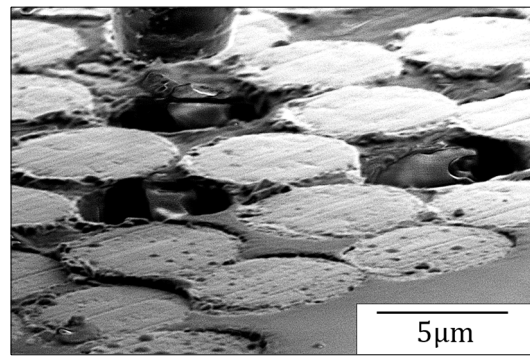


Figure 3.22 C/PA12 after fibres 1, 2 & 3 were pushed out

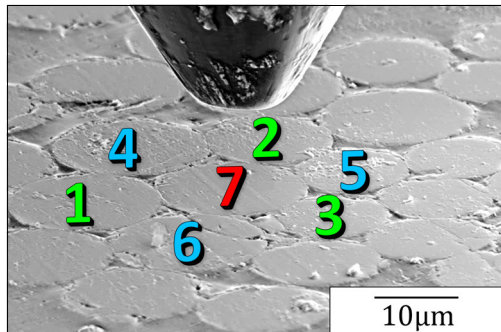


Figure 3.23 G/PP before fibres were pushed out in numerical order 1 to 7

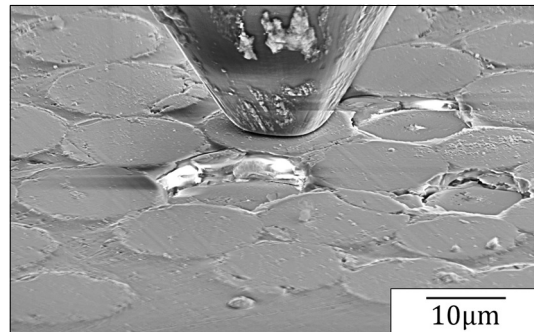


Figure 3.24 G/PP after fibres 1, 2 & 3 were pushed out

3.4.4 Differential scanning calorimetry analysis of polypropylene

Differential scanning calorimetry analysis was conducted on polypropylene specimens to identify their tacticity and crystallinity. Differential scanning calorimetry analysis (DSC analysis) is a thermoanalytical technique that is used to study the behaviour of materials as a function of temperature or time. It is often used to assess the melting point and glass transition temperature of polymers which is a reliable indicator of their crystallinity [199].

A DSC instrument measures the energy required to heat a sample at a constant rate. Figure 3.25 is a diagram of the differential scanning calorimetry technique. When analysing a sample using DSC, an empty reference crucible and a specimen in another crucible are heated or cooled at the same rate. As that happens, the difference between the heat flow supplied to the sample and the reference is recorded and plotted.

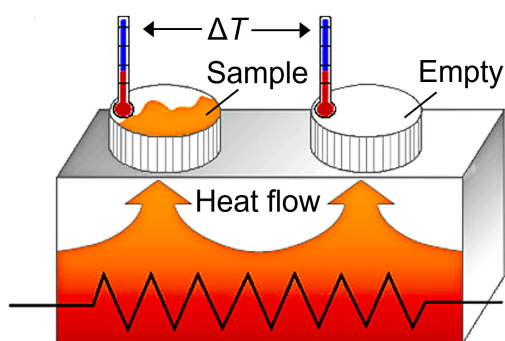


Figure 3.25 Diagram of the differential scanning calorimetry technique [231]

Differential scanning calorimetry was performed on G/PP, PP, and PA12 specimens using a Mettler-Toledo 821 DSC with STARe software. The DSC instrument was operated in the temperature range of 25°C to 300°C with heating and cooling rates of 20°C/min. Specimens were weighed on a Mettler Toledo analytical balance and reduced in size using a scalpel until they weighed 5 mg. Next, the samples were individually placed into crimped aluminium DSC sample pans which each had a pierced cover for nitrogen circulation. A 50 ml/min flow of nitrogen gas was maintained over the samples in the pans to create a dry, inert and reproducible atmosphere which prevented oxidative degradation. An empty reference pan was used to perform a blank run and calibrate the system before DSC scans took place.

Table 3.5 states the thermal program that was used for DSC analysis of the samples.

Polypropylene based specimen

- Pipe jacket (PP)
- Pipe reinforcement layer (G/PP)
- G/PP (from tape)

First heating scan

- Heat from 25°C to 300°C
- Hold at 300°C for 5 minutes

Cooling scan

- Cool from 300°C to 25°C
- Hold at 25°C for 5 minutes

Second heating scan

- Heat from 25°C to 300°C
- Hold at 25°C for 5 minutes
- Cool from 300°C to 25°C

(a) Polypropylene based specimen

Polyamide 12 based specimen

- PA12 (from PA12 sheet)

First heating scan

- Heat from 25°C to 240°C
- Hold at 240°C for 5 minutes

Cooling scan

- Cool from 240°C to 25°C
- Hold at 25°C for 5 minutes

Second heating scan

- Heat from 25°C to 240°C
- Hold at 25°C for 5 minutes
- Cool from 240°C to 25°C

(b) Polyamide 12 based specimen

Table 3.5: Thermal program that was used for DSC analysis of specimens

3.4.5 Tensile tests conducted on polyamide 12

Tensile tests were conducted on polyamide 12 to assess the effects of hydrothermal ageing on the mechanical properties of the polymer. Polyamide 12 was tensile tested in its state as received as well as after it had aged in distilled water at 100°C for 1, 3, 8, 24, and 72 hours.

The samples were cut from a sheet of polyamide 12 using a vertical milling machine so that they reached the dimensions shown in Figure 3.26, ± 0.3 mm (the samples were 0.5 mm thick).

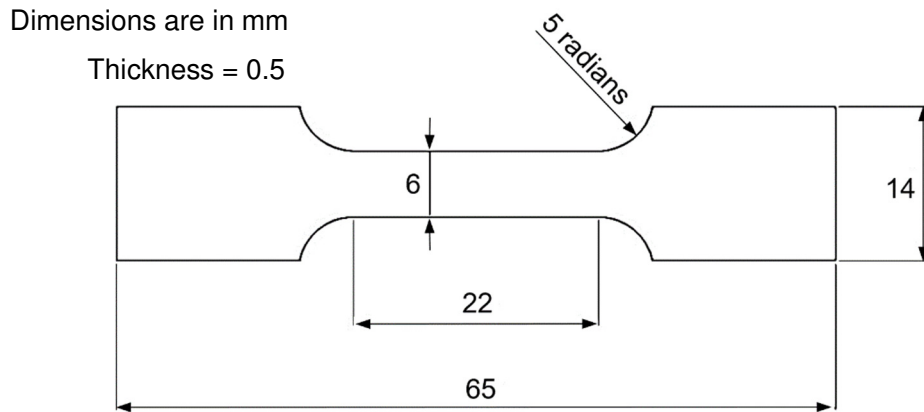


Figure 3.26 Dimensions of the polyamide 12 specimens that were tensile tested

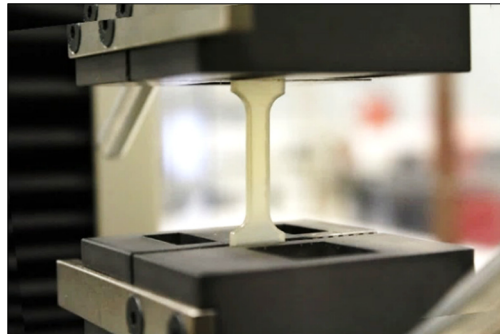


Figure 3.27 Polymer sample in the tensile testing machine

Polyamide 12 was tensile tested using a ZwickRoell Z010 universal tensile testing machine that was equipped with a 10 kN load cell. It was operated with a constant crosshead speed of 5mm/min, and tests were run with no preload. The gauge length between the jaws of the tensile tester at the start of each test was maintained at 45mm. Load and strain data were recorded using testXpert II software, and that data was used to generate stress-strain plots. Subsequently, engineering strain and engineering stress values were calculated using Equations 2.12 and 2.13, respectively, from which the tensile properties of the samples were determined.

3.5 Data treatment

Samples that are mounted upon a solid grooved substrate in preparation for push-out tests are not customarily placed flush and in constant contact with the upper surface of the substrate. That is because it tends to be challenging to prepare completely flat samples and mount them with submicron precision. The sample or the substrate may be slightly curved, even by less than a micron, which will affect load-displacement profiles. For example, that will cause a long trail in the load-displacement profile generated from a push-out test before the interface undergoes significant elastic deformation (see Figure 2.32, stage B-C).

In this work, shear stress-displacement curves generated from push-out tests were extrapolated when the sample was not flush with the substrate. Thus, to assist data analysis and to produce clearer plots, a line was drawn parallel to the modulus of the interface in the elastic region, as illustrated in Figure 3.28. The point at which that extrapolated line intersected with the x-axis (displacement axis) of the shear stress-displacement plot was redesignated as the origin of the plot. Subsequently, the plot was drawn from the new origin, whilst data preceding the new origin and the extrapolation line was omitted. Additionally, in some of the plots which feature multiple curves, data that was recorded during the unloading portion of the push-out test was omitted to keep the plot clear.

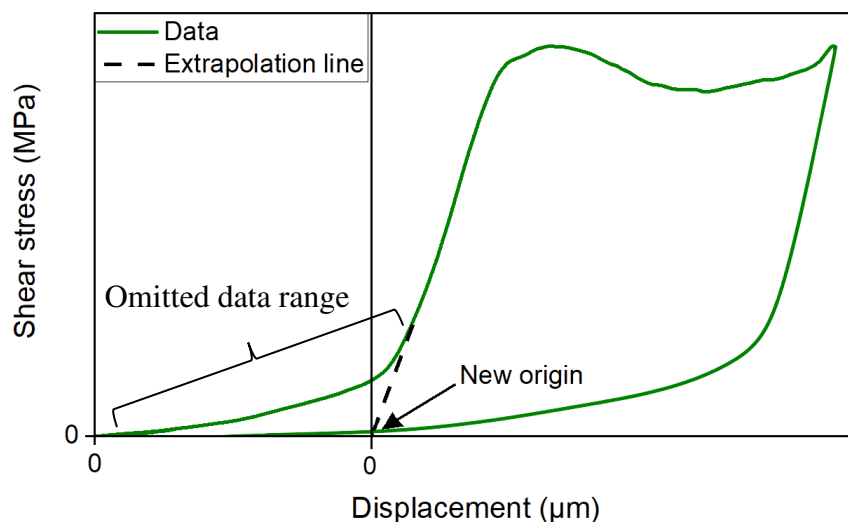


Figure 3.28 Illustration of how data treatment was performed

Figure 3.29 shows the outcome of conducting the data treatment procedure on a sample of G/PP that was push-out tested at 30°C and 70°C. Some of the stress-displacement curves have been omitted from the figure for clarity; Figure 5.8 features all of the curves.

At the start of the experiment, the sample was not flush with the substrate. It was out of the displacement range of the nanoindenter's piezo controlled actuator, which was employed to facilitate automatic and subtle movements of the flat punch. As a solution, the sample was manually pushed down with the flat punch while the applied load was recorded. Because of that, the shear stress values in Figure 3.29a begin slightly above zero.

In Figure 3.29b, the displacement values shown on the x-axis are reduced because of data extrapolation, and the shear stress values remain the same. This data extrapolation procedure has two main advantages. Firstly, it eliminates unnecessary data from stress-displacement profiles. Secondly, it can bring multiple stress-displacement curves closer to each other on charts which makes it easier to compare them.

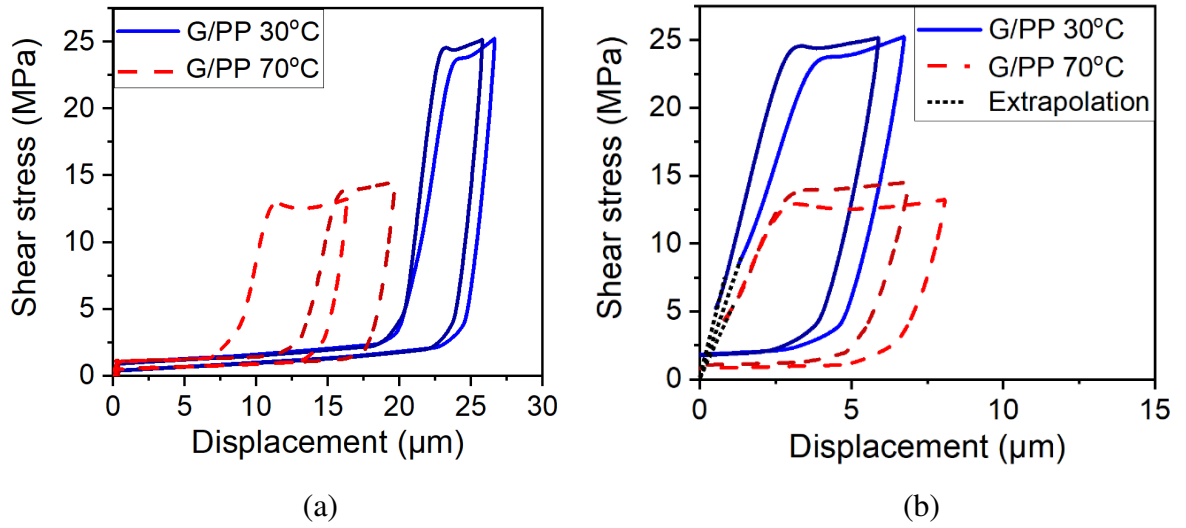


Figure 3.29 (a) original and (b) extrapolated IFSS profiles of G/PP, push-out tested at 30°C and 70°C

The G/PP used in this experiment was extracted from G/PP tape.

4. CHARACTERISTICS OF POLYMER COMPOSITES AT ROOM TEMPERATURE

This chapter presents findings regarding the characteristics of G/PP and C/PA12 composites at room temperature. It covers investigations that were conducted to; determine the tacticity of glass/polypropylene and polypropylene specimens (4.1), find the effect of fibre constraint on interface failure behaviour (4.2), develop and utilise a technique named the hybrid-push test as well as simulate different substrates for push-out tests (4.3), provide insight into the viscoelastic behaviour of interfaces in thermoplastic composites (4.4), and develop a method to incrementally damage interfaces while measuring their interfacial shear strength (4.5).

4.1 Tacticity of glass/polypropylene and polypropylene

Differential scanning calorimetry (DSC) was used to measure the melting point of the polymeric phase in each polypropylene-based specimen. Specifically, the reinforcement layer of the G/PP pipe (made of G/PP), the jacket of the G/PP pipe (made of PP), the G/PP tape, and a standard PP sheet. That data was used to find the tacticity and crystallinity of those materials. The device was programmed to heat each sample past its melting point twice and produce thermograms of the results. The first heating scan removed residual solvents from the polymer and erased its thermal history. The second heating scan revealed the temperature range in which the sample melted. The melting point (primary melting point) was determined from the peak of the heat flow/temperature curve in each thermogram (see Figures 4.1 to 4.4. and Table 4.1).

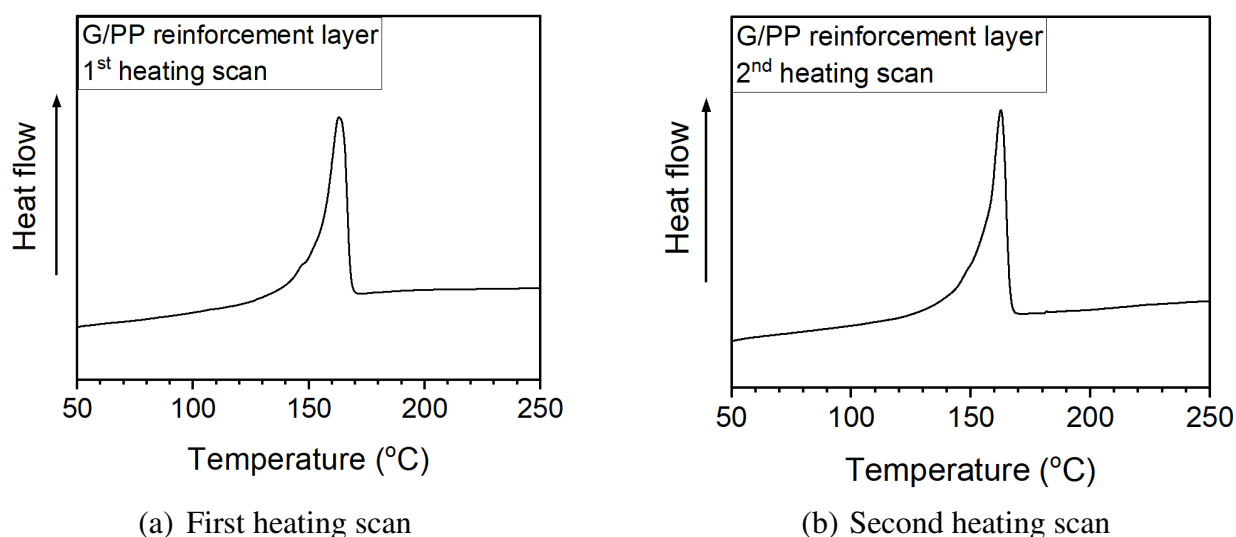


Figure 4.1 DSC heating scans of G/PP, extracted from a G/PP pipe

The melting point of the G/PP reinforcement layer in the pipe was 162.5°C

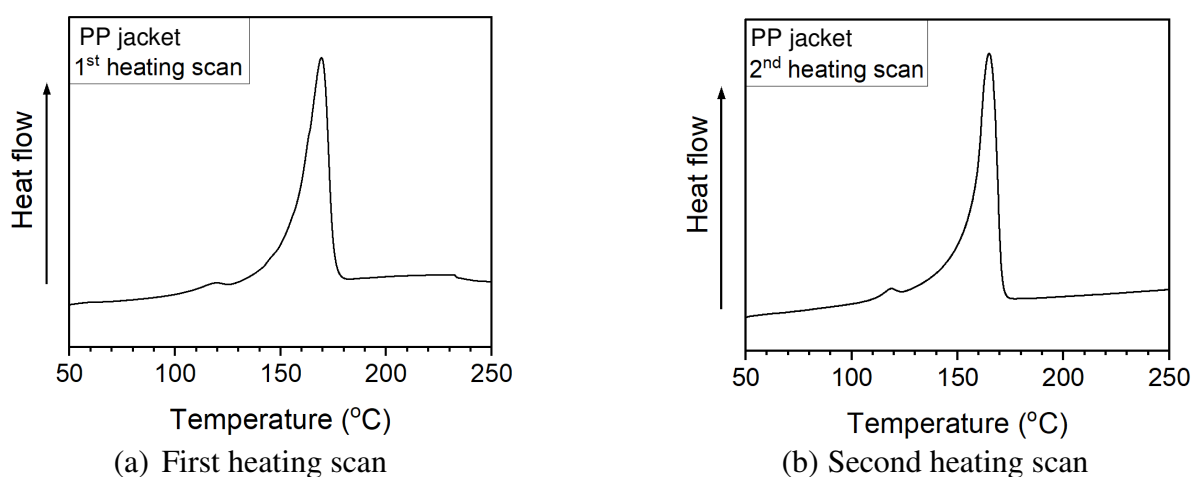


Figure 4.2 DSC heating scans of PP, that was extracted from the jacket of a G/PP pipe

The melting point of the polypropylene jacket was 164.8°C

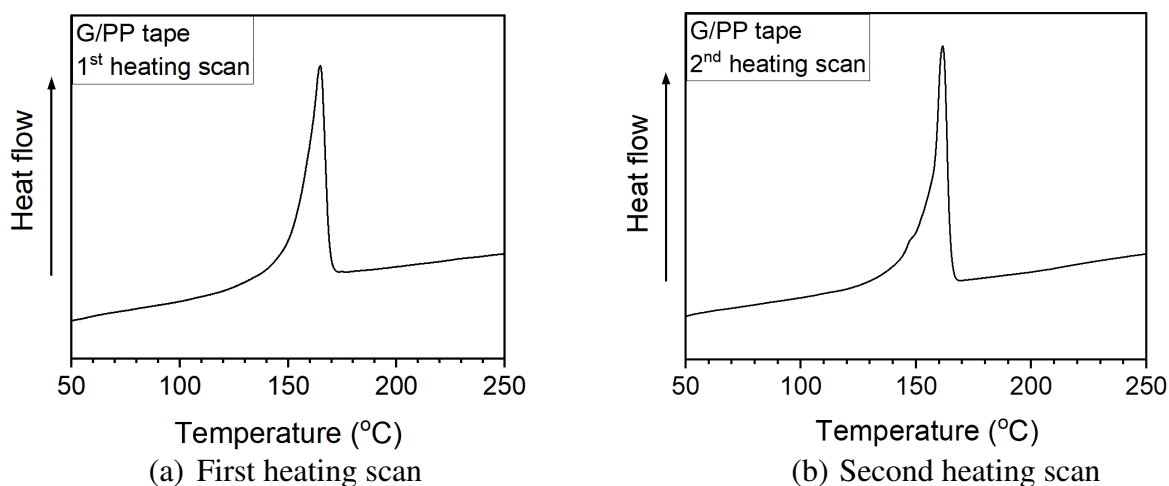


Figure 4.3 DSC heating scans of G/PP tape

The melting point of the matrix in the G/PP tape was 161.6°C

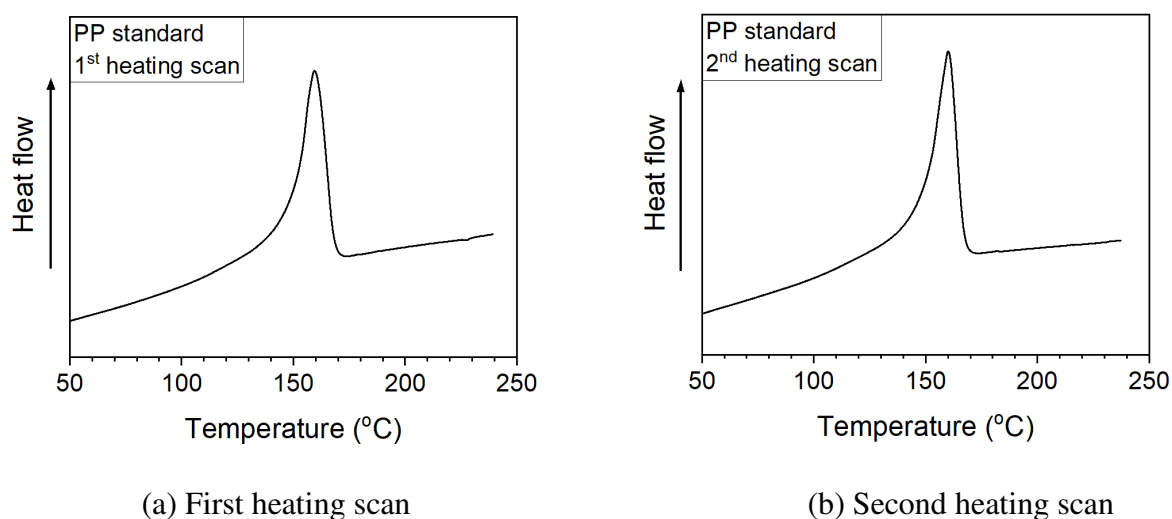


Figure 4.4 DSC heating scans of PP standard sheet material

The melting point of the standard polypropylene sheet was 160.5°C

Specimen (and source)	First heating scan	Second heating scan
	(°C)	(°C)
G/PP reinforcement layer (Pipeline)	163.0	162.5
PP jacket (Pipeline)	169.2	164.8
G/PP (Tape)	164.8	161.6
PP (Standard)	159.5	160.5

Table 4.1 DSC peak temperature (melting point) of polypropylene-based specimens

The polypropylene-based specimens were obtained from commercial sources and had a melting point in the range of 160 to 166°C, which is consistent with the melting point of isotactic polypropylene [62-64, 66]. Also, Tripathi [60] stated that atactic polypropylene “has little strength” and “only isotactic polypropylene has the requisite properties required for a useful plastic material”. With those findings, as well as research on the crystallinity of commercially produced polypropylene published by Crawford et al. [63] and Domininghaus [64]. The glass/polypropylene and polypropylene specimens were determined to be based on isotactic polypropylene and 25% to 75% crystalline.

4.2 Fibre constraint reduced interface shear strength values

Almost all mass-produced composites contain regions of high fibre density, where there are many fibres, and regions of low fibre density, where the presence of fibres is seldom. Therefore, an investigation was conducted in which G/PP and C/PA12 composites were push-out tested in their regions of high and low fibre density, as defined in Chapter 3.4.2. That was to quantify how local fibre density affects the behaviour of interfaces which are under an applied load. Another reason for that endeavour was to support the design of new composites in which the shear strength of interfaces is tailored, based upon the arrangement of fibres in the matrix and the fibre volume fraction.

Figure 4.5 shows stress displacement curves produced by push-out tests in which fibres in G/PP were pushed out from a region of high fibre density, and a region of low fibre density in the composite. During this experiment, fibres were consistently pushed out successfully. Also, before each type of test commenced, two fibres were pushed initially to gauge the correct settings to use on the nanoindenter.

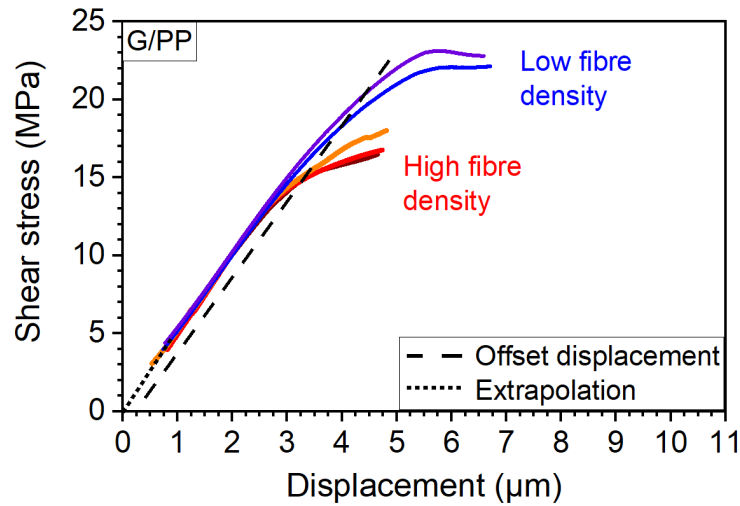


Figure 4.5 IFSS profiles of G/PP pushed-out tested in high and low fibre density regions

During this investigation, the G/PP specimens did not demonstrate a distinct point of interface failure. Therefore, a method was used to determine the interfacial shear strength of specimens which do not show a distinct point of interface failure. That involved utilising an offset displacement to provide an approximation of the point of interface failure. The interfacial shear strength was defined as the stress applied to the interface, which corresponded with the point of intersection between the stress-displacement curve and a line drawn parallel to that curve in the elastic region. The parallel line was horizontally offset by 0.2 μm .

That method of determining the interfacial shear strength is similar to the offset yield strength method, which has been used to determine the yield strength of materials from hardness measurements [232] and tensile strength measurements [233]. In the materials testing industry, the offset value is arbitrarily defined by a material testing standard (e.g. the ASTM or ISO), and it is expressed as a percentage of strain. The amount of offset selected can vary in accordance with the type of material being evaluated,

In this experiment, the fibres that were examined in the regions of high fibre density exhibited an interfacial shear strength of 15 MPa, which was 25% lower than those located in regions of low fibre density. Accordingly, the fibres that were located in regions of low fibre density exhibited an interfacial shear strength of 20 MPa.

4.2.1 Conclusions

Overall, during push-out tests conducted on G/PP, 25% less force was required to cause the interface of fibres located in regions of high fibre density to undergo shear failure, than those located in regions of low fibre density. That is likely because the matrix had greater freedom to yield in regions of low fibre density. Because of that, a greater proportion of the stress that the interface was subjected to was transferred to the matrix.

It is logical that when fibres in a composite are closely packed, the interface surrounding each fibre will have a narrower thickness at points where the fibre is in contact with, or very close to, a neighbouring fibre. Such that, depending on the chemistry, the interface surrounding a single fibre will merge with the interface surrounding a neighbouring fibre due to mutual interdiffusion (as illustrated in Figure 2.33). Thus, the chemistry gradient of the interface surrounding a single fibre will differ where it is merged with the interface surrounding a neighbouring fibre, and the thickness of that interface will be narrower due to its obstruction by an adjacent interface or fibre. If that occurred during the present work, those factors might have contributed to the fibres located in regions of high fibre density, exhibiting low interfacial shear strength. Also, it is thought that narrower interfaces in the regions of high fibre density would have caused the interfacial shear strength to decline in those regions, more than the modified gradient of interface chemistry near adjacent fibres (which may have improved the strength of interfaces). Hence, in the future, investigations regarding how the presence of neighbouring fibres affects the thickness and chemistry of interfaces, would be valuable to bring insight into that topic.

4.3 Investigation of the hybrid-push test method

The hybrid-push test method can be thought of as a combination of a push-out test and a push-in test. This chapter explains how the hybrid-push test was performed upon G/PP and the accuracy of the test. Subsequently, section 4.3.2 details how the accuracy of the test was improved with additional experimental work and mathematical formulae, which led to the invention of a substrate modelling technique. It also suggests practical use cases for the hybrid-push test and substrate modelling technique.

4.3.1 Hybrid-push tests conducted on G/PP

G/PP was push-out tested at room temperature, then the same specimen was hybrid-push tested on a wax substrate. Around six hybrid-push and four push-out tests were attempted. Results from those fibres which were successfully tested are provided in Figure 4.6. The figure shows that the composite exhibited an average interfacial shear strength of 35 MPa when it was hybrid-push tested, whereas it exhibited an interfacial shear strength of 22 MPa when it was push-out tested. Thus, there was a difference of around 45.6% between the shear stress required to cause interface failure in each type of test. That was because some of the load applied to the pushed fibre in the composite was opposed by the wax substrate.

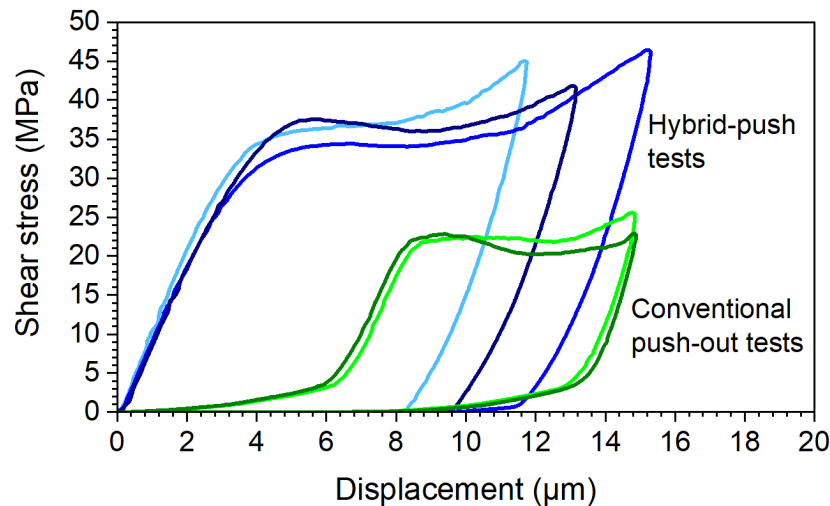


Figure 4.6 IFSS profiles of G/PP, during hybrid-push and conventional push-out tests

The G/PP used in this experiment was extracted from a flexible composite pipe

Figure 4.6 shows that the wax substrate reduced sample compliance, which occurred between 0 μm and 6 μm of indenter displacement during push-out tests. Sample compliance took place during push-out tests because the whole G/PP sample was pushed down by the flat punch until

it became level with the TEM grid. As such, sample compliance was a confounding variable. Hence, it was subsequently omitted from Figure 4.6 to produce Figure 4.7, which represents the modulus of the interface in the elastic region more accurately.

Figure 4.7 is derived from the same data which was used to produce the stress-displacement curves in Figure 4.6. In Figure 4.7, the stress-displacement curves generated from the push-out tests have been manually shifted closer to that of the hybrid-push tests to aid visual comparison of both curves (as demonstrated in Chapter 3.5).

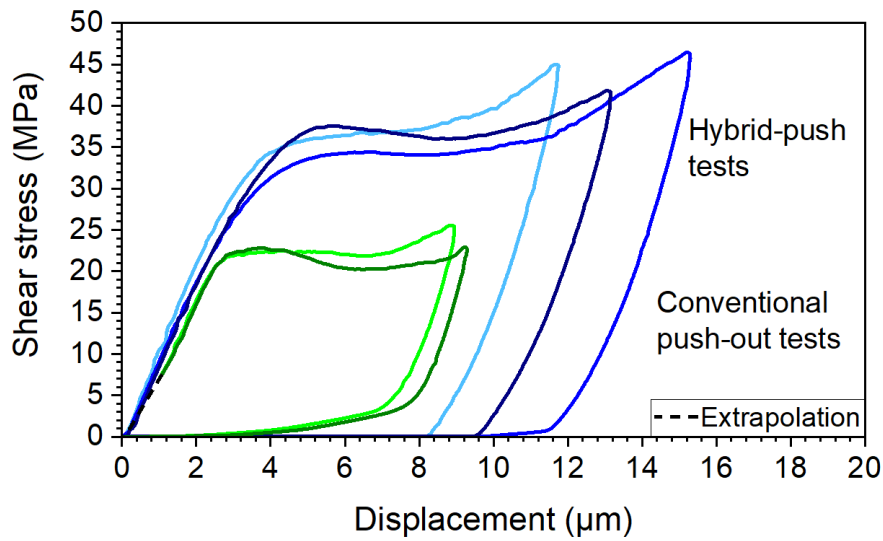


Figure 4.7 IFSS profiles of hybrid-push tested G/PP. Also, extrapolated IFSS profiles of push-out tested G/PP

In the elastic region, during the hybrid-push tests, the shear stress at the interface increased at a rate of 10.0 MPa/μm, whereas it increased at a rate of 8.3 MPa/μm when it was push-out tested in the same region. Thus, the interface appeared to be slightly stiffer when it was hybrid-push tested. That is logical because the wax substrate resisted indentation from the fibres that were pushed into it.

4.3.2 Substrate modelling technique

This section describes experimental procedures and mathematical formulae that were developed and mainly used to improve the robustness of the hybrid-push test method. Those actions led to the production of a semi-empirically derived graph which provided an estimate for the shear stress that would be required to cause interface failure in the hybrid-push tested G/PP sample as if it were absent of a wax substrate. Furthermore, those actions guided the production of a method to simulate push-out tests, as if they had been performed upon a substrate instead of over an empty space. That has potential to improve the ecological validity of experiments based on push-out tests.

The same flat punch that was used for hybrid-push tests and push-out tests on G/PP was also used to indent the wax substrate three times to a depth of approximately 15 μm . Figure 4.8 shows the response of the wax substrate to indentation. The load-displacement response of the wax and the G/PP specimen (mounted on wax) are presented in Figure 4.9.

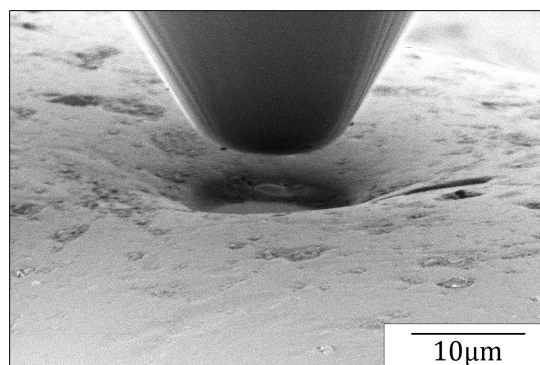


Figure 4.8 Indentation of the wax substrate which was used for hybrid-push tests

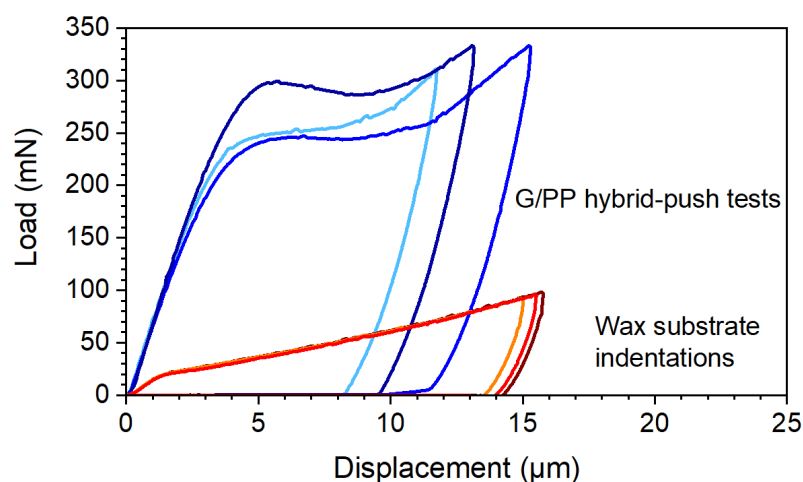


Figure 4.9 Load-displacement curves of G/PP generated from hybrid-push tests.

Also, load-displacement curves of the wax substrate.

The average load that was required to indent the wax substrate, P_s , was subtracted from the load applied to the hybrid-push tested fibre, P_f , at matching distances of indenter displacement (see Figure 4.9). Next, the resultant load values were converted into semi-empirically derived shear stress values, τ_{se} , by means of Equation 4.1.

$$\tau_{se} = \frac{(P_f \pm P_s)}{\pi dh} \quad 4.1$$

Where τ_{se} is the semi-empirically determined interfacial shear stress, P_f is the load applied to the fibre, P_s is the load applied to indent the substrate, d is the fibre diameter, and h is the thickness of the composite.

The term $(P_f - P_s)$ is used to mitigate the influence of a substrate from stress-displacement measurements. Whereas the term $(P_f + P_s)$ is used to simulate the effects that a flat substrate would have on the outcomes of a push-out test.

Figure 4.10 features the same stress-displacement curves for G/PP as Figure 4.7. Though the unloading portion of those curves has been omitted for visual clarity. In Figure 4.10, the dotted lines and straight lines are in pairs of an identical colour. The dotted lines display data corresponding to each fibre which was hybrid-push tested. Likewise, the solid lines of matching colour represent the stress-displacement curve of the same fibre, that curve having been adjusted by simulating the absence of the wax substrate via Equation 4.1. With the use of that equation, the load applied to indent the wax substrate, P_s , was subtracted from the load applied to the fibre, P_f . That led to the generation of semi-empirically derived stress-displacement curves for the hybrid-push test, which simulated the test as if it had been performed without a substrate present.

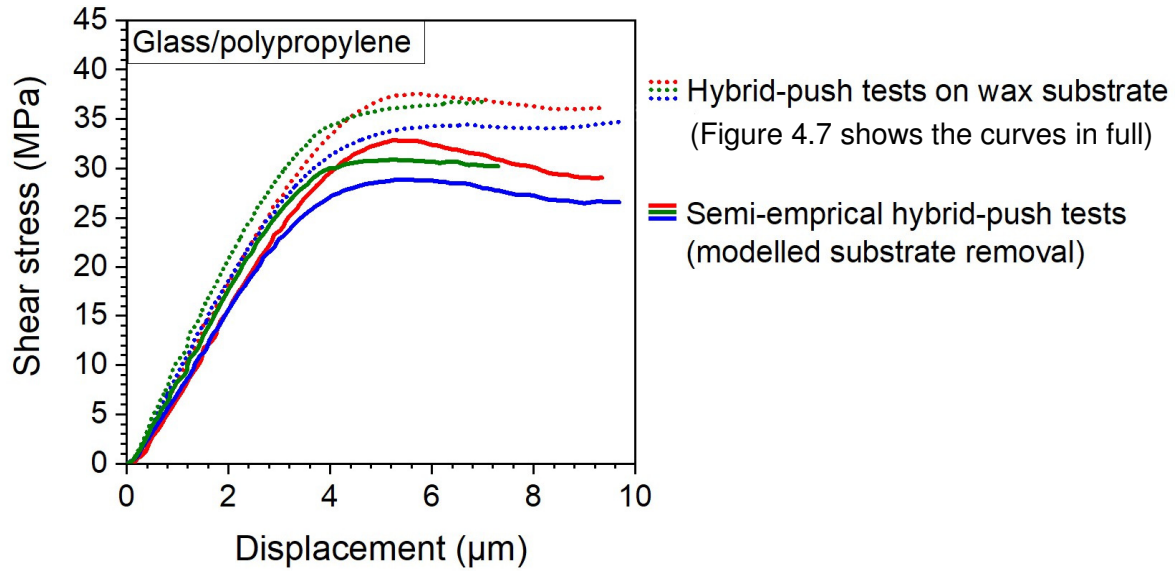


Figure 4.10 Graph of G/P hybrid-push tests results, with and without substrate modelling

Figure 4.10 shows that with the implementation of the substrate modelling technique, the average interface shear strength measured from the hybrid-push test reduced from 35 MPa to 30 MPa. The interfacial shear strength of the same sample, as determined by the push-out test, was 22 MPa (see Figure 4.7). Therefore, the substrate modelling technique reduced the difference between the average interface shear strength values measured in each type of test, from 45.6% to 30.8%.

Furthermore, the trend in the stress-displacement curves matched more closely with that of the specimen when it was push-out tested. Specifically, the point at which interface failure occurred, i.e. the peak shear-stress, became more distinct on the chart. Also, the period of fibre slide out after interface failure was indicated by a steeper stress-displacement gradient. That gradient being around 0.7 MPa/μm on average for the semi-empirically derived hybrid-push test and 0.1 MPa/μm on average for the original hybrid-push test.

Equation 4.1 was subsequently used to forecast how the mechanical behaviour of the G/PP composite would change if it was subjected to hybrid-push tests on an alternative substrate (in this case, the wax substrate). Figure 4.11 shows the outcomes of that analysis.

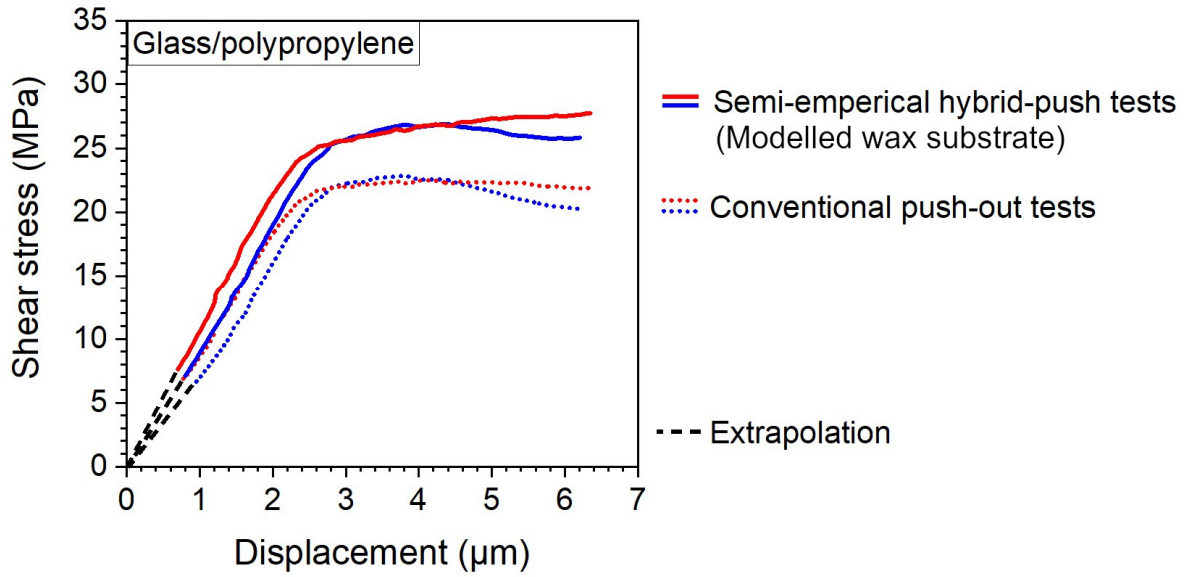


Figure 4.11 Graph of G/PP push-out tests results with and without substrate modelling

Figure 4.11 shows that when Equation 4.1 was utilised on the stress-displacement curves produced by push-out testing the G/PP sample. Those curves became more closely aligned with the stress-displacement curves produced from hybrid-push testing the same sample (see Figure 4.7). On average, the measured interfacial shear strength increased from 22 MPa, in the case of the push-out test, to 25 MPa. The interfacial shear strength of the sample according to hybrid-push tests was 35 MPa, which indicates that the application of Equation 4.1 diminished the difference between the interfacial shear strength measured via the push-out test and the hybrid-push test from 45.6% to 15.4%.

4.3.3 Conclusions

A hybrid-push test method was developed and used to measure the interfacial shear strength of a G/PP composite. The test involved pushing individual fibres out from the G/PP specimen, into a soft substrate; in this case, a wax substrate was used. The test method mitigated sample compliance which often influences stress-strain curves produced during conventional push-out tests. However, the interfacial shear strength values obtained by using the hybrid-push tests were higher than those obtained by conventional push-out tests on the same G/PP specimen. Thus, supplementary experimental procedures were developed to account for the influence of the wax substrate.

Those procedures improved the accuracy of results generated from the hybrid-push tests and provided a way to simulate push-out and hybrid-push tests as though they were performed on various types of substrates or no substrate at all.

For example, hybrid-push tests can be useful for situations wherein a specimen is not suited for conventional push-out tests. The specimen may be too brittle or too soft, such that mounting the specimen over a gap in preparation for conventional push-out tests would lead to problems such as bending or fracture.

As another example, composites that are used as fillings for teeth are designed to bond with tooth enamel, as well as underlying tooth dentine. Those composites must resist being pushed-out or displaced due to intense positive and negative pressures arising from brushing, flossing, chewing, sucking, and biting. Thus, performing hybrid-push tests or push-out tests with substrate-modelling, may provide an effective way to examine the stress-strain response of such composites in a more realistic setting. For instance, a tooth filling in a matrix of tooth enamel could be hybrid-push tested into a sample of the softer underlying tooth dentine or decaying tooth matter that it would be situated on during normal use.

4.4 Viscoelastic behaviour of glass/polypropylene interfaces

When a composite layer inside a flexible pipe is subjected to a hydrostatic overpressure, that composite may fail at the microscale through fibre microbuckling, kinking, and debonding at interfaces [41, 42, 46]. If that happens, a proportion of the load which was initially resisted by the embedded fibres will be transferred to neighbouring fibres which are already under hydrostatic pressure, making them more likely to fail. Subsequently, those fibres fail, and then the total load is transferred to the next neighbouring fibres. That happens repeatedly and contributes to the formation of kink bands, potentially leading to localised pipe collapse. Tianyuan et al. [40] noted that the rate at which a pipe collapses under hydrostatic pressure increases with time. Therefore, it is logical that the interfaces that are embedded within it fail at an increasing rate as well. Hence, this chapter reports an investigation that was conducted to evaluate how the viscoelastic behaviour of interfaces in G/PP changed as they were subjected to a load which was applied at different rates.

Push-out tests were conducted on G/PP (from G/PP pipe) at displacement rates of 0.1, 5, and 10 $\mu\text{m/s}$. Around four attempts were made to push-out test a fibre at each displacement rate. Data from the successful tests are shown in Figure 4.12. The figure shows that, on average, the fibres that were pushed at 0.1 $\mu\text{m/s}$ (the slowest rate) exhibited the lowest shear strength, that shear strength being 24.5 MPa. In contrast, the fibres which were pushed at 5 and 10 $\mu\text{m/s}$ exhibited a higher shear strength, 29.3 MPa and 29.0 MPa, respectively.

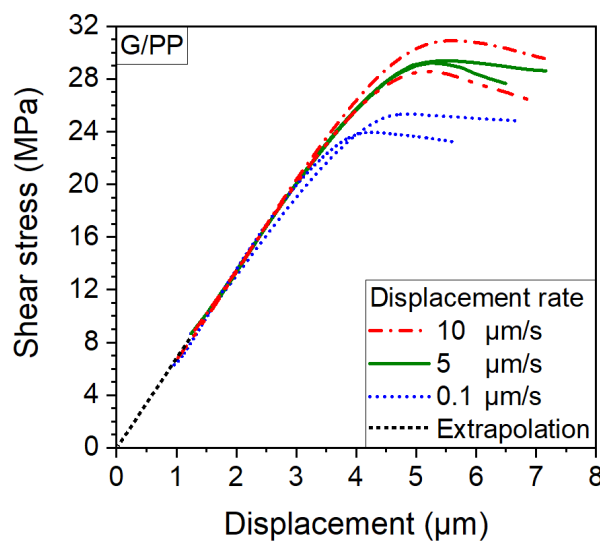


Figure 4.12 IFSS profiles of G/PP tape that was push-out tested at 0.1, 5 and 10 $\mu\text{m/s}$

Figure 4.12 shows that the interfacial shear strength of the G/PP composite increased with faster fibre displacement rates. A probable cause for that outcome is that creep had less time to take place and influence the deformation of the interface.

Creep (sometimes called cold flow) is a time-dependent type of material deformation that occurs at stresses below the yield strength of a material. Viscoelastic materials are affected by creep, and isotactic polypropylene is a viscoelastic material [234]. Therefore, it is likely that the stress which was applied to the interface of G/PP at 0.1 $\mu\text{m/s}$ in this experiment allowed it to creep significantly before failure.

Further insight into the creep behaviour of an interface in a polymer composite can be attained from analysing its behaviour immediately after it undergoes shear failure and is held under a constant load. Gallo et al. [235] took that approach by conducting push-out tests on a sample of carbon fibre-reinforced epoxy in which the pushed-out fibres were held under a constant load. The indenter was operated under a load-controlled displacement-terminated mode. It applied a load to the composite until that load reached 200 mN, or a displacement of 2 μm was reached (whichever condition was reached first). The fibres that were pushed out at 0.1 mN/s had a shorter strain time per unit of dwell time (constant load) than those which were pushed out at faster rates of 1 mN/s and 10 mN/s.

During this present experiment, the fibres that were pushed out at 0.1 $\mu\text{m/s}$ were more resistant to sliding out under friction after failure than the fibres which were pushed out at faster rates. That is evident in Figure 4.12, as after fibre failure, shear stress at the interface of the fibres which were pushed out at 10 $\mu\text{m/s}$ and 5 $\mu\text{m/s}$ decreased at a faster rate than those fibres which were pushed out at 0.1 $\mu\text{m/s}$. After fibre debonding occurred the frictional shear stress, τ_f at the interface decreased at a rate of approximately 1.2 MPa/ μm regarding the fibres that were pushed out at 10 $\mu\text{m/s}$, 0.89 MPa/ μm regarding the fibres that were pushed out at 5 $\mu\text{m/s}$, and 0.11 MPa/ μm regarding the fibres that were pushed out at 0.1 $\mu\text{m/s}$.

In other words, increasing the rate at which fibres were pushed out, by a factor of 50 and 100, corresponded with the frictional shear stress at the interface decreasing 7.9 and 9.9 times faster, respectively. In short, increasing the rate at which load was applied to the fibres, had a small effect of increasing the rate at which frictional shear strength was lost as the fibres slid out from the matrix.

4.4.1 Conclusions

Overall, the results attained from this experiment showed that the interfacial shear strength of G/PP increased with faster rates of applied load, from 24.5 MPa with a 0.1 $\mu\text{m/s}$ rate of applied load to 29.0 MPa with a 10 $\mu\text{m/s}$ rate of applied load. Those results suggest that the influence of creep should be considered during advanced analysis of interfacial shear strength in polymer composites, and particularly during single-fibre interface shear strength tests. Because if such tests are conducted at unduly slow rates, creep will significantly alter the stress-strain behaviour of the interface. However, as explained in Chapter 2.3, the rate at which a pipe collapses under hydrostatic pressure increases with time. Therefore, it follows that the rate at which the interfaces in a pipe fail will also accelerate over time. In addition, Chapter 2.5.2 describes how flexible pipes are subjected to different types of stress, such as tensile stress, compressive stress, and alternating stresses during service. Those stresses are applied at a range of rates; however, information regarding how an interface in a thermoplastic composite will respond to a load which is applied to it at different rates is scarce. Therefore, experiments which involve measuring the interfacial shear strength of a composite would likely be more valuable if those experiments took a range of interface loading rates into account. That would also increase the utility of interface shear strength measurements for oil and gas producers by covering a greater range of the stress situations to which flexible pipes are subjected during service and mechanical failure.

4.5 Induction and measurement of incremental interface damage

As flexible composite pipes collapse under hydrostatic pressure, the fibres and interfaces in the composite layers of the pipe fail in succession. Evidence of that can be seen at the macroscale, from observing the progression of global bending to localised collapse to the total flattening of pipes. Also, future evidence of that can be seen at the microscale, from the growth of kink bands in unidirectional composites, as explained in Chapter 2.3.

Also, interface failure under compressive stress typically occurs through a shear mode, in which the fibres which are near each other fail in progression and at an increasing rate, starting with the fibres which are under the most stress. Thus, it would be useful if experiments were conducted to identify how the shear failure of a single fibre in a composite under compressive stress affects the shear strength of remaining local fibres in the composite. Therefore, this chapter reports findings from an experiment that was conducted to investigate how interfaces in polymer composites lose strength due to being progressively damaged by the failure of local fibres under shear stress.

In this experiment, fibres in G/PP and C/PA12 composites were push-out tested in a systematic order and at a select distance from each other to cumulatively damage the interface surrounding target fibres while measuring their remaining shear strength.

The G/PP and PA12 composites were push-out tested according to the method described in Chapter 3.4.3. Next, they were flipped over and inspected on their underside to confirm that the pushed fibres had debonded from the matrix. Figures 4.13 and 4.14 show that the fibres which were pushed during this experiment jutted out from the underside of the composites, which indicated that the push-out tests were successful.

It was noticed that elongated filaments of polymer remained adhered to the exposed curved surface of a glass fibre in Figure 4.13. Because of that, another glass fibre was pushed out of the G/PP sample to a depth of 20 μm to obtain a clearer perspective of how polymeric filaments remained adhered to the glass fibres after interface failure occurred. That fibre is shown in Figure 4.15.

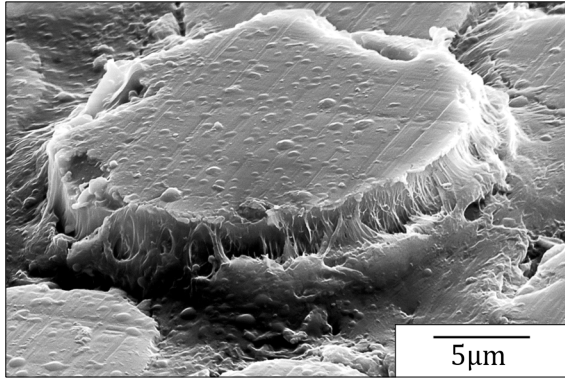


Figure 4.13 Underside view of a glass fibre pushed out from G/PP specimen

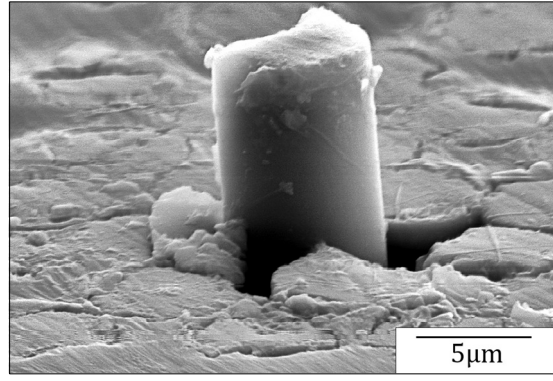


Figure 4.14 Underside view of a carbon fibre pushed out from C/PA12 specimen

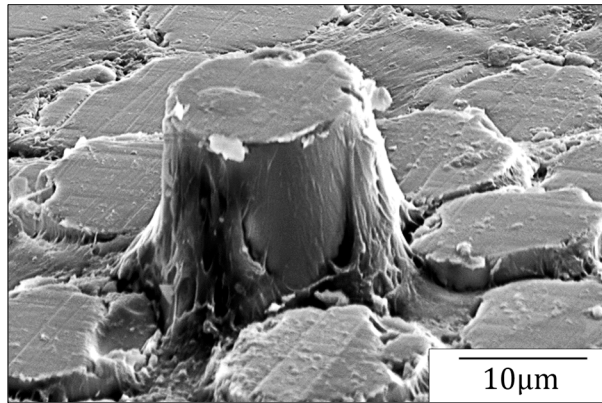


Figure 4.15 Underside view: glass fibre pushed out from G/PP

Figure 4.16a shows that there was a negligible difference in the measured interfacial shear strength of G/PP when fibres 1, 2, and 3 were pushed-out. On average, those fibres all underwent interfacial failure when 14 MPa of shear stress was applied, and that value reduced by 43% for fibres 4, 5, and 6, which failed under a shear stress of 8 MPa. Lastly, the central fibre, fibre 7 exhibited an interfacial shear strength of 3.5 MPa, which was 75% lower than fibres 1, 2, and 3 (which had not been damaged in advance).

Likewise, in the case of C/PA12, there was a negligible change in the measured interfacial shear strength of the composite when the first fibres, 1, 2, and 3, were pushed out from the specimen (see Figure 4.16b). On average, those fibres failed at 40.2 MPa of imposed stress. That declined by 20.4% for fibres 4, 5, and 6 as they debonded when 32.0 MPa of shear stress was applied. Lastly, fibre number 7 debonded when 15.0 MPa of shear stress was applied, which was an additional 53.1% decrease. That corresponded with a 62.7% total reduction in the initial interface shear strength values.

In contrast to the stress-displacement curves produced from push-out tests on G/PP (Figure 4.16a). The stress-displacement curves produced by push-out tests on C/PA12 feature a distinct peak corresponding to the degree of fibre displacement that was required to cause interface failure. After that peak, the gradient of each stress-displacement curve declines in correspondence with the pushed fibre sliding out from the PA12 matrix under friction (see Figure 4.16b).

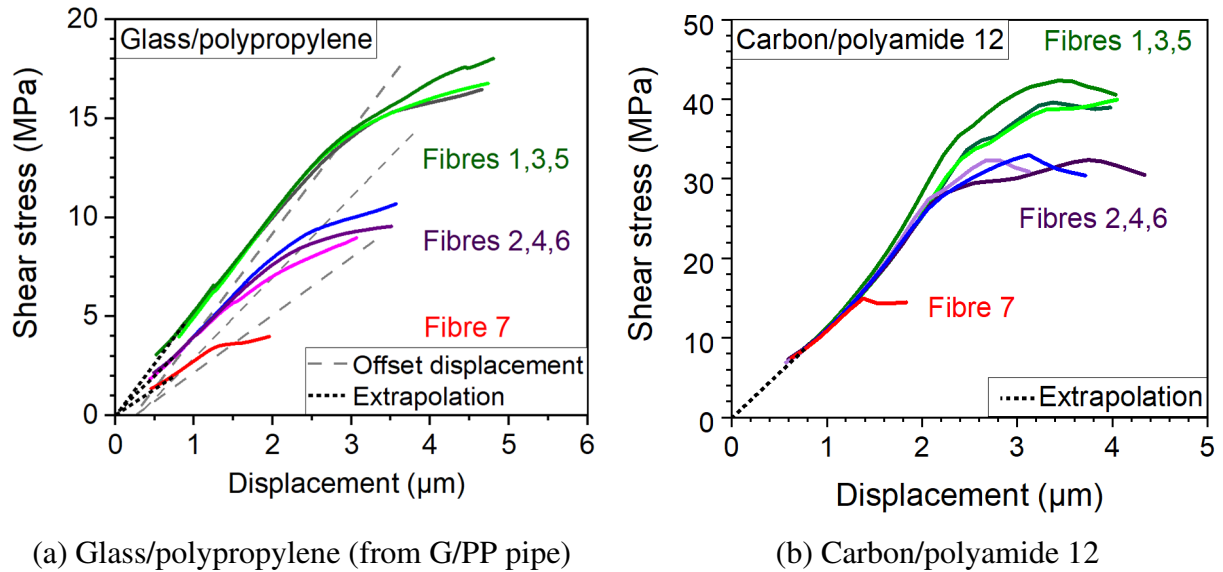


Figure 4.16 IFSS profiles of push-out tested (a) G/PP and (b) C/PA12 composites.

The stress-displacement curves which were generated from the glass fibres that were pushed out from G/PP featured a slight inflexion (see Figure 4.16a). That was because as the fibres were being pushed out by the flat punch, the interface surrounding the fibres deformed in a viscoelastic manner and remained partially intact before the flat punch was retracted. Accordingly, Figures 4.13 and 4.15 show that remnants of the matrix remained adhered to the glass fibre surfaces in the form of elongated filaments. Those filaments became elongated due to being under tensile stress as the interface was failing. A greater degree of debonding would have occurred if the tensile strength of those filaments was overcome by pushing the fibre further out. However, that was not possible during this experiment because the flat punch would have made contact with the surrounding fibres due to its conical shape. Conversely, that was not an issue for the push-out tests which were conducted on C/PA12 because a cylindrical flat punch was used to conduct push-out tests on that composite. Unlike the fibres which were pushed out from the G/PP composite, fibres in the C/PA12 composite debonded with a negligible amount of residue remaining upon their exposed surface (see Figure 4.14).

4.5.1 Conclusions

Fibres in C/PA12 and G/PP composites were push-out tested in a systematic order and close to each other. As the number of fibres which had been pushed-out nearby a neighbouring fibre increased, the interfacial shear strength of the final remaining fibre decreased. For example, the shear strength of the interface surrounding a fibre in the centre of six neighbouring fibres which had been pushed-out reduced by 75% in the case of G/PP, and 53% in the case of C/PA12. Those outcomes demonstrate that the shear failure of the interface surrounding a fibre in a composite can significantly impair the interfacial shear strength of neighbouring fibres. Furthermore, the push-out test can be used to incrementally cause mechanical damage to interfaces in composites and measure the remaining shear strength of those interfaces.

Inspection of the underside of the samples revealed that the exposed surface of the G/PP fibres was covered in considerably more polymer matrix than the C/PA12 fibres, which indicated that the interface surrounding the carbon fibres had been damaged and debonded considerably more than the interface surrounding the glass fibres. That correlated with the stress-strain curves produced. Specifically, the gradient of the stress-displacement curve of the C/PA12 composites became negative after interface failure occurred, which indicated the onset of fibre slide out under friction. In contrast, the gradient of the curves in the G/PP composites declined but did not become negative because the interface remained considerably intact before the indenter was retracted.

Those results indicate that the matrix surrounding a fibre which has failed under shear stress can be inspected alone and in post-mortem, to gather information about the historical shear stress-displacement behaviour of that fibre and the initial strength of its bond with the interface before the failure occurred.

5. CHARACTERISTICS OF POLYMER COMPOSITES AT ELEVATED TEMPERATURES

At present flexible composite pipes are being used in oil and gas fields wherein they are constantly exposed to elevated temperatures. Therefore, this chapter describes research findings that have provided insight into how the strength of the interface and the hardness of the matrix in composites, specifically glass/polypropylene and carbon/polyamide 12, changes when they are exposed to elevated temperatures, within the range of temperatures present in oil and gas wells.

In addition, it is common for flexible composite pipes to experience temperature fluctuations during service in oil and gas production operations. For instance, during production startup, shutdown, and maintenance operations. Therefore, this chapter also describes how far interfaces in a G/PP composite recovered their strength after being heated from room temperature up to 70°C, and then cooled back down to room temperature.

5.1 Interfacial shear strength of C/PA12 at elevated temperatures

G/PP and C/PA12 specimens were individually mounted on a nanoindenter and subsequently heated inside a scanning electron microscope. The heat caused the matrix in the samples to expand. Figures 5.1 and 5.2 show how that affected the C/PA12 sample at 120°C, while Figures 5.5 to 5.7 show how it affected G/PP specimens at 70°C.

The specimens were fixed to a TEM grid at both ends, which caused their centre portion to rise away from the grid by over 50 µm as they expanded. Consequently, sample compliance rose considerably, and each fibre needed to be pushed down further to become level with a free space in the TEM grid. That resulted in the load-displacement curves produced, showing significant indenter displacement distances at low loads, which obscured observation of elastic behaviour of the interface. Subsequently, the flat punch was moved towards one of the ends of the specimen to solve that issue. The fibres in that region were push-out tested. Figure 5.1 illustrates that solution as it was carried out on a C/PA12 specimen. That solution would not

have been possible if the composites were mounted to a substrate the conventional way, that is upon a substrate with a single groove, as done by several past researchers [11, 227, 228].

Nonetheless, as the C/PA12 sample was still curved at elevated temperatures, around four attempts were made to push a fibre at each temperature. That was also the case for the push-out tests that were performed on the G/PP specimen at elevated temperatures. A reason why not every attempt to push a fibre was successful was that the flat punched often pushed the whole sample down to become level with the TEM grid before interface failure occurred. That occasionally caused the tip of the flat punch to move away from the centre of the fibre that it was pushing and onto the matrix. Consequently, results from those test attempts were unsuccessful.

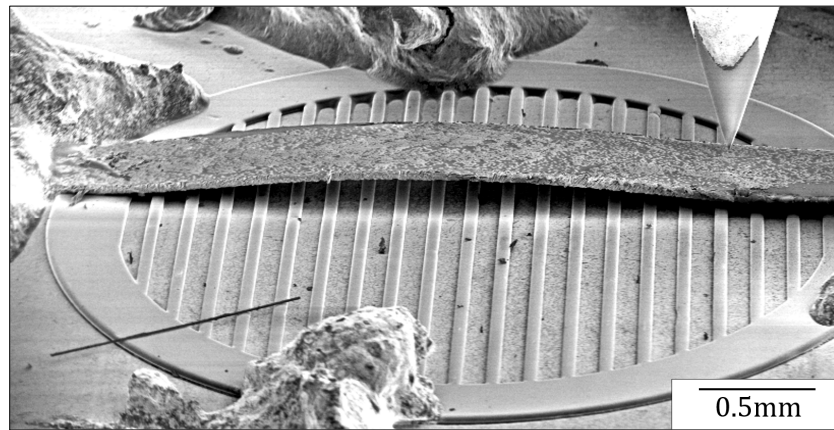


Figure 5.1 C/PA12 sample expanded and bowed when heated to 120°C

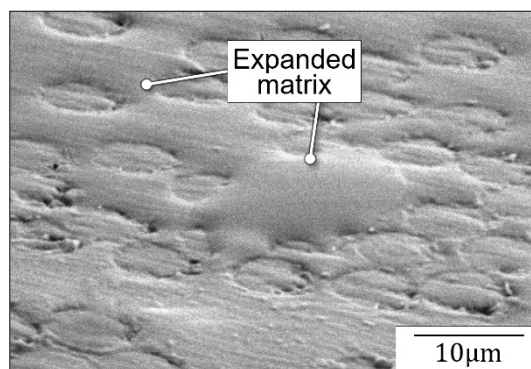


Figure 5.2 C/PA12 matrix expanded when heated to 120°C (close view)

C/PA12 was push-out tested at room temperature (30°C), then 80°C and lastly 120°C. At 30°C. On average, its initial shear strength was about 38.0 MPa; it fell to 27.0 MPa at 80°C which was a 29% decrease, then at 120°C, it diminished to 17.5 MPa which was equivalent to a total reduction of 54% overall (see Figure 5.3).

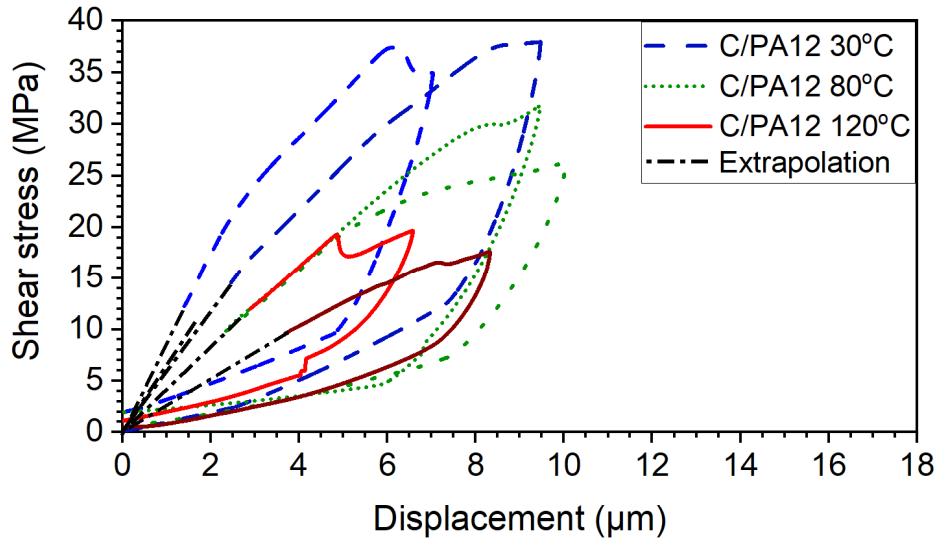


Figure 5.3 IFSS profiles of thermally aged C/PA12

The glass transition temperature of polyamide 12 is in the range of 35 to 36°C [22, 23]. Therefore, during this experiment, the C/PA12 specimen was heated through the glass transition temperature of its polyamide 12 matrix.

To investigate the behaviour of the polyamide 12 matrix alone. Matrix rich regions of the composite were indented using the same flat punch that was used to push-out the carbon fibres. That was done at the same temperatures at which the composite was heated, i.e. 30, 80, and then 120°C. Figure 5.4 shows the load-displacement curves produced from indenting the matrix under those conditions.

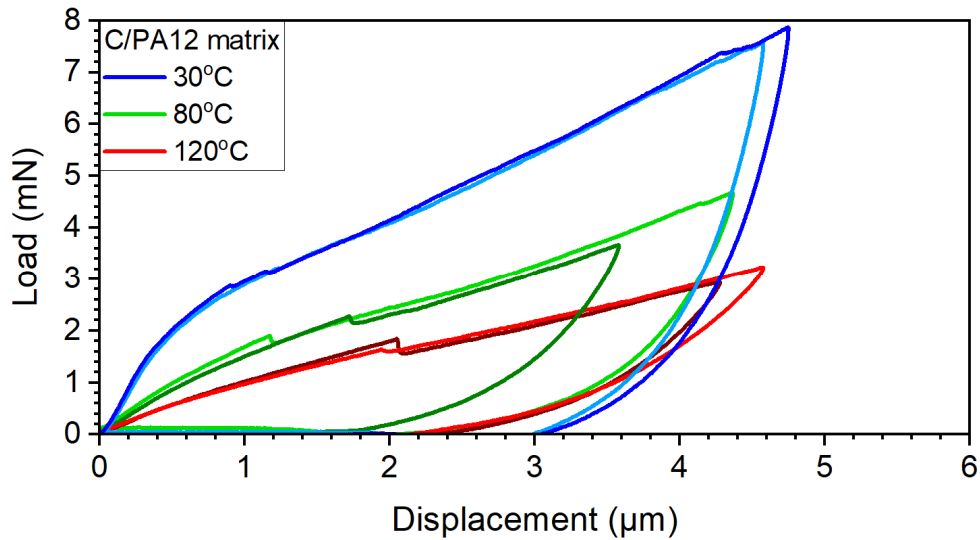


Figure 5.4 Indentation of C/PA12 matrix at 30, 80 and 120°C

Figure 5.4 shows that at room temperature (30°C), the polymer matrix of C/PA12 behaved elastically as it was indented to a depth of 2 μm . After that period, the flat punch popped into the substrate and began to indent it plastically.

When the composite was heated to 80°C and 120°C, those temperatures exceeded its glass transition temperature. Consequently, its matrix softened and the period of elastic deformation which occurred before the flat punch popped into the matrix became progressively less pronounced at higher temperatures. Specifically, indenting the matrix at room temperature to a depth of 4 μm required an applied load of 5.4 mN. That load requirement fell to 3.2 mN at 80°C, which was a 40% reduction, and 2.2 mN at 120°C, which was a 59.3% reduction. That trend is reasonable because a polymer will naturally change from being a hard, glassy material to a relatively soft, rubbery material when it is heated to a temperature that is higher than its glass transition temperature [21]. At each elevated temperature, the percentage by which the C/PA12 matrix lost stiffness remained similar to the percentage by which the C/PA12 interfaces lost shear strength.

5.2 Interfacial shear strength of G/PP at elevated temperatures

A sample of G/PP was mounted onto a TEM grid in preparation for push-out tests which were arranged to be conducted at room temperature (25°C), then 70°C, and finally at room temperature again. At 70°C, the sample expanded, causing it to undergo upheaval buckling and rise away from the TEM grid that it was mounted upon by over 100 μm (see Figures 5.5 to 5.7). A similar phenomenon was also encountered when the C/PA12 sample was push-out tested at elevated temperatures (see Figure 5.1). As a solution, the samples were consistently pushed out at one of their ends near the silver-epoxy paste because they were closer to the TEM grid at those locations.

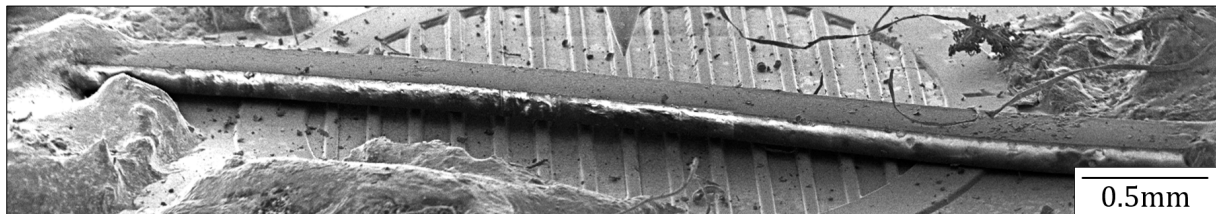


Figure 5.5 Micrograph of G/PP, at room temperature (25°C)

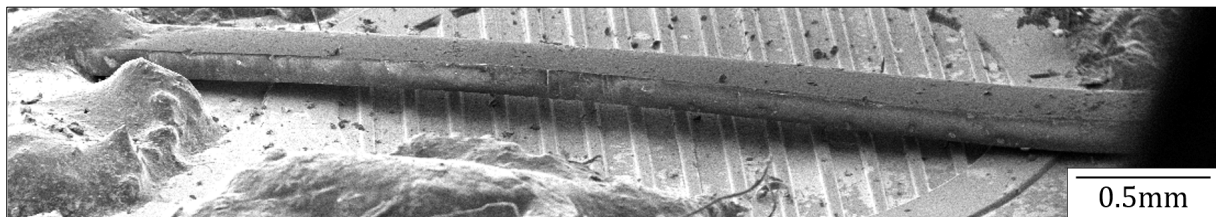


Figure 5.6 Micrograph of G/PP, exhibiting expansion at 70°C

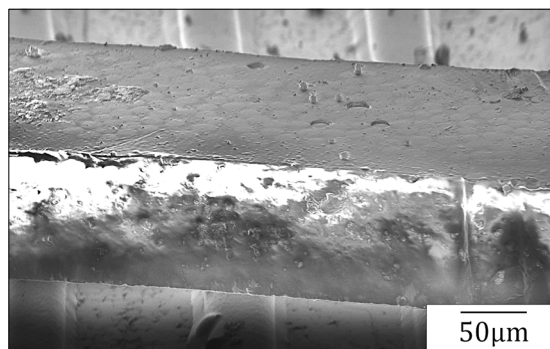


Figure 5.7 Micrograph of G/PP, exhibiting expansion at 70°C (close view)

Figure 5.8 shows that upon raising the temperature of G/PP from room temperature to 70°C, the average shear strength of interfaces within it fell from 23.3 MPa to 13.5 MPa, which was a 42% reduction. After the sample was allowed to cool back to 25°C under ambient conditions,

its interfacial shear strength recovered. That outcome implies that the interface had a lower shear strength at 70°C mainly due to it softening and becoming more ductile as it was heated, rather than fracturing, which would have caused considerable irreversible damage. Overall, interfaces in G/PP weakened at elevated temperatures, and that strength loss was strongly reversible upon cooling the composite back to room temperature.

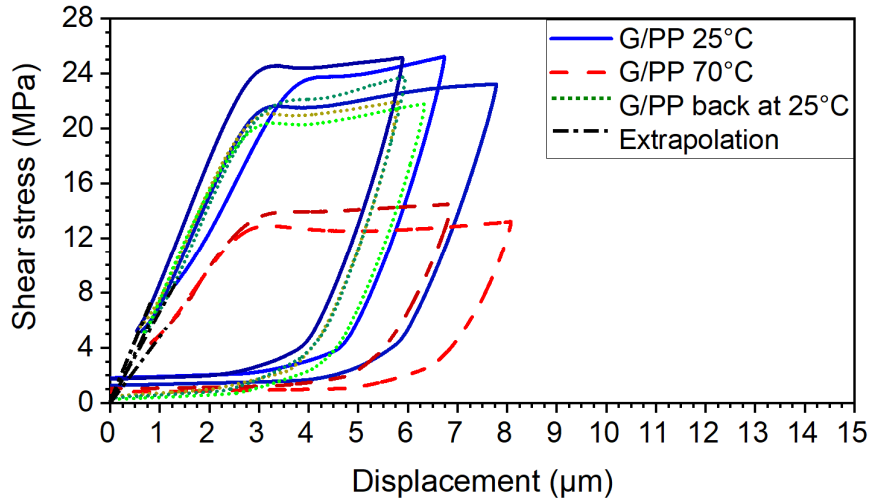


Figure 5.8 IFSS profiles of G/PP that was push-out tested at 30°C and 70°C

The G/PP used for this experiment was extracted from G/PP tape

To investigate the thermomechanical behaviour of the matrix in G/PP alone, the flat punch was used to indent the matrix of the G/PP specimen at the same temperatures that interfaces in the material were push-out tested, i.e. at room temperature (25°C), then 70°C and finally 25°C again (see Figure 5.9).

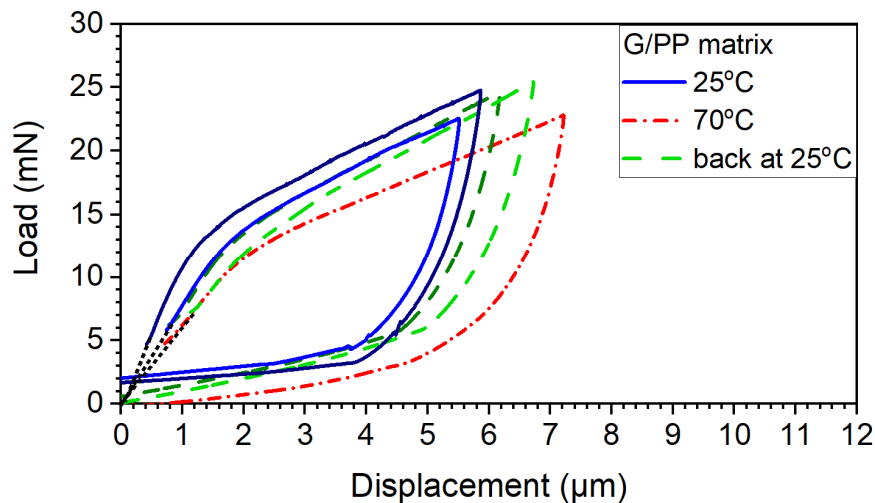


Figure 5.9 Load displacement profile of the G/PP matrix at 30°C and 70°C

On average, the load that was required to achieve an indentation depth of 4 μm was 20 mN when the sample was held in the microscope at 30°C, 16 mN when the sample was held at 70°C, and 19 mN after the temperature of the sample was returned to 30°C.

The behaviour of the interface in terms of load applied per unit of fibre displacement in the elastic region remained consistent at each temperature. It did not change by more than 25%, even when the composite was tested at 70°C, at which point its interfacial shear strength diminished by 42%.

5.2.1 Conclusions

Experiments were conducted in which the interfacial shear strength of G/PP and C/PA12 composites was assessed at elevated temperatures by means of push-out tests. The specimens expanded and bowed upwards as they were heated in the nanoindenter, which had the potential to strongly influence load-displacement measurements during each test. However, that issue was overcome, mainly because an advanced method was developed and used to mount the specimens in preparation for mechanical tests at elevated temperatures.

The interfacial shear strength of G/PP and C/PA12 reduced as they were heated from room temperature, up to 70°C (G/PP) and 130°C (C/PA12). At those temperatures, the interfacial shear strength of G/PP declined by 42%, while the interfacial shear strength of C/PA12 reduced by 54%. Those temperatures were above the glass transition temperature of the PP and PA12 matrices. Therefore, the matrix would have been in a relatively soft state at those temperatures.

Nonetheless, it is not clear whether the elevated temperatures were mainly detrimental to the mechanical properties of the interface or the mechanical properties of the matrix in the composites. A preferable way to examine the hardness and stiffness properties of the interface and matrix might be by using a nanoindenter that is equipped with a Berkovich tip. Nanoindentation can provide resolutions which are suitable for the micromechanical analysis of composite materials, and Chapter 2.7 of this thesis describes how nanoindentation has gained an excellent reputation for evaluating the hardness and stiffness of materials at elevated temperatures.

6. CHARACTERISTICS OF AGED POLYMER COMPOSITES

This chapter explores how the morphology and interfacial shear strength of glass/polypropylene and carbon/polyamide 12 composites altered after those materials underwent hygrothermal ageing in distilled water and oil (a 50/50 pentane/toluene solution). It begins with details of the effects of water on the characteristics of G/PP (6.1), then the effects of oil on the characteristics of G/PP (6.2). Next, it covers the effects of water on the characteristics of C/PA12 (6.3). Subsequently, it details the effects of oil on the characteristics of C/PA12 (6.4). Finally, it closes with examples of how the location and progression of interface failure in G/PP changed after it was aged in water and push-out tested (6.5).

6.1 Effects water on the characteristics of glass/polypropylene

6.1.1 Glass/polypropylene: Kinetics of water absorption

Two 0.5mm thick coupons of G/PP were cut and extracted from a G/PP tape. One of those coupons was aged in distilled water for thirteen days at 80°C, whereas the other was left as received. Figures 6.1 and 6.2, show that blistering took place in the aged sample.

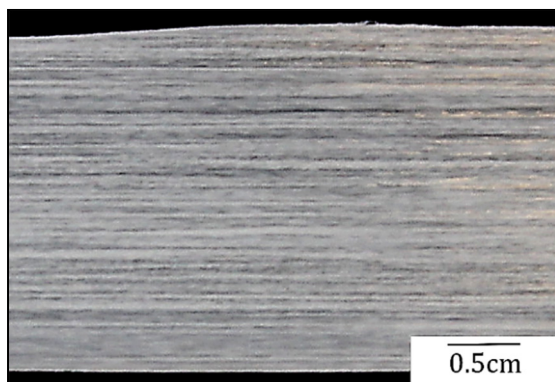


Figure 6.1 Photograph of G/PP sample as received

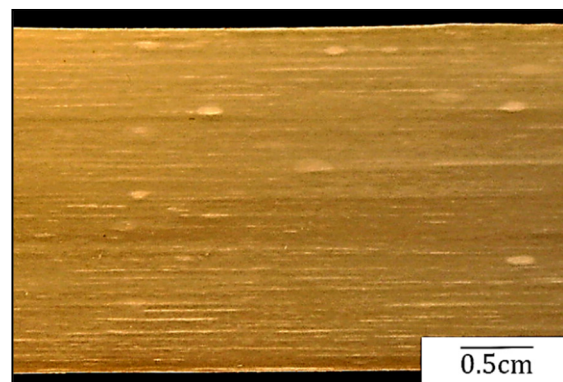


Figure 6.2 Photograph of G/PP sample after it was aged in water

Polypropylene can absorb water and swell due to osmosis. Osmosis is the spontaneous net movement of solvent molecules through a semipermeable or selectively permeable membrane, into a region of higher solute concentration, towards the direction that equalises the solute concentrations on both sides of the membrane [236]. Therefore, it is likely that water diffused into the G/PP specimen and combined with water-soluble molecules (such as short molecular chains, sizing, or plasticisers) to form large molecules. As that occurred, osmotic pressure built up in the matrix, which caused blisters to form. Those blisters may have enabled fluids to reach and penetrate the interfaces in the specimen with greater ease, causing fibre/matrix bonds to weaken.

G/PP, from G/PP tape, was aged in water for 35 days at 80°C. The condition of the sample after it was aged under those conditions is shown in Figure 6.3.

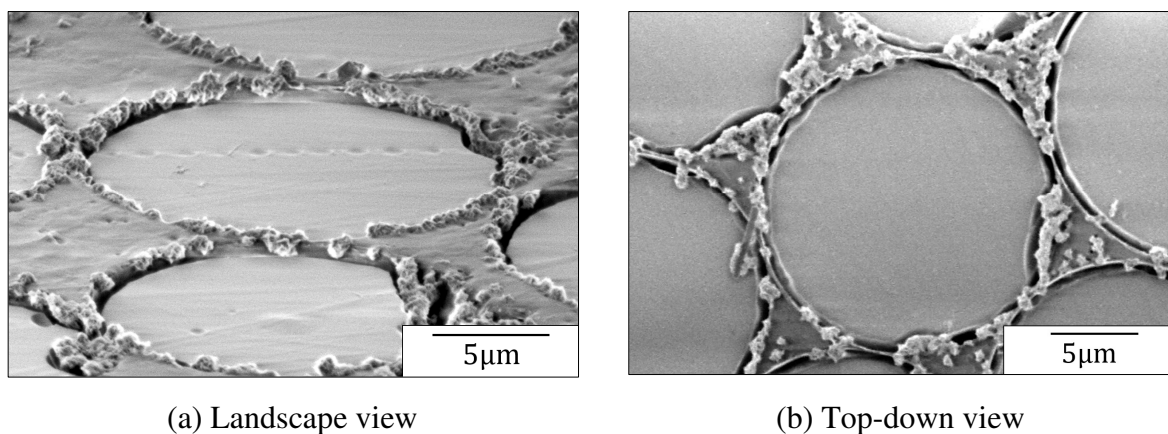


Figure 6.3 Surface of G/PP (from tape) after it was aged in water for 35 days at 80°C

Figure 6.3 shows that the matrix of the G/PP sample swelled, causing it to rise to a height around 0.6 µm above the surface level of the embedded fibres.

G/PP was aged in water at 50°C and 80°C for seven days. Likewise, polypropylene was aged in water at 50°C and 80°C for up to 23 days. Figure 6.4 shows that the rate of moisture diffusion through the materials was a strong function of water temperature. Each datapoint in the figure has been derived from the average gravimetric measurement gathered from four individual samples.

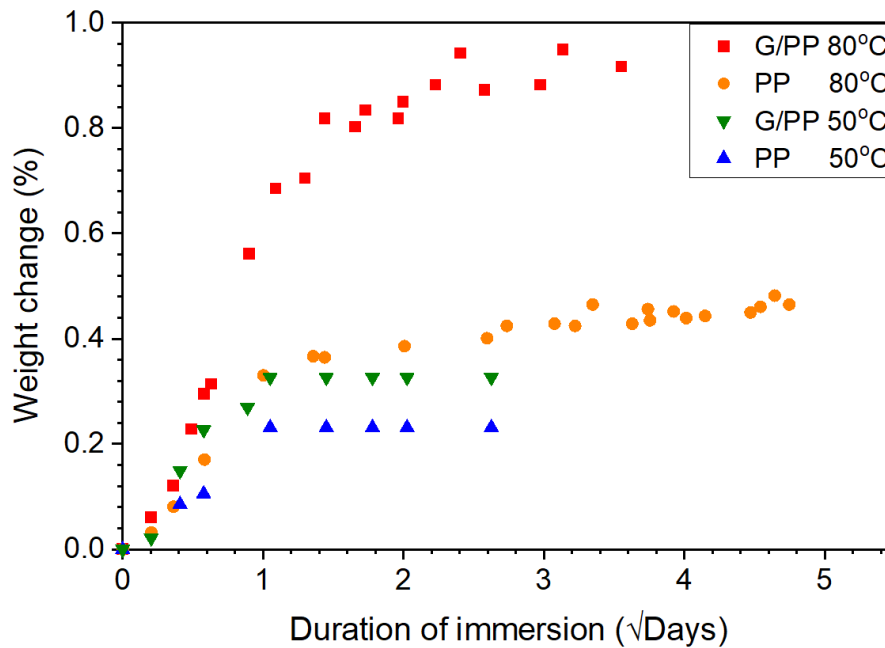


Figure 6.4 Weight change of G/PP (from tape) and polypropylene, both aged in water at 50°C and 80°C

Figure 6.4 shows that during each test of water uptake, the material which was aged at the higher temperature absorbed the most water. That indicates that the rate at which diffusion took place was temperature dependant. Specifically, the equilibrium moisture content of the polypropylene sample increased by 0.23%, whereas the equilibrium moisture content of the G/PP composite increased by 0.32% when both specimens were aged at 50°C (i.e. the composite increased in moisture content by 0.1% more than the polymer on a percent change basis). Also, when both specimens were aged in water at 80°C, the equilibrium moisture content of the polypropylene specimen increased by approximately 0.47%, whereas the equilibrium moisture content of G/PP increased by around 0.91% (i.e. the composite increased in moisture content by 0.44% more than the polymer on a percent change basis).

In each assessment of water absorption, the G/PP composite absorbed more water than non-reinforced polypropylene. That difference may have occurred because the composite was more porous than the unreinforced polypropylene. However, micrographs of the surface of the sample indicate that the sample was considerably non-porous (see Figures 3.19b and 3.20)

An alternative suggestion is that the wetting characteristics of the interface caused capillary action to occur at the interface. Capillary action, also called wicking, describes the phenomenon wherein a liquid spontaneously flows in a narrow space without assistance from

external forces. It occurs when adhesive intermolecular forces between a liquid and the walls of a narrow space are stronger than the cohesive intermolecular forces in the liquid. That causes a concave meniscus to form where the liquid contacts a vertical surface. Figure 6.5 illustrates that phenomenon.

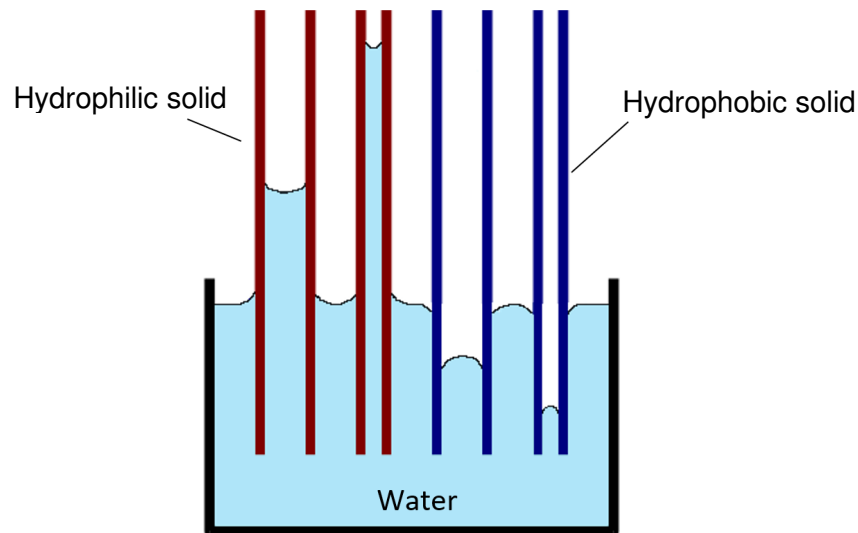


Figure 6.5 Illustration of capillary action, as well as positive and negative contact angles in large and small bore capillaries

Where red hydrophilic solid wall = contact angle less than 90° and blue hydrophobic solid wall = contact angle greater than 90° with water [237, 238]

Glass is hydrophilic, which means that it has a strong affinity for water. That is because its surface contains oxygen and hydrogen atoms which readily form hydrogen bonds with water. In general, if water is poured on a glass, it will spread out with a low contact angle to form a thin and uniform film over the surface, as illustrated in Figure 6.6b. That occurs because adhesive forces between the water and glass are strong enough to pull the water molecules out of their spherical arrangement and hold them against the glass surface [239].

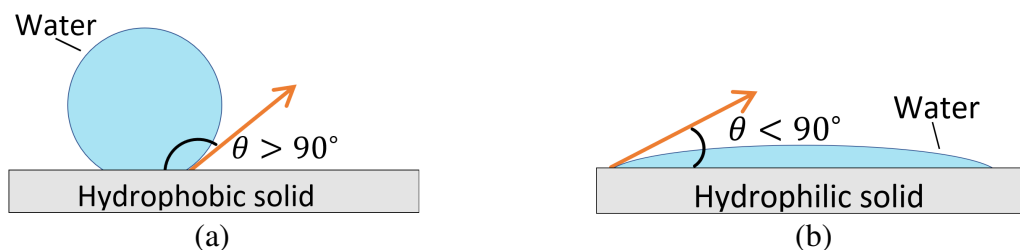


Figure 6.6 Liquid wetting on (a) hydrophobic solid and (b) hydrophilic solid surface

Where θ is the contact angle

Overall, the results presented in this chapter suggest that water infiltrated the interface in the G/PP composites and spread through them rapidly and extensively because the glass fibre surfaces were hydrophilic. That led to the formation of blisters in the hydrothermally aged G/PP specimens. Consequently, the G/PP specimens exhibited faster water uptake and a greater volume of water uptake than neat polypropylene.

6.1.2 Effects of water on the interfacial shear strength of G/PP

In this work, a sample of G/PP was extracted from G/PP tape and then push-out tested at room temperature (25°C), which revealed that it had an average interfacial shear strength of 18.2 MPa. Next, another sample of G/PP was extracted from the tape and aged in water at 80°C for 35 days before being push-out tested. Its interfacial shear strength was approximately 15.3 MPa. That interfacial shear strength was low compared to the unaged specimen. During the experiment, around four attempts were made to push out fibres at each temperature. Results from the push-out tests, which were performed successfully, are shown in Figure 6.7.

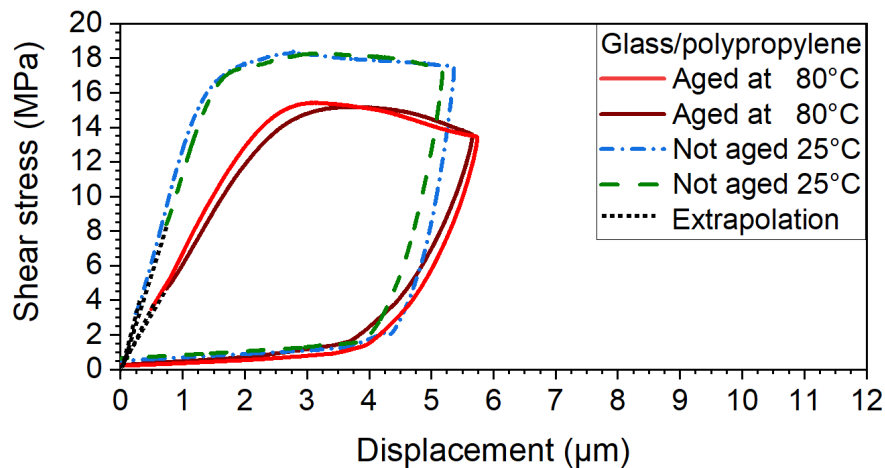


Figure 6.7 Interface shear strength profiles of G/PP that was extracted from G/PP tape and aged in water at 80°C for 35 days

Figure 6.7 shows that after G/PP composites were aged during this experiment, their interfacial shear strength diminished by 15.9%. Additionally, the frictional shear strength of the fibres which were pushed out of the aged specimens reduced at the fastest rate. That is evident as the gradient of the stress/displacement curve during fibre slide-out was 0.44 MPa/μm with regard to the specimens which were not aged, whereas it was 0.73 MPa/μm regarding the specimens that were aged.

6.1.3 Conclusions

The interfacial shear strength of G/PP diminished by 15.9% after it underwent hydrothermal ageing in water at 80°C for 35 days. Also, the amount of stress that was required to push fibres out from the polypropylene matrix under friction reduced from 0.44 MPa/μm to 0.73 MPa/μm. Those outcomes are consistent with predictions made by Tucker and Brown [161]. Specifically, Tucker and Brown [161] investigated how graphite fibre-reinforced vinyl ester composites absorb water. In that work, they suggested that in addition to moisture absorption by diffusion, composites that are subjected to high hydrostatic pressure will experience capillary flow of moisture along the fibre-matrix interface, as well as the influx of moisture through cracks. That will likely promote further damage, and open volumes within the composite wherein moisture can accumulate. In line with those predictions, as G/PP was aged in the present work open volumes were seen in the specimen as blisters. Those blisters may have formed due to osmosis, capillary action, or a combination of those phenomena. The general mechanism of those phenomena has been described in this chapter.

6.2 Effects of oil (pentane/toluene) on the characteristics of G/PP

6.2.1 Glass/polypropylene: Kinetics of pentane/toluene absorption

Figure 6.8 shows how the weight of polypropylene specimens (from a polypropylene standard sheet) changed as they were immersed in pentane/toluene at 25, 85 for 51 days. The average of two measurements is shown at each datapoint in the figure.

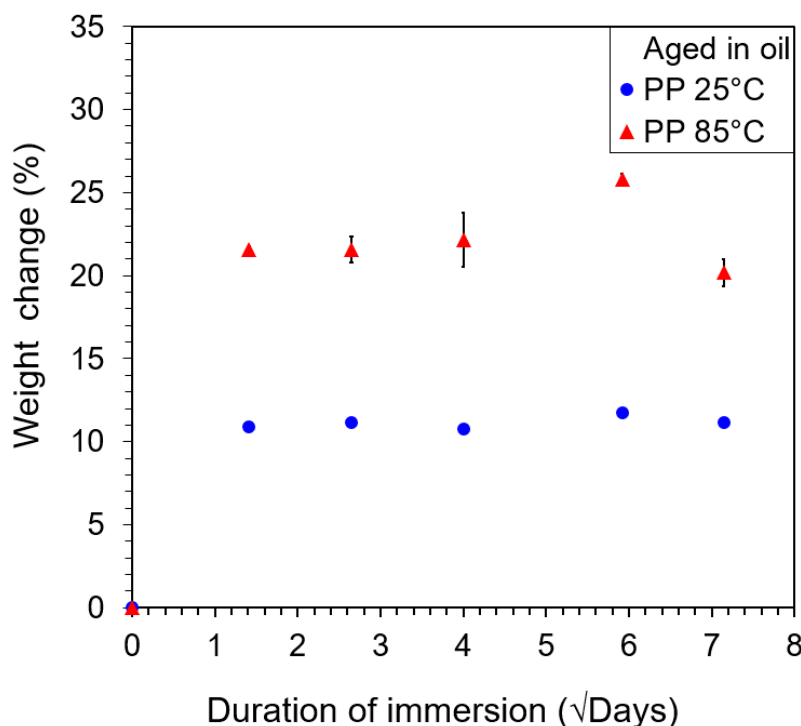


Figure 6.8 Weight change of PP (from PP sheet), aged in pentane/toluene at 25°C and 85°C

Figure 6.8 shows that, on average, when the polypropylene specimens (from the polypropylene standard sheet) were aged in pentane/toluene at 25°C for 51 days, their weight rose 11.1% within two days and remained considerably stable. Likewise, when the polypropylene specimens were aged in pentane/toluene at 85°C, their weight rose by 21.5% and remained did not deviate substantially from that value over the course of 51 days of immersion. Polypropylene specimens were also immersed in pentane/toluene, for the same duration, at 100°C. However, those specimens partially dissolved and fused together at that temperature. Consequently, they could not be examined further.

Interestingly, the weight of the polypropylene specimens that were aged at 85°C rose by up to 26% and then began to decline after 35 days of immersion. When the experiment

ended, the weight of the specimens had increased by 20% overall. Polypropylene is a petroleum sorbent that can absorb 7 to 9 times its weight in oils [240, 241]. It is also a low-cost material with low water uptake and low density [242, 243]. Because of those characteristics, it is a preferred material for marine oil-spill recovery.

In most cases, when polypropylene is immersed in oil, that oil will only be absorbed at the surface of the material. The core of the polymer will not come into contact with the oil in the short term, and its surface will slowly bind over as it absorbs the oil, significantly reducing further ingress [244]. Thus, the measurement of the 26% weight gain, which the polypropylene specimen incurred during this experiment, was reasonable.

Figure 6.9 shows how the weight of G/PP specimens (from G/PP tape) changed as they were immersed in pentane/toluene at 25, 85, and 100°C for 51 days. The average of two measurements is shown at each datapoint in the figure.

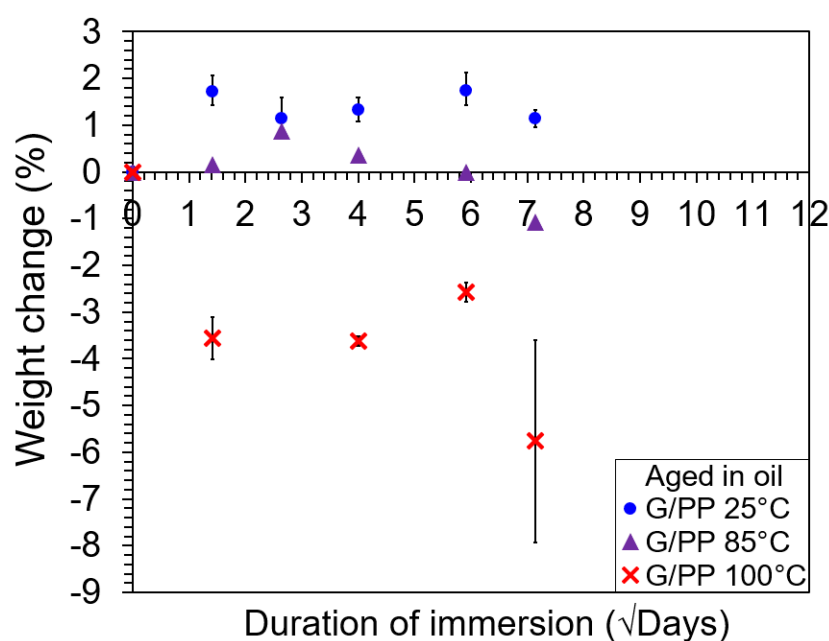


Figure 6.9 Weight change profile of G/PP, aged in pentane/toluene at 25, 85, and 100°C

On average, when the G/PP specimens were aged in pentane/toluene at 25°C, their weight rose by a maximum of 1.7% within two days of immersion. Subsequently, their weight began to decline, such that by day 51 of immersion, their overall weight gain was 1.2%. When G/PP was aged at 85°C in pentane/toluene, its weight rose to a maximum of 0.9% and then began to decrease until it reached an overall weight loss of 1.1% on the 51st day of immersion. All gravimetric measurements show that the weight of G/PP declined when it was aged at 100°C.

In actuality, its weight likely rose within the first few hours of immersion due to pentane/toluene permeation. However, no gravimetric measurements were taken during that period (see Figure 6.9).

The weight of the G/PP specimens began to decline after 35 days of immersion in pentane/toluene at 85°C and 100°C because the pentane/toluene solution functioned as a solvent to the polypropylene matrix. Evidence of that can be seen in Figures 6.10 to 6.14.

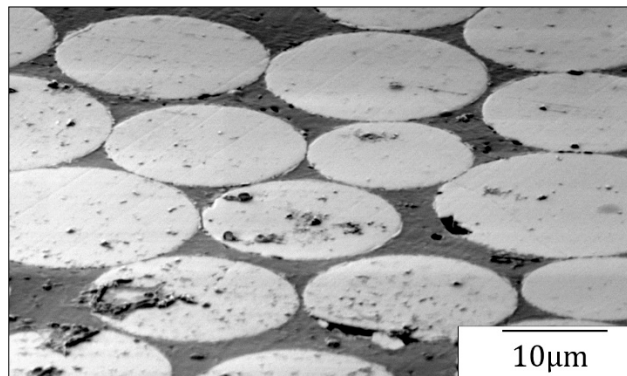


Figure 6.10 Surface condition of G/PP as received

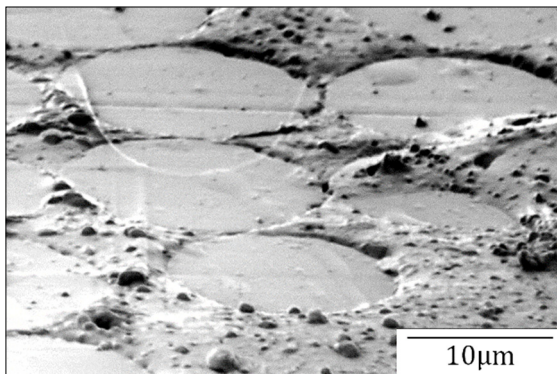


Figure 6.11 Surface of G/PP aged in pentane/toluene at 85°C for 51 days



Figure 6.12 Surface of G/PP aged in pentane/toluene at 100°C for 51 days

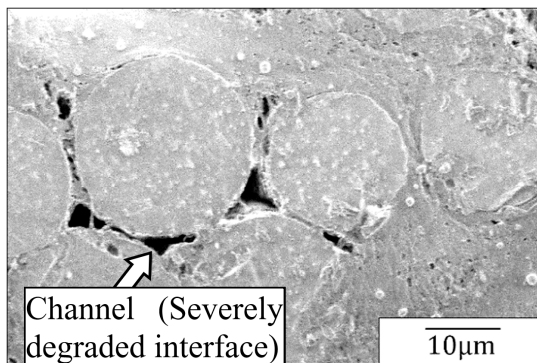


Figure 6.13 Top-down view of G/PP aged in pentane/toluene at 100°C for 51 days

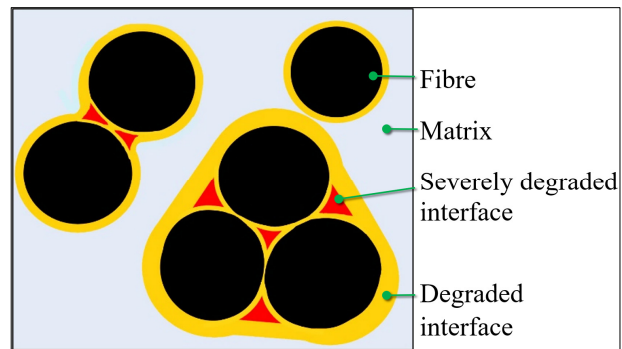


Figure 6.14 Distribution of degradation in a hygrothermally aged composite

Figures 6.9 to 6.14 show that at the first stage of degradation, on balance, pentane/toluene absorbed into the polymer matrix, which caused it to swell and its weight to increase. After the equilibrium moisture content of the polymer was reached, its weight declined as it dissolved.

Overall, the eventual weight loss that the polypropylene-based specimen exhibited during 51 days of immersion in pentane/toluene was due to the dissolution of polypropylene in the pentane/toluene solution. That evaluation is supported by Figures 6.10 to 6.14 as those images illustrate how and where the matrix within the G/PP sample was lost while it was aged in pentane/toluene at 85°C and 100°C for 51 days. Additionally, the images show that the matrix rich region between tightly packed fibres dissolved, leaving a channel that facilitated further matrix dissolution.

6.2.2 Effects of pentane/toluene on the interfacial shear strength of G/PP

A sample of G/PP, from G/PP tape, was push-out tested at room temperature (25°C). Also, another sample of G/PP, which was extracted from the G/PP tape, was aged in oil (pentane/toluene) at room temperature (25°C), 85 °C, and 100°C for 51 days before being push-out tested. Figure 6.1 shows a graph that illustrates the outcomes of those tests on the interfacial shear strength of the specimens.

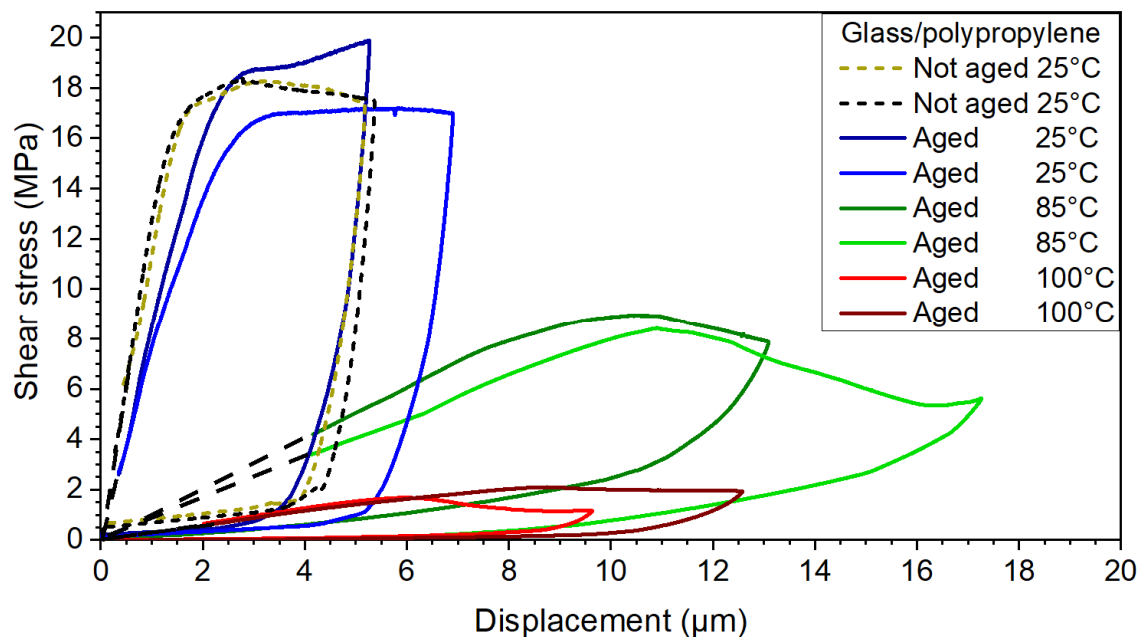


Figure 6.1 Interface shear stress profiles of G/PP aged in pentane/toluene at 25°C, 85°C, and 100°C

Figure 6.1 shows that the interfacial shear strength of the specimens that were not aged was 18.2 MPa. On average, the interfacial shear strength of the specimens which were aged at room temperature in oil was around the same value (18MPa). The specimens which were aged at 85°C had an interfacial shear strength of 8.7 MPa, which was 57.6% lower than the non-aged specimens. Lastly, the samples which were aged at 100°C exhibited an interfacial shear strength of 1.8 MPa, which was a drastic 90.1% reduction in interfacial shear strength when compared to the original non-aged specimen.

Interestingly, the interfacial shear strength of the specimens that were not aged, and those that had been aged in oil at 25°C for 51 days were similar. In effect, ageing the G/PP specimens in oil at room temperature had a negligible effect on their interfacial shear strength, even though the polypropylene matrix that those specimens are based on is renowned for its capability to absorb oil. Those outcomes emphasise that the temperature of a flexible composite pipe is a critical factor for its service life.

6.2.3 Conclusions

G/PP was hygrothermally aged in oil (pentane/toluene) at 25, 85 and 100°C for 51 days before being push-out tested. The elevated temperatures both increased the rate of moisture sorption and the maximum moisture content of both G/PP and neat polypropylene at saturation. The maximum weight gain that G/PP experienced under those conditions was 0.8%, and likewise, the maximum weight gain that neat polypropylene reached was 26%. Both of those materials lost weight after prolonged ageing due to the dissolution of polypropylene in the immersion fluid. In correspondence with that, images provided by SEM microscopy indicated that interfaces in G/PP mainly deteriorated in regions of high fibre density. The material primarily degraded by swelling at first, and subsequently, dissolution was the leading mechanism of degradation after the equilibrium moisture content of the matrix had been met (see Figures 6.10 to 6.14).

The G/PP specimens that were not aged and those that had been aged in pentane/toluene at 25°C for 51 days had a similar interfacial shear strength of approximately 18 MPa. In contrast, the G/PP specimens that had been aged in pentane/toluene at 85 and 100°C for the same duration had an interfacial shear strength of 8.7 and 1.8 MPa, respectively. Those results show that the extent to which the interfacial shear strength of G/PP decreased was highly dependent upon the temperature of the immersion fluid rather than the duration of immersion over a period of 51 days.

6.3 Effects water on the characteristics of carbon/polyamide 12

6.3.1 Carbon/polyamide 12: Kinetics of water absorption

C/PA12 was aged by means of immersion in distilled water at 130°C for 72 hours. Figures 6.15 to 6.18 show the condition of the sample before and after it was aged. The aged sample did not show prominent swelling due to moisture absorption. Instead, some of the matrix was lost, causing the exposed flat surface of the carbon fibres to be slightly protruded from the sample by around 1 micron in various regions. Also, the surface of the aged sample was rougher and featured a greater volume of microcavities.

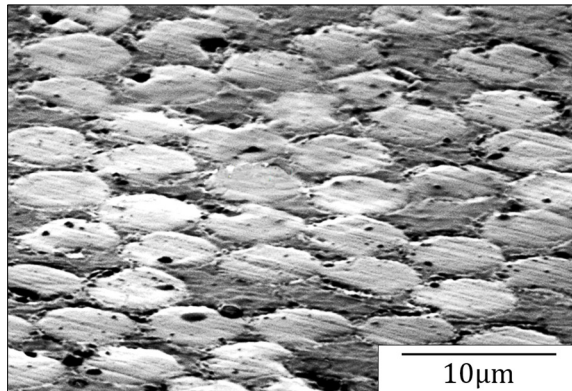


**Figure 6.15 C/PA12 as received
(top-down view)**

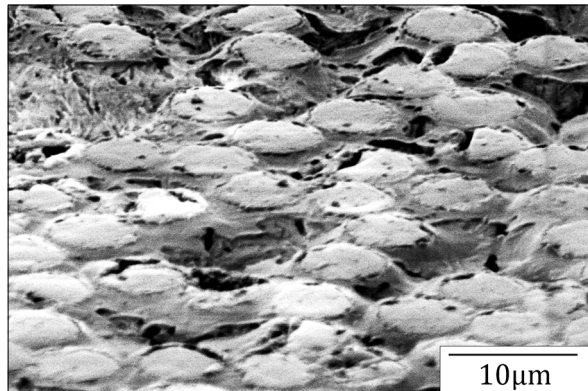


**Figure 6.16 C/PA12 that was aged in water
for 72 hours at 130°C (top-down view)**

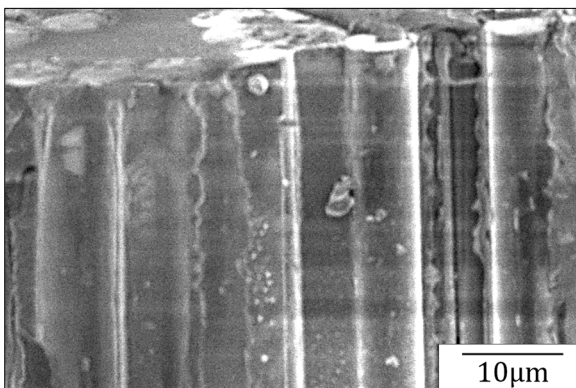


Figure 6.17 C/PA12 as received (side view)

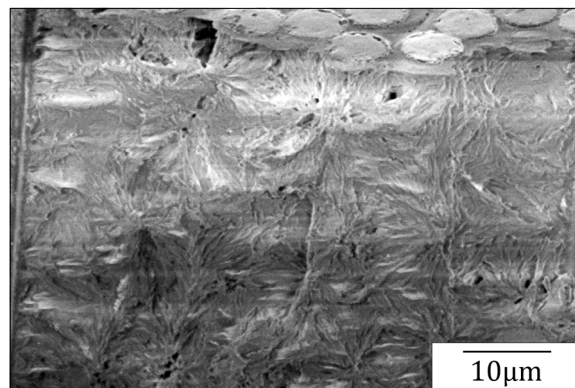


**Figure 6.18 C/PA12 that was aged in
water for 72 hours at 130°C (side view)**

Polyamide 12 coupons were aged in water at 50, 80, and 85°C for up to 16 days. Each sample reached saturation within two days. The sample that was aged at 50°C took the longest to reach that state. It had a maximum weight gain of 0.75%, while the accompanying samples that were aged at 80 and 85°C increased in weight by 1.25 and 1.3%, respectively. After that, the weight of those samples began to decline at a rate of 0.24% per day, as shown in Figure 6.2.

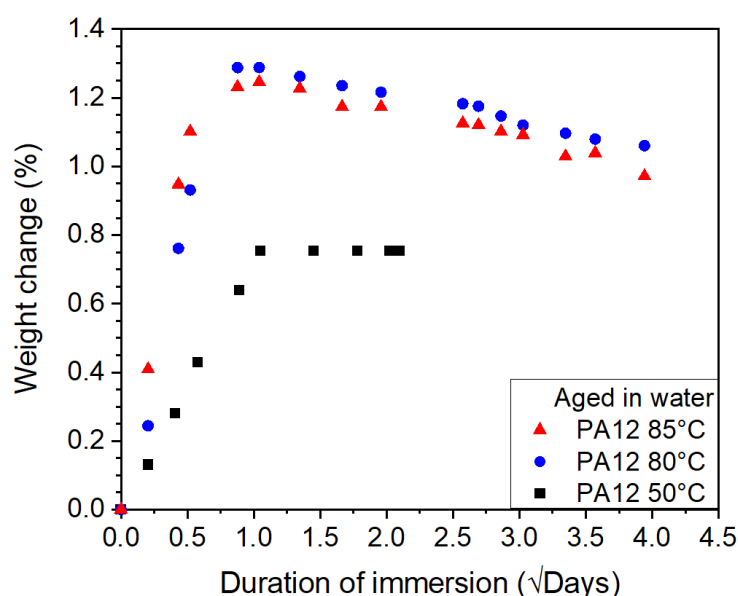


Figure 6.2 Weight change of PA12 aged in water at 50°C, 80°C, and 85°C

Overall, Figure 6.2 shows that elevated temperatures raised the rate at which polyamide 12 absorbed water, its maximum percentage weight gain at equilibrium and the rate at which it was chemically degraded. Mazan et al. [179] artificially aged polyamide 11 in water and explained that hydrolysis causes chain scissions in polyamides, which lowers their molecular weight. Hence it is likely that the samples that were aged at 80 and 85°C began to lose weight after two days because they had reached saturation. Thus, they could not gain more weight from absorbing water, and chain scissions occurred within their structure, which lowered their molecular weight. The resultant shorter molecular chains (oligomers) and monomers diffused out from the polymer and into the surrounding water.

6.3.2 Effects of water on the interfacial shear strength of C/PA12

Figure 6.19 shows that, on average, the interfacial shear strength of C/PA12 (from the flexible pipe) diminished from 40 to 15 MPa after it was aged in water at 130°C for 72 hours, which is

a 62.5% decrease. Furthermore, plots generated from push-out tests conducted on the aged specimens featured a sharp peak, indicating that interfaces in the composite became more brittle after it was aged. Polyamide 12 is susceptible to hydrolysis; therefore, it is likely that hydrothermal ageing of the composite in water caused it to undergo hydrolysis, which caused the embrittlement. That evaluation is supported by Mazan et al. [179], who stated that hydrolysis causes chain scissions which contribute to softening of the amorphous phase as well as its embrittlement. Also, they found that plasticisers within carbon/epoxy composites were lost within two weeks of hydrothermal ageing in water at 120°C. Thus, it is likely that plasticisers were lost in the C/PA12 composite that was hydrothermally aged in the present work, which could be another significant reason for the difference in how the fibres underwent shear failure.

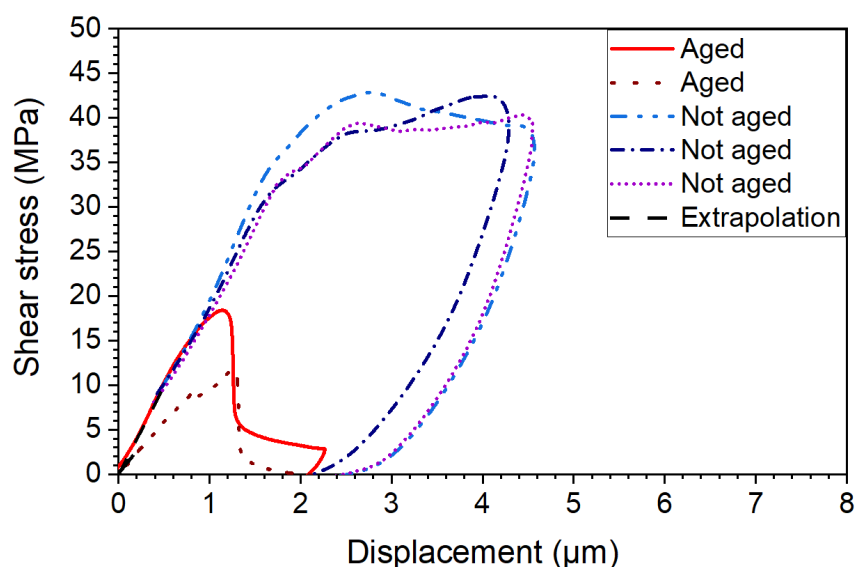


Figure 6.19 Interfacial shear strength profiles of C/PA12 (from flexible pipe) as received and after hydrothermal ageing at 130°C for 72 hours

To investigate how the mechanical behaviour of the polyamide 12 matrix changed in response to hydrothermal ageing. Polyamide 12 was tensile tested both in its state as received and after it was aged in water at 100°C for 72 hours (see Figure 6.3).

Within 72 hours of ageing under those conditions, polyamide 12 exhibited an increase in its yield strength from 20 to 40 MPa, while its ultimate tensile strength increased from 30 to 65 MPa, and its failure strain declined by 70%. Those results are consistent with findings obtained by Mazan et al. [179], who artificially aged polyamide 11 in water at 120°C for up to ten weeks. Initially, they saw that the compliant behaviour of the polymer ended after one week

of ageing, and during that time the tensile strength of the material increased. They affirmed that the initial increase in mechanical strength was anticipated due to the rapid initial dissociation of plasticiser. Nevertheless, a reduction of strength and modulus was also expected from the decrease in molecular weight. They suggested that the reduction in mechanical properties was not observed because reduced plasticiser content concealed the possible decrease in properties caused by reduced molecular weight.

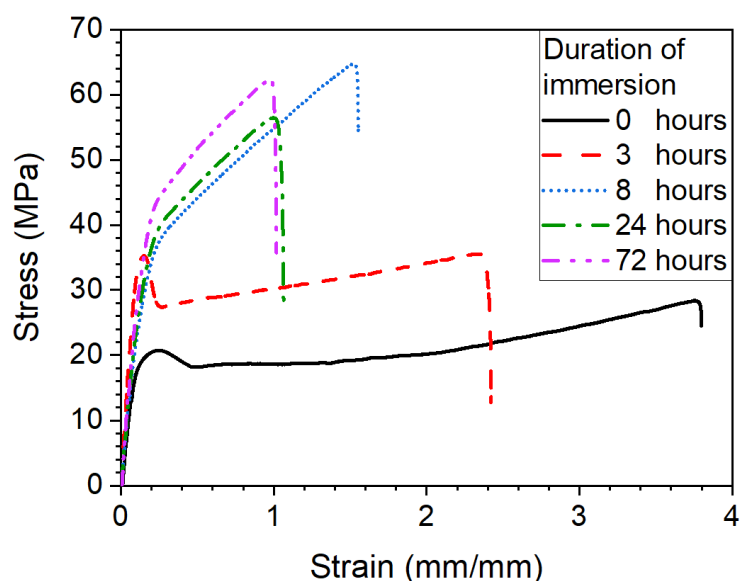


Figure 6.3 Stress-strain profiles of PA12 that had been hydrothermally aged at 100°C for 72 hours and tensile tested

6.3.3 Conclusions

Polyamide 12 coupons were hydrothermally aged at 50, 80 and 85°C. Within two days of ageing under those conditions, the polymer became saturated with water and its weight increased by a maximum of 0.75, 1.25, and 1.3%, respectively. After that duration of ageing, the specimens which were aged at 80 and 85°C steadily lost weight. That was likely due to hydrolysis, which reduced the molecular weight of the specimens. Additionally, push-out tests showed that the interfacial shear strength of C/PA12 diminished by 62.5% after it was aged in water at 130°C for 72 hours. Analysis of the stress-displacement curves generated from those push-out tests implied that the interface/matrix within the aged specimen became brittle. Subsequent tensile tests were conducted on neat polyamide 12, and the test results confirmed that was the case for the matrix.

6.4 Effects of oil (pentane/toluene) on the characteristics of C/PA12

6.4.1 Carbon/polyamide 12: Kinetics of pentane/toluene absorption

A thin sample of C/PA12 and two pairs of PA12 coupons were aged in oil (pentane/toluene) for 51 days at 100°C and 130°C. Figures 6.20 to 6.22 show that the surface of C/PA12 exhibited negligible swelling and little degradation after being exposed to those conditions. Those results are reasonable because both carbon fibre and PA12 are well known for being highly resistant to hydrocarbons [113, 245]. On average, the polyamide 12 coupons reached saturation within 72 hours of being exposed to those conditions. At that point, the weight of the coupons that were aged at 130°C had risen by 8%, while the weight of the coupons that were aged at 100°C rose by 7% (see Figure 6.23).

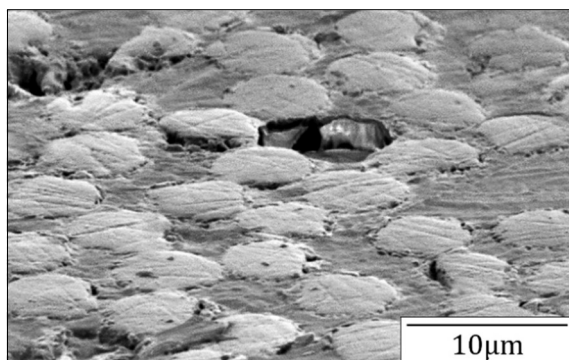


Figure 6.20 C/PA12 as received
(image features a pushed-out fibre)

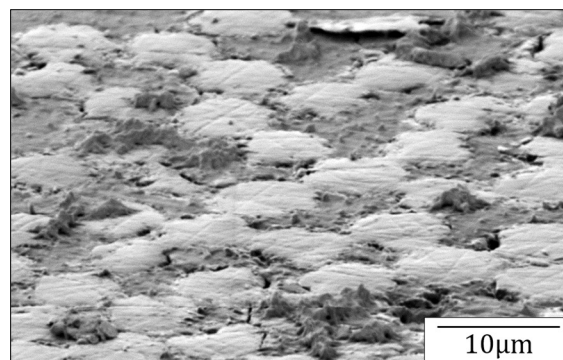


Figure 6.21 C/PA12 aged in pentane/toluene
for 51 days at 100°C

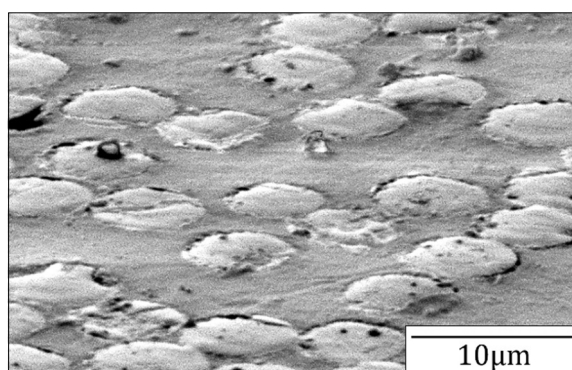


Figure 6.22 C/PA12 aged in pentane/toluene for 51 days at 130°C

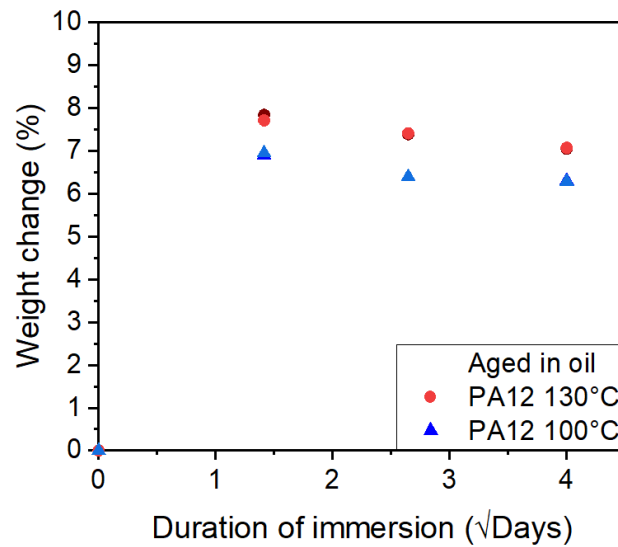


Figure 6.23 Weight change of PA12 aged in pentane/toluene at 100°C and 130°C for 35 days

6.4.2 Effects of pentane/toluene on the interfacial shear strength of C/PA12

Samples of polyamide 12 were push-out tested in their condition as-received and after they were artificially aged in pentane/toluene for 51 days. On average, the specimen that was not aged had an IFSS of 36.5 MPa, whereas the specimen that was aged at 100°C had an IFSS of 43 MPa, and the specimen that was aged at 130°C had an IFSS of 42 MPa. Those results show that the aged samples did not lose interfacial shear strength. Instead, the average interfacial shear strength that was measured increased by 17.8% for the specimen that was aged at 100°C and 15.1% for the specimen that was aged at 130°C (see Figure 6.24).

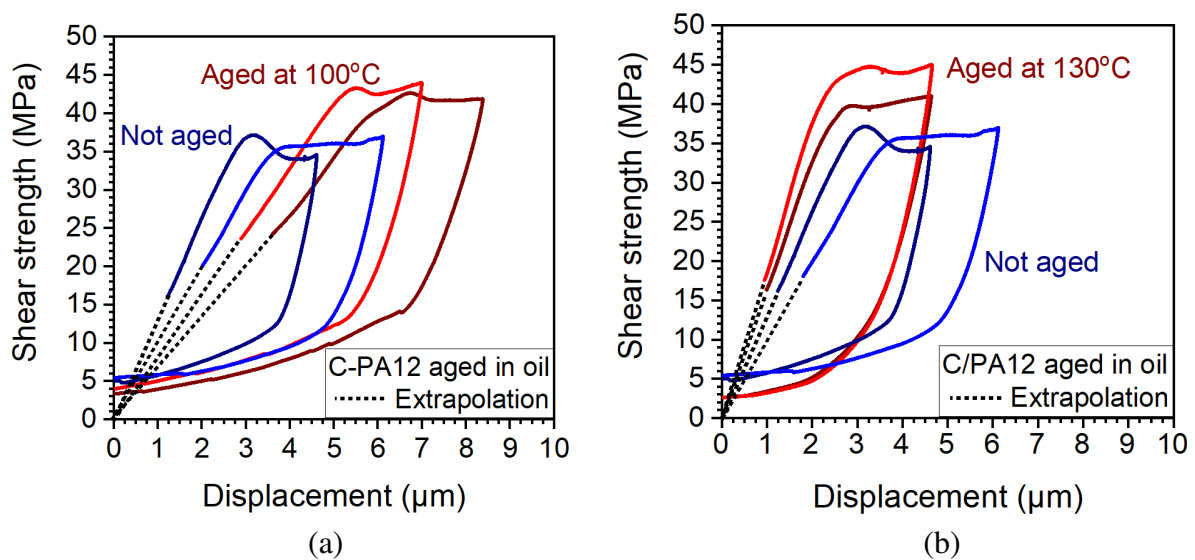


Figure 6.24 IFSS profile of C/PA12 aged in pentane/toluene at (a) 100°C and (b) 130°C

Differential scanning calorimetry analysis of PA12

Samples of PA12 from the PA12 standard sheet were analysed through differential scanning calorimetry before and after they were aged in pentane/toluene for 51 days. That was done to provide insight into the thermochemical and mechanical characteristics of the PA12 matrix in the C/PA12 composites. Results of that analysis are shown in Figures 6.25 to 6.27 and Table 6.1. Those figures indicate that the melting point of PA12 increased with the temperature of the pentane/toluene solution in which it was aged. That was from 175.3°C, to 177.7°C, and 179.0°C, regarding the samples that were not aged, aged at 100°C, and aged at 130°C respectively. Furthermore, when the sample was cooled its crystallisation temperature was 142.3°C, 143.7°C and 147.0°C, regarding the samples that were not aged, aged at 100°C and aged at 130°C respectively. Those trends indicate that the crystallisation temperature of the polymer rose after it was aged at higher temperatures.

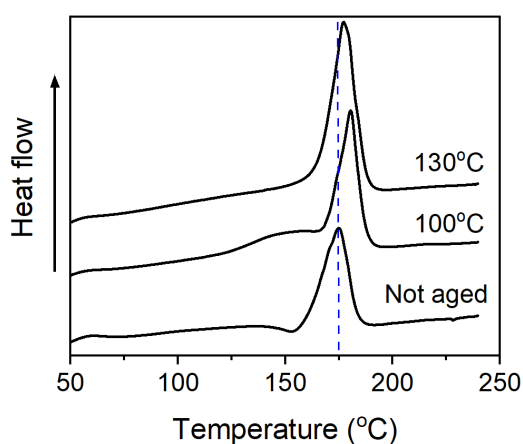


Figure 6.25 DSC. First heating scan, PA12 aged in pentane/toluene

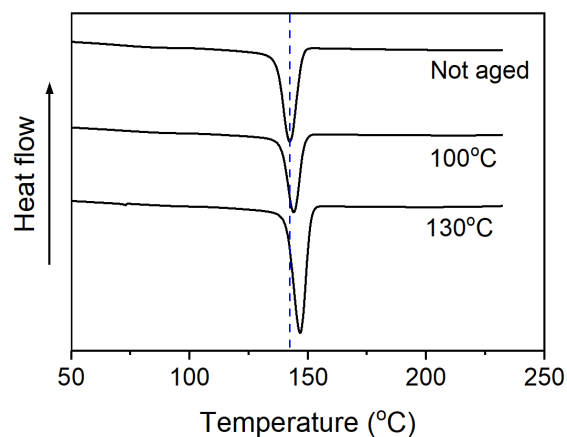


Figure 6.26 DSC. Cooling scan, PA12 aged in pentane/toluene

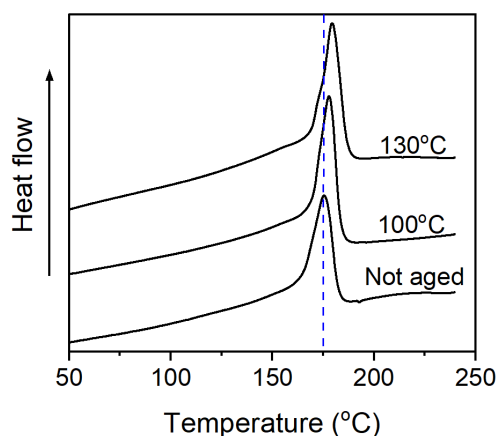


Figure 6.27 DSC. Second heating scan, PA12 aged in pentane/toluene

Aged in pentane/toluene at temperature	First heating scan (°C)	Cooling scan (°C)	Second heating scan (°C)
Not aged	175.0	142.3	175.3
100°C	180.3	143.7	177.7
130°C	179.3	147.0	179.0

Table 6.1 DSC analysis, peak temperatures of PA12 aged in pentane/toluene for 51 days

Polymorphism describes the existence of a solid material in more than one crystal structure or form. Four well-known polymorphs of PA12 are the α , α' , γ , and γ' form.

Hiramatsu [246] explained that the γ -form of polyamide 12 can be obtained by slow cooling the melt at atmospheric pressure, annealing the γ' -form above 110°C, or by high-pressure annealing the α -form at high temperature (above 150°C). Subsequently, Aleman and Casanovas [247] conducted a theoretical study based on force-field calculations to determine that the γ -form is the most stable polymorph of polyamide 12. Still, it should be noted that the α -form is more stable than the γ -form under high pressure (above 500 MPa) [246].

Li et al. [248] used WAXS (wide-angle X-ray scattering) and SAXS (small-angle X-ray scattering) to analyse PA12. From their research, they concluded that the crystalline transition γ to α' occurs upon heating PA12 to around 120°C, and they explained that the α' -phase is independent of the thermal history of the polymer [248].

The γ' -form consists of small crystals that have the same structure as the γ -form, albeit with numerous defects [249, 250]. Hiramatsu et al. [246] investigated crystalline transformations in polyamide 12 by using wide-angle X-ray diffraction (WAXD), X-ray fibre patterns, and differential scanning calorimetry. With that research, they observed that the γ' to γ transformation occurred began when PA12 was annealed above 110°C at atmospheric pressure, and it was almost complete at 150°C. They also noted that the γ' to γ transition took place upon annealing PA12 at 150°C for 10 seconds, and the γ and γ' forms coexist below 50°C or above 110°C. Figure 6.28 shows a summary of the polymorphic transition behaviours of PA12 from a melt.

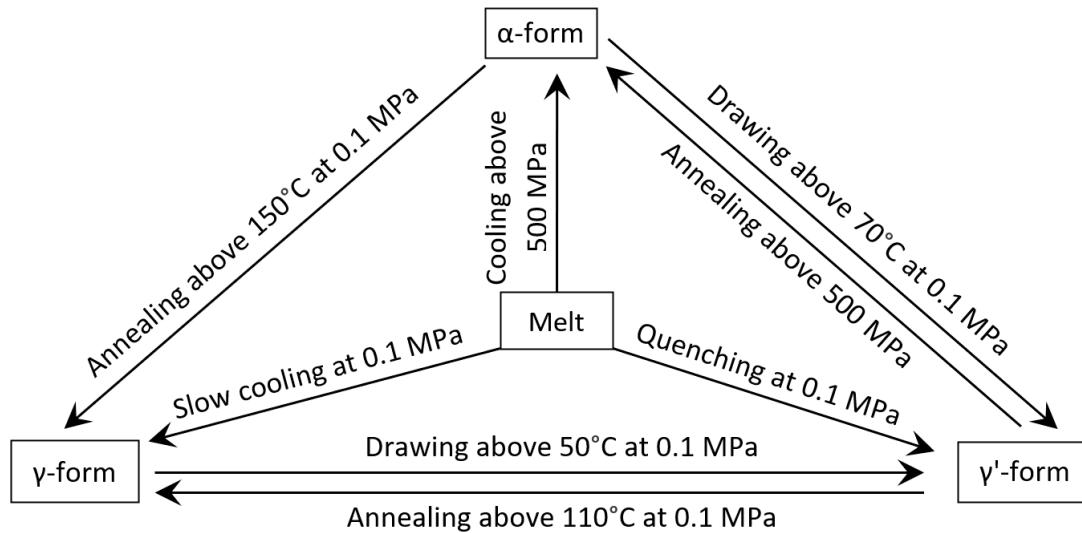


Figure 6.28 Polymorphic transformation behaviours of polyamide 12 [246] from a melt

In polymer solution casting, a polymer is dispersed or dissolved in a solution and then coated onto a carrier substrate. Subsequently, the solvent is removed by drying to generate a solid layer on the carrier [251]. Ma et al. [252] found that an α -form and a mixed ($\alpha + \gamma$)-form of PA12 can be obtained by casting at 30°C and (40°C to 80°C), respectively. Also, the γ -form of PA12 can be obtained by either casting at 90°C. Figure 6.29 shows a summary of the polymorphic transformation behaviours of polyamide 12 obtained from a solution.

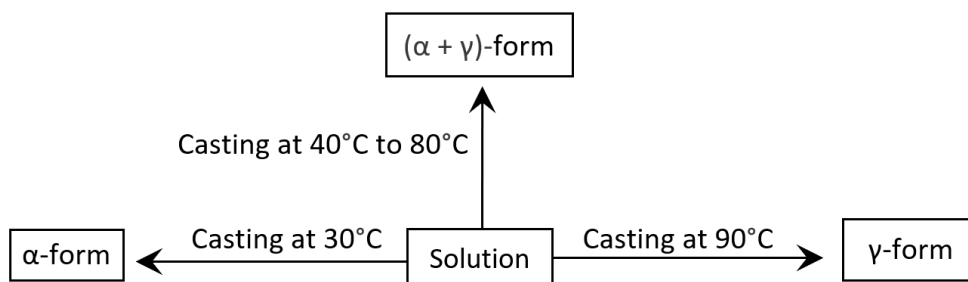


Figure 6.29 Polymorphic transformation behaviours of polyamide 12 from a solution (Adapted from [252])

The C/PA12 specimens that were tested in this work were commercially manufactured. Consequently, the specific conditions under which they were manufactured are currently unknown to the author of this thesis. However, it is likely that the specimens mainly consisted of the γ -form. A reason for that is because both the γ and γ' forms of PA12 exhibit a single melting peak, whereas the α -form exhibits two melting peaks [252]. Figures 6.25 and 6.27

show that the neat PA12 specimens featured a single melting peak, which is consistent with PA12 exhibiting the γ and γ' form. A second reason is that the layers which make up bonded flexible pipes are melt-fused together, in line with that C/PA12 specimens were machined from bonded (melt-fused) flexible pipe in the present work. In PA12, the γ -form is easily and simply obtained by cooling from the melt at atmospheric pressure, whereas high pressure (above 500 MPa) and fast quenching production conditions are required to produce the α -form and γ' -form of PA12 from a melt, respectively (see Figure 6.28). Considering that the layers in the C/PA12 specimens were obtained from flexible pipe had been melt-fused together, it is likely that they underwent slow cooling, not only because of the ease of manufacture but also because the γ -form is stable under 500 MPa [246] and has superior mechanical properties to those of γ' -PA12 [248], accordingly slow cooling would have improved the mechanical properties of the C/PA12 flexible pipe. Thus, it is likely that the polyamide 12 specimens that were examined in the present work mainly consisted of the γ -form polymorph.

Hence, it is worth bearing in mind that the PA12 specimens may have undergone a polymorph transition as they were aged in pentane/toluene during the present work because PA12 is resistant to both toluene and pentane, and because the specimens were aged in pentane/toluene at 100°C and 130°C. If the PA12 based specimens were produced by fast quenching from the melt, they would have primarily consisted of the γ' polymorph; thus the γ' to γ transformation would have occurred as the specimens were aged at 130°C, which is above the 110°C threshold for that transition [246]. Nonetheless, it is worth considering that the polymer is likely to have also transformed into the α' structure when aged at 130°C because the crystalline transition from γ to α' occurs upon heating at around 120°C [248].

Li et al. [248] explained that the mechanical properties of γ -PA12 are superior to those of γ' -PA12, mainly because the γ -form obtained by cooling slowly from the melt leads to closely packed molecular chains and higher crystallinity. Thus, because PA12 and C/PA12 were aged in pentane/toluene for 51 days in this work, believed that the PA12 matrix may have undergone a significant transition to the γ -form at 100°C, that is even more likely to have occurred at 130°C, leading to the improvement of its interfacial shear strength, as indicated by the IFSS profiles of C/PA12 shown in Figure 6.24.

Furthermore, Starkweather et al. [253] found that when the crystallinity of 66 nylon (a type of polyamide) was increased, its stiffness, yield point, tensile strength, and hardness improved. The DSC analysis conducted during the present work showed that the crystallisation temperature of PA12 increased after it was aged in pentane/toluene. Thus, it is likely that its crystallinity, stiffness, yield point, tensile strength, and hardness also improved. That is likely

to have contributed to the heightened interface shear stress values that were measured in C/PA12 after it was aged in pentane/toluene, by improving toughness between the fibres and resin (which is similar to the findings of Min et al. [254]).

Jacques et al. [181] discovered a situation in which the molecular weight of polyamide 11 increased while being aged in oil. Specifically, Jacques et al. [181] aged polyamide 11 in water and normalised oil (diesel) at 140°C for 1000 hours (41.7 days). The polyamide 11 specimens that were aged in water lost molecular weight with immersion time, whereas the polyamide 11 specimens that were aged in the oil attained a higher molecular weight with immersion time. Those outcomes are related to the mechanical strength of polymer composites because, in general, the strength, stiffness, toughness, viscosity and glass transition temperature of a polymer increases as its molecular weight increases [255, 256]. The higher degree of entanglement between long molecular chains allows the material to be placed under a greater amount of strain before the molecular chains and molecular bonds break. Thus, it is believed that as the C/PA12 specimens were aged in pentane/toluene at 100 and 130°C for 51 days in the present work, not only did their crystallinity improve, but their molecular weight also increased. That led to measurements of higher interfacial shear strength in the aged specimens (see Figure 6.2).

Min et al. [254] conducted an experiment in which a G/PP composite gained interfacial shear strength after it was hydrothermally aged. In that experiment, G/PP composites were aged by immersion in water that was held at 50, 75, and 100°C. The glass fibres in the composites were coated with a size that had a high molecular weight and low functionality. As the composite was aged at 50°C, its interfacial shear strength increased with longer immersion times because those conditions improved toughness between the fibres and resin. At 75°C, the interfacial shear strength of the composite decreased with longer ageing durations. That mainly occurred because at that temperature, the water degraded the size. The size was destroyed at 100°C.

Still, investigations by Cho et al. [257], plus Cho and Drzal [258], infer more reasons for why the IFSS measurements of the C/PA12 specimens that were aged in pentane/toluene, were higher than those of the non-aged C/PA12 specimen. Cho et al. [257] found that the storage modulus and thermal properties of carbon fibre/BMI improved after it was sized with LaRC PETI-5 at 150°C (which is a higher temperature than the maximum 130°C that composites were aged at in this work). They suggested that the properties of the composite may have improved because while it was sized with LaRC PETI-5 at 150°C, physical interdiffusion

and chemical co-reactions occurred at fibre-matrix interfaces. Also, Cho and Drzal [258] heated LaRC PETI-5 in air at 100°C and 150°C for 1 hour and found that it reached approximately 2 to 5% of full cure during that timeframe. Considering that during this present work, C/PA12 was aged at 100°C and 130°C for 51 days, it could be argued that the temperature and duration at which composites in this work were aged, promoted further cure of the sizing. However, Cho and Drzal [258] saw that the extent of curing at those temperatures was around 1 to 5% of the maximum possible, which makes it less likely that post-cure of the sizing would have significantly improved the functionality of the size. Nonetheless, in contrast to that deduction, Kumar et al. [259] investigated the effect of post-curing on the thermal and mechanical behaviour of glass/epoxy composites. Those composites were cured and then post-cured by heating. The molecular crosslink density at interfaces in those composites increased rapidly with the amount of time that the composite was post-cured at 140°C. After 6 hours of post-curing at 140°C, the interlaminar shear strength of glass/epoxy rose 25% higher than that of glass/epoxy that was not post-cured.

6.4.3 Conclusions

C/PA12 was aged by immersion in pentane/toluene at 100°C and 130°C for 51 days. Subsequently, the composite was push-out tested, which revealed that it did not lose interfacial shear strength after that treatment. Instead, the average interfacial shear strength measured in the aged specimens was 17.8% and 15.1% higher in each case, respectively.

In the past, researchers have seen the mechanical properties of composites and interfaces improve after the bulk composite had been exposed to elevated temperatures. That has been observed in metal matrix composites [209] and polymer composites [254, 259], which supports the findings of the present work. With further consideration of past research, it is thought that the heat that C/PA12 was exposed to during the present experiment may have improved the shear strength of interfaces within it due to physical interdiffusion and chemical co-reactions of components within the interfaces. Also, a general change in the crystalline structure of PA12, at the interface and matrix, from γ' -PA12 to γ -PA12 could have taken place, resulting in improved mechanical performance [248]. In line with research carried out by Jacques et al. [181], who aged PA11 in oil (diesel) at 140°C for 41.7 days. During the present work, the molecular weight of the polymer may have improved as it was aged in pentane/toluene at 100 and 130°C for 51 days, causing the shear strength of interfaces in the specimens to rise. Additionally, the shear strength of interfaces may have improved due to a

post-curing occurring within the size, improving the functionality of the size and molecular crosslink density (depending on the chemistry of the size).

Nonetheless, it is common for the sizing formula that composite manufacturers use to be patented, kept private, and highly proprietary. Consequently, the sizing formula that was used on the C/PA12 composites that were tested during the present work is unknown. However, a possible sizing formula is LaRC PETI-5 [260], another is Hydrosize [261]. Fittingly, Hydrosize HP-1632 is polyamide-based and compatible with polyamide 12. Its onset of degradation is above 500°C. Therefore, the unknown sizing formula that was added to the C/PA12 specimens might not have been negatively affected to a significant extent by the pentane/toluene solution at elevated temperatures. That further supports the suggestion that the elevated temperatures at which C/PA12 was aged while immersed in pentane/toluene during the present work, caused the shear strength of interfaces within the composite to improve.

6.5 Location of interface failure in aged composites under shear stress

Fibre push-out tests were performed upon a coupon of G/PP that had been aged in water at 80°C for 13 days, then reduced to a thickness of 80 μm thick in preparation for the push-out tests. Figure 6.30 shows that during one of those tests, the interface remained in contact with the pushed fibre while it was pulled apart from a neighbouring fibre. That indicates that the strength of interfaces in the aged composite was inhomogeneous, to the extent that it could change where fibre-matrix debonding took place as fibres underwent shear failure.

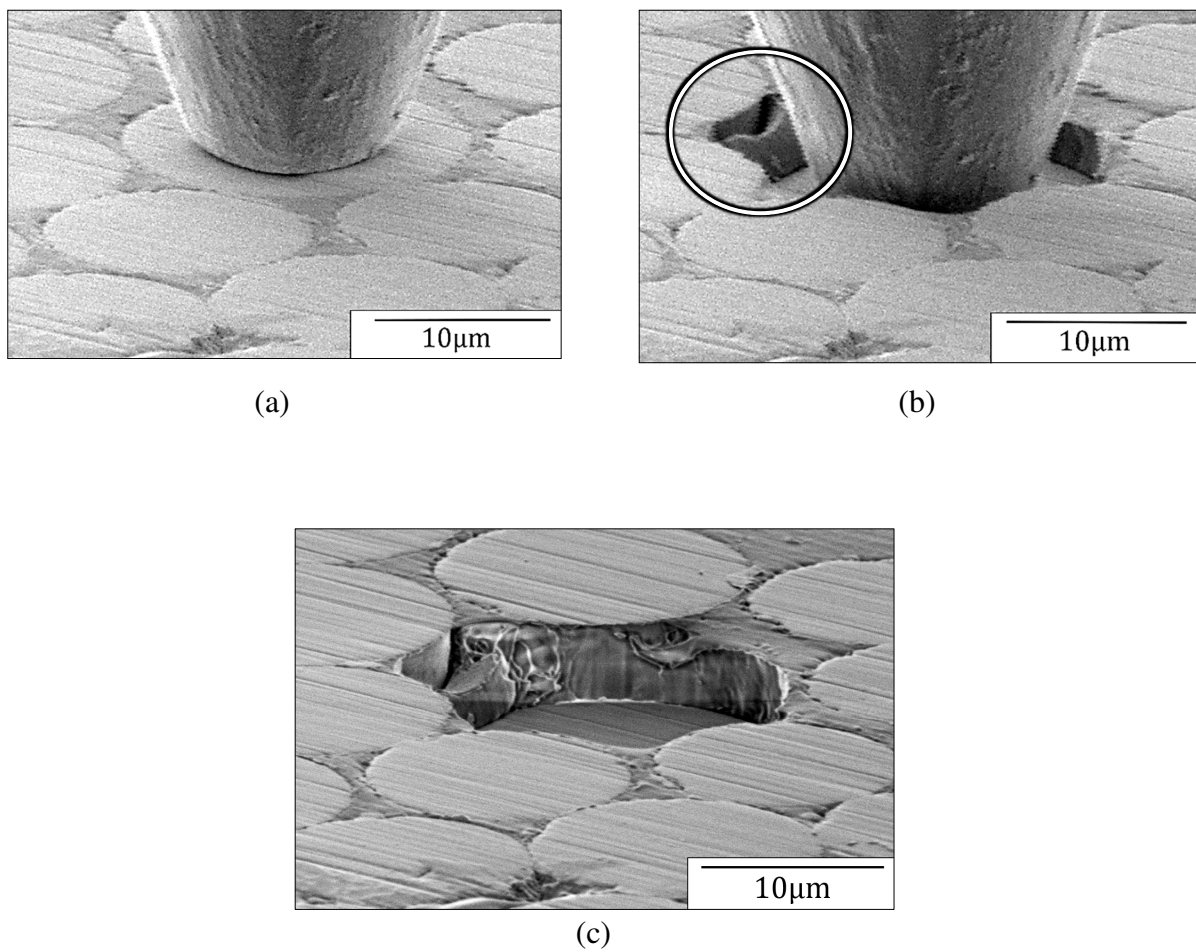


Figure 6.30 G/PP push-out tested (a) and exhibiting the pulloff failure mode (b and c)

Figure 6.31 depicts a push-out test that was conducted on a G/PP specimen. The sample originated from a composite tape which was aged in water for 13 days at 80°C. When the sample was inspected in detail, it was noticed that some fibres slightly protruded from it after it was ground and polished. It was thought that could be an early indicator that the interface surrounding those specific fibres was particularly weak. To test that hypothesis, a fibre located nearby but not next to a raised fibre was pushed out.

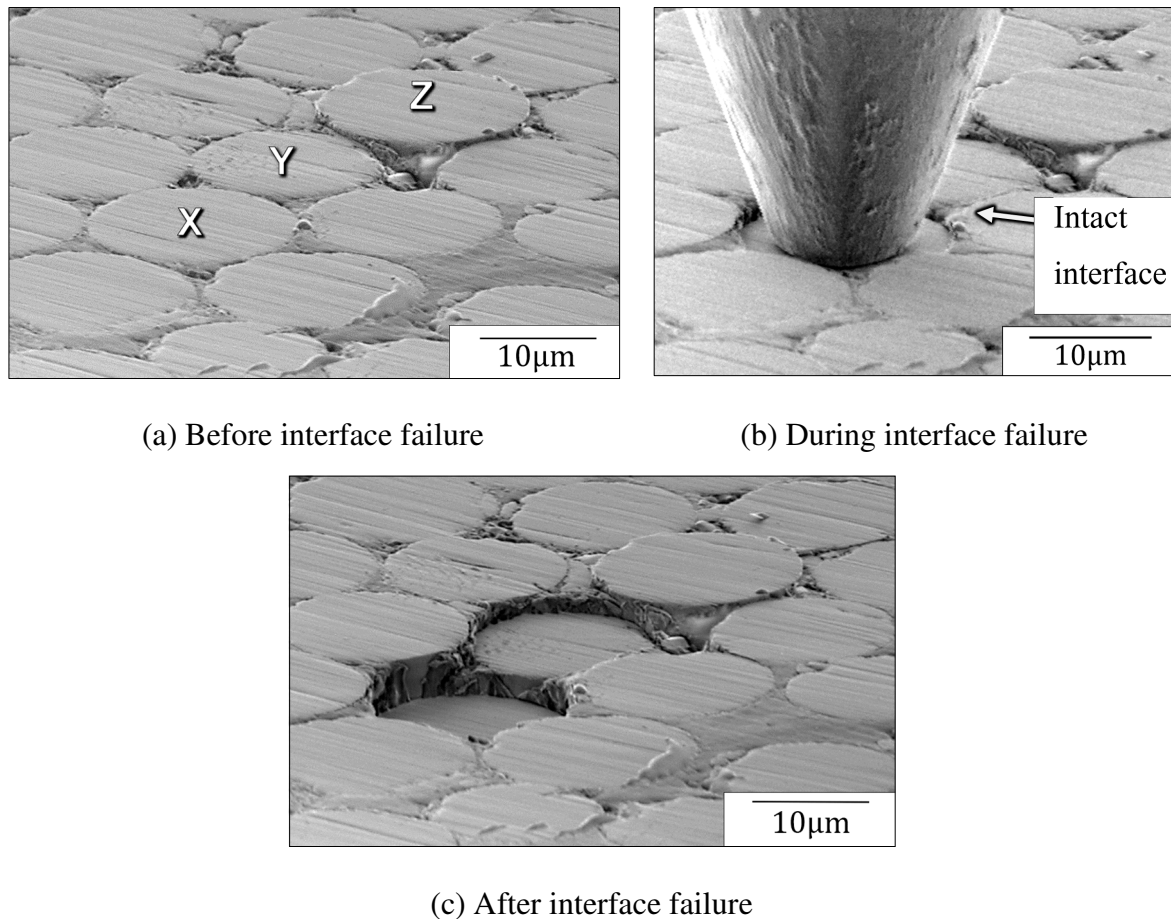


Figure 6.31 G/PP (from tape) aged in water at 80°C for 13 days, then ground and polished

The label, Z, in Figure 6.31a marks the fibre that was slightly protruded, while the X label indicates the fibre that was pushed by the indenter. The outcome of this test was that not only did fibre X that was pushed by the indenter debond, but so did fibre Y, which resided between fibre X and fibre Z (Figure 6.31b). That supports the prediction that the height of fibres in a polished sample can be an indicator of regions in a composite wherein interfaces have weakened to a greater extent than the average found in the rest of the material. Interestingly it

also shows that the small region between fibres X and Y, which remained intact as fibre X was pushed, had a stronger shear strength than the rest of the interface surrounding fibres X and Y.

Around five attempts were made to push-out test fibres from a sample of G/PP that had been aged in water at 80°C for 13 days. Figure 6.32 shows stress-displacement data from the successful push-out tests. Stress-displacement data from the fibres that were pushed out individually is shown in the figure (red dotted and red dashed lines). The shear stress values in those curves were calculated using Equation 2.11. In contrast, shear stress values for the fibres, which exhibited the pulldown mode of failure, are represented by a solid green line in the figure. For those fibres, Equation 6.1 was used to calculate total shear stress across the debonded interfaces, τ_i , and plot the associated stress-displacement curve.

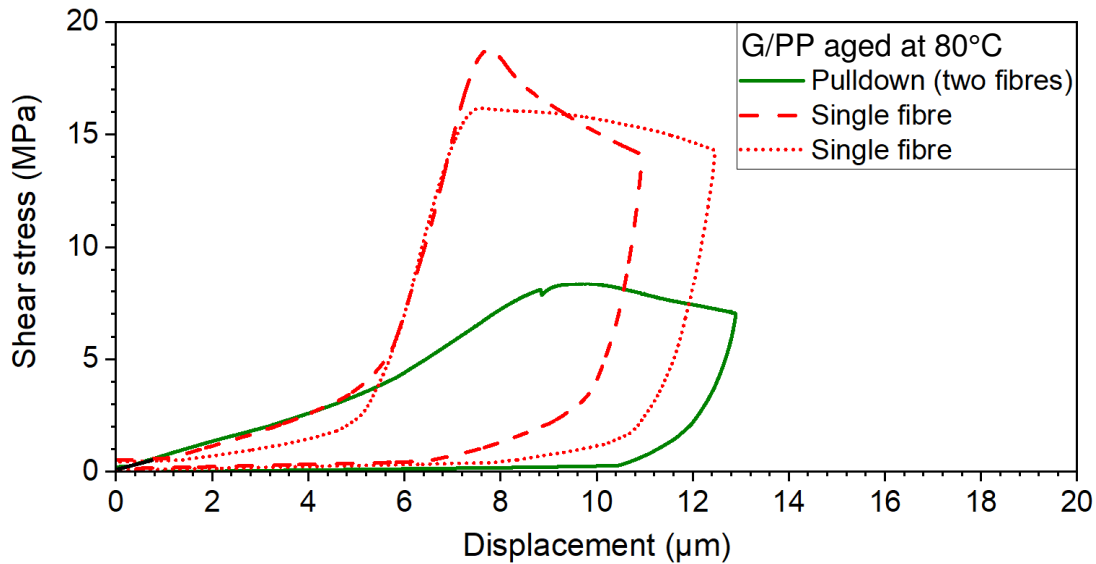


Figure 6.32 IFSS profiles of G/PP (from tape), aged in water at 80°C for 13 days

The solid green curve in Figure 6.32 represents the total surface area of fibres, X and Y, which was debonded from the matrix as the fibres were pushed out. By modification of Equation 2.11, Equation 6.1 was derived and used to generate that curve.

$$\tau_i = \frac{P_f}{\pi d_i h} \quad 6.1$$

Where τ_i is the total shear stress across the debonded interfaces, P_f is the load applied to the fibre which was pushed by the indenter, d_i is the total fibre diameter that had undergone interfacial failure, and h is the specimen thickness.

Together, the shear strength of fibres X and Y, having been pushed out simultaneously, was around half that of the single fibres that were also pushed out from the sample. That is logical given that the surface area of fibres X and Y together was around double that of the single fibres. The partial interface between fibres X and Y was strong enough to pulldown fibre Y, while fibre X was pushed. That is evidence that interfaces weakened in an inconsistent manner around the circumference of each individual fibre.

6.5.1 Conclusions

G/PP was aged in water at 80°C for 13 days and then push-out tested. Interfaces in the composite degraded unevenly around the circumference of the embedded glass fibres. As a result, the fibres underwent shear failure through different modes during the tests. Those modes were named ‘pulloff’ and ‘pulldown’ failure modes in this chapter. In the pulloff failure mode, a single glass fibre was placed under an axial load so that it was pushed through the polypropylene matrix. That fibre pulled the interface surrounding its neighbouring fibre apart while its own interface remained intact. In the pulldown failure mode, a glass fibre was pushed through the polypropylene matrix by a flat punch, and while that fibre was pushed out from the matrix, it pulled down a neighbouring fibre with it, causing the neighbouring fibre to debond from the matrix and begin to slide out. Essentially, multiple fibres were pushed out while the interface between them had not completely debonded. Thus, an equation was developed and used to produce a more valid calculation of the shear strength of the interface, which had failed surrounding those fibres.

7. CONCLUSIONS AND FURTHER WORK

Due to the depletion of onshore and offshore oilfields, the need to obtain oil from greater depths is pushing the design of flexible pipes to their technical limits. Flexible pipes frequently offer a better balance between service weight, chemical, and mechanical performance than steel pipes. That has driven the oil and gas industry towards using flexible composite pipes in challenging high-pressure, high-temperature oil and gas production environments.

The main goals of this thesis were to provide detailed insight into how the shear strength of fibre-matrix interfaces in G/PP and C/PA12 thermoplastic composites, which are typically used in flexible pipes, changes due to prolonged exposure to water, oil (pentane/toluene) and elevated temperatures, as well as short term exposure to elevated temperatures alone. Thus, a literature review of popular single fibre shear strength test methods was conducted, and from that review, the push-out test was identified to be the most promising technique for the fulfilment of those goals. That test was used to evaluate how the strength of the interface surrounding individual fibres was affected by the local fibre density, the rate at which the fibre was put under an applied load, the temperature of the fibre and matrix, and mechanical damage caused by the failure of neighbouring fibres under shear stress.

For example, it was found that interfaces in G/PP had greater resistance to shear failure when the embedded fibres were subjected to an applied load at faster rates. Those interfaces also exhibited less frictional shear stress after fibre failure. That was likely because the interface had less time to deform under the influence of creep when the fibres were pushed at faster rates.

Moreover, G/PP fibres that were examined in the regions of high fibre density (where fibres were closely packed) exhibited an interfacial shear strength that was 25% lower than those located in regions of low fibre density. Reasons for why that difference occurred were proposed, the first suggestion being that the matrix was constrained and had less freedom to yield in regions of high fibre density, which limited stress transfer from the interface to the matrix. Additional suggestions were that the interface had a narrower average thickness and different chemical make up in regions where fibres were close or in contact with each other, which reduced the shear strength of the interface in regions of high fibre density.

When a continuous unidirectional composite is subjected to overwhelming compressive stress, it will typically fail through the shear mode [41, 42]. During that process, the embedded fibres break and fibre-matrix interfaces fail in succession, leading to the formation of a kink band which propagates through the composite. Thus, in the present work, fibres in G/PP and C/PA12 were systematically pushed-out in a specific sequence to investigate the effects of gradual, cumulative mechanical damage to the interface surrounding a single glass or carbon fibre which was closely surrounded by six matching fibres in a hexagonal arrangement. In one case, glass fibres in G/PP were push-out tested in succession. The fibres which were situated between two neighbouring fibres that had been pushed out had an initial interfacial shear strength which was subsequently reduced by 43%, and the initial interfacial shear strength of a central fibre surrounded by six neighbouring fibres was reduced by 75% after the neighbouring fibres were pushed out. Likewise, in the case of C/PA12, the initial interfacial shear strength of carbon fibres adjacent to two fibres which had been pushed out diminished by 20%, and the interfacial shear strength of fibres that were surrounded by six neighbouring fibres diminished by 53%, after the neighbouring fibres were pushed out. Importantly, the results demonstrated that the push-out test can be used to cause and measure cumulative damage at interfaces. The findings also showed examples of how far the shear strength of the interface surrounding a given fibre in a composite can diminish due to prior failure of its neighbouring fibres under shear stress.

G/PP and C/PA12 composites were aged in water and pentane/toluene at temperatures ranging from room temperature up to 130°C for up to 51 days. The interfacial shear strength of the G/PP and C/PA12 specimens weakened as they were hydrothermally aged. Specifically, the interfacial shear strength of G/PP reduced by 15.9% after it was aged in water at 80°C for 35 days. Also, the interfacial shear strength of C/PA12 reduced by 63% after it was aged in water at 130°C for 72 hours. The critical factor for reduction of the interfacial strength in the G/PP specimen after hydrothermal ageing was deemed to be water penetration into the-fibre matrix interface. That penetration of water could have been enhanced by the glass fibres, which would have naturally attracted water because glass is hydrophilic. A critical factor that caused interfacial shear strength reduction in the C/PA12 specimen after hydrothermal ageing was deemed to be the hydrolysis of the interface. Evidence for that view came from previous literature regarding the mechanism of polyamide hydrolysis, as well as trends in the stress-displacement curves produced by push-out tests on the specimens. Those trends indicated that the interface became brittle, which is typical for PA12 that has undergone plasticiser loss or hydrolysis.

The interfacial shear strength of G/PP reduced by 90% after it was aged in pentane/toluene at 100°C for 51 days. that decrease in interfacial shear strength was mainly due to dissolution of the matrix and interface in the pentane/toluene solution.

In contrast, the interfacial shear strength of C/PA12 was measured before and after it was aged by immersion in pentane/toluene at 100°C and 130°C for 51 days. On average, after that treatment its interfacial shear strength was measured as being 17.8% higher, regarding the specimen that was aged at 100°C and 15.1% higher regarding the specimen that was aged at 130°C. Several possible reasons for that outcome were put forward in this thesis. For example, the hygrothermal ageing conditions may have closed defects at interfaces [262], improved how well sizing wet the fibres [263], enhanced interface adhesion through post-cure of the sizing [239], improved interface morphology through physical interdiffusion and chemical co-reaction of the size with the matrix [254], or improved the structure of the matrix in terms of its molecular weight [95, 181] and crystallinity [246, 262].

A hybrid-push test was devised. In that test, glass fibres from a G/PP composite were pushed into a soft wax substrate. The hybrid-push test provided an effective way to eliminate the period of sample compliance that usually occurs before a sample comes into full contact with a grooved substrate during conventional push-out tests. However, performing the test resulted in the interfacial shear strength of the composite being inaccurately measured as 59% stronger than it was in reality due to the substrate resisting fibre displacement. To mitigate that outcome, a supplementary experimental method and equation were devised and used to improve the accuracy of interface shear stress values produced from the hybrid-push tests by around 9%. Those inventions also provided a way to simulate push-out tests as if they were performed on a composite that is situated on a given soft substrate, rather than over a gap.

Moreover, it was found that as composites absorb moisture the interfaces within them can weaken in a significantly inhomogeneous way, which can cause the strength of the interface surrounding an individual fibre to be inconsistent from one region of the fibre circumference to another. That strength may vary to the extent that when a fibre in a hygrothermally aged composite is subjected to an applied load, it may transfer enough force through the matrix to break the interface surrounding a neighbouring fibre, while its own interface remains intact. It can also be divergent enough that when a single fibre is pushed down, it will pulldown another fibre with it. Here those failure mechanisms were named as pulloff and pulldown failure modes, respectively.

7.1 **Further work**

G/PP was push-out tested in regions wherein it had a high fibre density and in regions wherein it had a low fibre density. It is thought that the matrix of G/PP had greater freedom to yield in its regions of low fibre density, and that caused the interfacial shear strength of G/PP to be higher in those regions. A way to provide additional evidence for that proposition in future work could be to push-out test fibres which are located in regions of high and low fibre density. Then to measure how far the matrix yields and how much polymeric material remains adhered to the exposed curved surface of each fibre, in correlation with the local fibre density.

In this work, it was suggested that glass fibre surfaces in G/PP were hydrophilic, which caused G/PP to exhibit faster water uptake and a greater volume of water uptake than neat polypropylene. A way to assess that proposal in future work could be to fabricate fibre-reinforced polypropylene composites which are reinforced by hydrophilic fibres. Then to assess how far they absorb moisture compared to polypropylene alone. The hydrophilicity of the composite could be adjusted by using different types of fibre, different types of sizing, or no sizing at all on the fibre. The wettability of the fibres alone could be measured using a Wilhelmy balance, which is a device that can measure the wettability of a single fibre in a tensiometer. Qiu et al. [264] developed that technique of using a Wilhelmy balance to measure contact angles and used it to measure the dynamic contact angles of water on carbon fibres of different diameters.

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