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Thermal cycling effects on the durability of a pultruded GFRP material for off-shore civil engineering structures

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Abstract

This paper investigates the effects of thermal cycles on the structural integrity of a pultruded Glass Fibre Reinforced Polymer (GFRP). Through a critical review of current literature alongside a comprehensive experimental campaign, the material’s response to cyclic thermal loading has been ascertained, defined by the rate of degradation of its physical, mechanical and visco-elastic properties. Matching sets of both dry and soaked samples conditioned in distilled water for 224 days. Freeze-thaw cycling of both dry and soaked samples was conducted between 20°C and -10°C for a total of 300 cycles. Computed tomography scanning (CT-scan) was undertaken to assess the microstructural physical changes throughout freeze-thaw cycling. After exposure, GFRP samples exhibited a minor decrease in Glass Transition Temperature ($T_g$) which indicated minor structural degradation. Dry GFRP sample’s mechanical response exhibited negligible changes in both tensile and in-plane shear properties. However, as a result of the higher induced thermal stresses, soaked samples showed a significant degradation of their tensile and shear strengths. Yet, the soaked material’s stiffness remained largely unaffected due to the potential reversible nature of plasticization, which acts to increase the material’s molecular mobility when initially moisture-saturated, but is later recovered as the soaked samples lose moisture throughout freeze-thaw cycling.

Keywords: pultruded composite; polymer matrix composite; FRP; freeze-thaw thermal cycling; mechanical properties; Computed Tomography (CT-scan)

1. Introduction

Fibre-Reinforced-Polymer (FRP) materials in their simplest form consist of fibres embedded in a polymeric resin matrix, combining the high stiffness and strength of structural fibres with the lightweight, low-cost and environmental durability of polymer resins. The growing need for infrastructure renewal throughout the developed world, alongside the ever decreasing cost of FRP materials, has led to a new found interest in their civil engineering applications. As such, FRPs are now being increasingly used as structural materials in the construction industry [1].

Across a range of civil engineering sectors, Glass Fibre Reinforced Polymers (GFRP) are becoming the most commonly used form of composite materials, due to their reduced cost and high chemical resistance to environmental attack. For structural sections in particular, the economic and consistent process of pultrusion has become the standard method of fabrication. As discussed within several studies [1-3], pultruded composite sections and profiles present great potential for the civil engineering industry, offering high specific strength and stiffness, low self-weight, ease of handling, electromagnetic transparency, low maintenance requirements and high durability even in relatively harsh environments [1-3].
2. **Background**

2.1. FRPs in civil engineering applications

To date, composite materials have been used in a range of applications within the construction industry [4]. GFRP profiles in particular have been used as both primary and secondary structural elements, with only a handful of demonstration projects of footbridges, highway bridges, and buildings that utilise GFRPs as primary structural members [3]. As awareness and knowledge of composite structures has grown within the construction industry, a range of promising applications for GFRP profiles have become available. As highlighted by Bakis *et al.* [1], one of the most promising fields of application of GFRP materials are in bridge structures, such as lightweight footbridges or bridge deck replacements. The potential of GFRP materials for these applications stems largely from the material’s high fatigue and corrosion resistance, alongside its increased strength and stiffness per unit weight as compared to traditional steel and reinforced concrete structures.

More recently, the rapid growth of the offshore renewable energy sector has generated several new potential areas of application for GFRP materials. Following the continuous demand for increased efficiencies in wind, wave and tidal energy, designers now require larger blades and structures, which in turn require significantly higher strength/stiffness-to-weight ratios, alongside non-corrodibility and low maintenance requirements [5]. To date, only FRP materials are known to meet these design requirements. In each of these major applications of GFRPs, the presence of water, chemical exposure, sustained loading and both high and low extremes of temperature calls into question the composite’s long-term durability within such harsh environmental conditions. This requires the designer to understand and accommodate for the specific aging and degradation mechanisms that will ultimately affect the material’s structural properties throughout the design life of the structure. It is in this vein that the widespread use of FRP materials in construction encounters its greatest obstacle; such an understanding of the material’s structural response to environmental degradation is yet to be explored and fully understood.

In this work, the thermal cycling degradation process of a pultruded GFRP profile is investigated. In particular, the effects of freeze-thaw cycles on durability, and the compounding effects of pre-existing water molecules within the composite structure are studied. The main goal is to outline both the physical mechanisms behind the freeze-thaw process, alongside the rate of degradation of specific mechanical properties in both dry and moisture saturated environments. This field of research is of particular interest to the aforementioned applications of such materials within the construction industry. The presence of water alongside freeze-thaw conditions is unique to such structures, which are located in regions of low extremes of temperature and tidal water levels.

2.2. Freeze-thaw degradation

To date, a range of research has been carried out in the field of freeze-thaw durability of FRP profiles. However, the combined effects of both moisture saturation and thermal cycling has received little attention. In order to properly define the test conditions (due to the current lack of freeze-thaw testing standards), reference has been made to previous research to ensure comparable parameters are selected for testing. A vast range of such test parameters are considered in the current literature [2, 6-15] and discussed below. Each study focuses on a specific variable affecting the composite’s durability, which when viewed in combination, has developed the current understanding of the mechanisms that drive the freeze-thaw degradation of FRPs. The focus of the studies undertaken to date, although frequently used in combination,
can be separated into three categories: (i) fibre structure and manufacturing process; (ii) matrix structure, and (iii) combined environmental conditions.

2.2.1 Fibre structure and manufacturing process

Dutta et al. [6] investigated the effects of thermal cycles between -60°C and 50°C (2 h at each temperature) on the flexural properties of two polyester based GFRPs of E-glass and S2-glass. After just 100 cycles, the E-glass specimens had developed extensive cracking and so no further tests were undertaken. Whereas, the S2-glass samples showed no visible signs of degradation following 250 cycles and so were tested further, leading to minor degradation of both the tensile modulus (-6.2%) and shear modulus (-6.3%). All samples tested were of substantial thickness (12.7 to 44.5mm), therefore induced post-cure stresses are highly likely as the heat distribution is unlikely to be uniform during curing. In addition, the high extremes of temperature used during thermal cycling would possibly accelerate these post-cure phenomenon, whilst the lower bound temperature would induce significantly high thermal stresses within the samples, which would combine to exceed their tensile strength.

Zhang et al. [7] also investigated the extent to which the constituent fibre material affects the composite’s resistance to freeze-thaw cycling, subjecting E-glass (wet-layup), aramid (wet-layup) and carbon (automated winding) fibre reinforced polymers to 180 cycles between -26°C and 23°C (48 h). In addition, all samples were submerged in a 5% NaCl solution (5 weeks) prior to thermal cycling to simulate moisture absorption through road spray. The samples showed overall reductions in tensile strength (-10.1 to -16.1%), with a more severe degradation of interlaminar shear strength (-7.8 to -25.3%), except for the carbon fibre composite which exhibited an insignificant increase compared to the likely experimental error (+2.2%). It was also shown that constant exposure to low extremes of temperature (-15°C) has negligible permanent effects on the composite’s mechanical properties. The increased degradation shown may come as a result of the additional stresses induced as salt deposits expand within the composite structure, however it was noted that the samples were unlikely to have reached full saturation following only 5 weeks of submersion. The varying manufacturing processes involved in the use of each fibre material possibly influenced the increased degradation, stemming from the incomplete curing and pre-existing voids of the ambient cured; wet-layup samples in particular.

Rivera et al. [8] and Karbhari et al. [9] further assessed the effects of varying fibre structures on the composites freeze-thaw durability, using ambient cured carbon/vinylester and E-glass/vinylester composites, and subjecting samples to 100 cycles between -10°C and 22.5°C (24 h). These cycles were completed in both dry conditions and in aqueous solutions of deionised water and salt water. The dry samples exhibited significant reductions in their tensile (-8.2 to -9.1%) and compressive (-9.5 to -17.5%) strengths and to a lesser degree, in their tensile modulus (-3.9 to -6.0%) and glass transition temperature (-6.8 to -7.3%). The immersed samples exhibited accelerated degradation; in particular the tensile (-9.6 to -16.1%) and compressive strengths (-25.8 to -29.8%). The reduction in tensile strength was comparable to that found by Zhang et al. [7] under relatively similar cyclic conditions. Li et al. [10] supplemented these previous works into the effects of varying fibre structures, evaluating the freeze-thaw resistance of unidirectional E-glass, carbon and basalt reinforced epoxies between -30°C and 30°C. This resulted in insignificant degradation of the tensile properties of both the glass and basalt fibre samples, with a much more severe degradation exhibited by the carbon fibre samples in both tensile strength (-16%) and tensile modulus (-18%). This was attributed to the inertness of the carbon fibres, which results in weaker fibre-matrix bonding. In comparison with the studies of Rivera et al. [8] and Karbhari et al. [9], the temperature range of these tests were significantly higher (approximately double), whilst the results show a significantly lower degree of degradation of the composite’s tensile properties.
2.2.2 Matrix structure

Di Ludovico et al. [11] investigated the behaviour of Carbon Fibre Reinforced Polymer (CFRP) laminates under freeze-thaw conditions (210 cycles between -5°C and 40°C), focussing upon the durability of a range of innovative resin structures, namely neat epoxy and nano-modified composite systems. Samples were subjected to 210 cycles between -5°C and 40°C (24 h). This resulted in a minor depression of tensile strength (-8.5%) in the commercial epoxy samples, whilst the nano-modified resin samples showed minimal degradation throughout freeze-thaw cycling. The degradation exhibited was much less severe than the CFRP samples tested by Li et al. [10]. This was attributed by the authors to the increased resistance of the epoxy systems, however it can be seen that several mechanisms may have also contributed to these findings. The lower bound temperature used within this study (-5°C) is significantly higher than that of the previous studies, resulting in much lower induced thermal stresses within the samples. Furthermore, the high upper bound temperature used (40°C) may have resulted in an additional post-cure of the epoxy resins (which were cured for 1 hour at 60°C), resulting in an increase in their mechanical properties throughout each thaw phase. The recent work of Sousa et al. [2] again focused on the effects of the composite’s matrix structure on the material’s degradation throughout thermal cycling. Samples cut from GFRP profiles of both polyester and vinylester matrix structures were subjected to 190 cycles from -5°C to 40°C (14 h). This resulted in minor degradation of the samples’ viscoelastic properties, and minimal degradation of their mechanical properties. It was also found that the vinylester samples exhibited reduced overall degradation compared to the polyester samples [2]. The similar thermal cycle conditions used in the work of Di Ludovico et al. [11] led to significantly lower degradation than that reported by Sousa et al. [2]. This likely stems from the use of a different fibre material (CFRP), which is known to have a negative coefficient of thermal expansion, thus inducing lower thermal stresses within the samples. In addition, the high upper bound temperature (especially in the vinylester samples whose glass transition temperature is significantly lower than that of the polyester samples) would likely have caused some residual curing (or post-curing) phenomenon [15], counteracting the freeze-thaw degradation of mechanical properties.

2.2.3 Combined environmental conditions

Wu et al. [12] were one of the first to apply these basic testing principles to the assessment of the freeze-thaw durability of modern composite bridge deck materials, with a focus on simulating the environmental conditions of such structures and assessing their compound degradation effects. Samples of E-glass/vinylester composite were subjected to 250 cycles from -17.8°C to 4.4°C (5 h). Both dry and wet samples (submersion in distilled water or salt water for two weeks) were cycled under a constant applied load of 25% of the composites ultimate load to simulate the service exposure conditions of such bridge deck structures. This resulted in minimal degradation of the samples’ flexural strength and glass transition temperature. The minimal submersion time for each sample alongside the addition of epoxy to each of the samples’ cut edges will have resulted in insignificant water uptake in the sample, thus inducing no additional thermal stresses. It may be postulated that the low temperature difference between -17.8°C and 4.4°C, when compared to previous studies, resulted in a thermal gradient which was not great enough to induce the necessary thermal stresses within each sample to cause degradation. The latter was apparent in the insignificant degradation of the dry samples shown in this study. Kim et al. [13] further investigated the synergistic effects of various long-term degradation processes, testing two types of E-glass/vinylester rods under a range of environmental conditions (moisture, chloride, alkali and freeze-thaw). During freeze-thawing, samples were subjected to 60 cycles between -25°C to 30°C in alkaline conditions. It was found that severe degradation of the composite’s interlaminar shear strength occurred in the commercial vinylester sample (-29.3%)
and to a lesser degree in the modified vinylester (-5.9%). It was noted that this strength reduction was very similar to that shown during alkaline aging, thus the degradation was dominated by the alkaline condition during freeze-thaw cycling. As such, it is very difficult to compare the results of this work to previous research. A further study into the freeze-thaw flexural properties of polyester based pultruded GFRP profiles under combined environmental conditions was undertaken by Aniskevich et al. [14], who subjected both dry and soaked (moisture saturated) samples to 125 cycles from -30°C to 20°C. This resulted in a minor increase in the dry sample’s flexural strength (+2.5%) with the soaked sample exhibiting substantial degradation (-13.3%). The flexural modulus of the dry samples exhibited a minor increase (+5.9%), whilst the soaked samples showed significant increases (+14.4%). Both dry and soaked samples also showed a slight decrease in their glass transition temperatures (-3.0% and -5.2% respectively). As the dry samples showed insignificant losses in flexural strength, the degradation shown by the soaked samples are likely to have stemmed from the additionally induced thermal stresses, resulting from the formation of ice crystals within the composite structure. In addition, the hygrothermal degradation of the glass fibres themselves may have led to the substantial losses of flexural strength, which have been shown to effect the matrix and fibres to a greater degree than the effects of freeze-thaw cycling. Table 1 summarizes the results reported by previous studies into the freeze-thaw resistance of FRPs.
There is a general consensus within the discussed literature that matrix embrittlement, microcracking, and the fibre-matrix interface failure are the key degradation mechanisms that drive the freeze-thaw process. However, the experimental work in this field is severely limited by the lack of a consistent test methodology with varying exposure conditions, cycle definitions, raw materials, manufacturing processes and test procedures. These inconsistencies lead to several contradictory and incomparable studies that cannot provide the level of confidence required by designers in the establishment of design standards and material specifications for FRP materials. In addition, the combined degradation effects of moisture and thermal cycling have been highlighted by Karbhari [4] as one of the key gaps in the knowledge of FRP’s long-term durability. However, very few of the recent studies investigate this combined condition. Those that do mostly fail to adequately moisture-saturate each sample or investigate the combined degradation mechanisms that occur. The majority of the research outlined also fails to fully understand each of the predicted failure mechanisms, with very few studies investigating the extent to which each mechanism has resulted in the degradation of specific mechanical properties. This prevents the creation of mathematical or computational models able to simulate the composite’s long-term durability throughout thermal cycling based on physical test data. This paper aims to bridge the above mentioned gaps identified within current literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Fibre</th>
<th>Matrix</th>
<th>Adhesive</th>
<th>Matrix Interface</th>
<th>Autoclave</th>
<th>Thermal Cycles</th>
<th>Results</th>
<th>Property</th>
<th>Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data and Bai</td>
<td>1996</td>
<td>E-Glass</td>
<td>Polyester</td>
<td>Adhesive bonding</td>
<td>-</td>
<td>Ambient Humidity</td>
<td>4</td>
<td>290</td>
<td>%</td>
<td>-6.8</td>
</tr>
<tr>
<td>Zhang et al.</td>
<td>2001</td>
<td>E-Glass</td>
<td>Polyester</td>
<td>Adhesive bonding</td>
<td>2% NaCl Immersion (for 5 weeks prior to thermal cycles)</td>
<td>-</td>
<td>-10 to 23</td>
<td>%</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Wu et al.</td>
<td>2002</td>
<td>Carbon</td>
<td>Vinylester</td>
<td>Unclassified</td>
<td>Immersion in deionized water, salt water and ambient humidity</td>
<td>-</td>
<td>24</td>
<td>%</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Lin et al.</td>
<td>2007</td>
<td>E-Glass</td>
<td>Polyester</td>
<td>Adhesive bonding</td>
<td>-</td>
<td>Ambient Humidity</td>
<td>24</td>
<td>60</td>
<td>%</td>
<td>10.5</td>
</tr>
<tr>
<td>Li et al.</td>
<td>2011</td>
<td>E-Glass</td>
<td>Polyester</td>
<td>Adhesive bonding</td>
<td>-</td>
<td>Ambient Humidity</td>
<td>24</td>
<td>60</td>
<td>%</td>
<td>10.5</td>
</tr>
<tr>
<td>Ludovico et al.</td>
<td>2012</td>
<td>Carbon</td>
<td>Commercial Epoxy</td>
<td>Adhesive bonding</td>
<td>25% of ultimate load</td>
<td>24</td>
<td>5 to 40</td>
<td>%</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Sousa et al.</td>
<td>2014</td>
<td>E-Glass</td>
<td>Polyester</td>
<td>Adhesive bonding</td>
<td>25% of ultimate load</td>
<td>24</td>
<td>50 to 30</td>
<td>%</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Summary of results from previous studies into the freeze-thaw resistance of FRP materials.

There is a general consensus within the discussed literature that matrix embrittlement, microcracking, and the fibre-matrix interface failure are the key degradation mechanisms that drive the freeze-thaw process. However, the experimental work in this field is severely limited by the lack of a consistent test methodology with varying exposure conditions, cycle definitions, raw materials, manufacturing processes and test procedures. These inconsistencies lead to several contradictory and incomparable studies that cannot provide the level of confidence required by designers in the establishment of design standards and material specifications for FRP materials. In addition, the combined degradation effects of moisture and thermal cycling have been highlighted by Karbhari et al. [4] as one of the key gaps in the knowledge of FRP’s long-term durability. However, very few of the recent studies investigate this combined condition. Those that do mostly fail to adequately moisture-saturate each sample or investigate the combined degradation mechanisms that occur. The majority of the research outlined also fails to fully understand each of the predicted failure mechanisms, with very few studies investigating the extent to which each mechanism has resulted in the degradation of specific mechanical properties. This prevents the creation of mathematical or computational models able to simulate the composite’s long-term durability throughout thermal cycling based on physical test data. This paper aims to bridge the above mentioned gaps identified within current literature.
3. Material

A 5-layer commercially available pultruded GFRP flat sheet provided by ‘Creative Pultrusions Inc.’, PA, USA (FS040.101.096A) was selected for this study. The nominal thickness of the profile was approximately 6.4 mm. The external surface of the profile is covered by an additional protecting polyester non-structural film (veil). The profile is made of E-CR glass fibres reinforcing the isophthalic polyester resin which served as the matrix of the composite, yielding a fibre volume fraction of approximately 45%. Fig. 1 displays the structure of the tested composite profile, which consists of 3 continuous strand mats (CSM, of which 33.3% in volume is glass fibres) and 2 unidirectional (UD, of which 54.5% in volume is glass fibres) roving layers.

![Figure 1. Construction of the investigated pultruded FRP profile.](image)

All test specimens were cut from the same composite flat sheet using a water-cooled diamond saw. No sealing was applied to the cut edges of the investigated samples. A set number of samples were then split into two distinct pre-conditioning regimes, producing two controlled sets of specimens – dry samples and soaked samples. The direct comparison of these sets would indicate the effects of pre-existing water molecules within the composite structure.

The dry samples were conditioned within a ventilated environment (25°C ± 2°C) to minimise any water ingress prior to thermal cycling (as-received by the manufacturer).

The soaked samples were pre-conditioned within a medium of distilled water at a constant temperature of 25°C for 224 days [16]. Measurements of the absorbed moisture content were monitored throughout the soaking period, with 200x200x6.4mm³ samples reaching approximately 1% of mass increase. Once conditioned, the soaked samples were then stored within sealed polyethylene bags and kept in a refrigerated environment to minimise any water loss.

4. Experimental Procedure

4.1. Freeze-thaw cyclic regime

Freeze-thaw cycles were achieved using an environmental conditioning chamber supplied by Temperature Applied Science Ltd., UK, of model HT CL135. Each cycle had a total duration of 2 h, consisting of a 20 minute freezing state at -10°C and a 20 minute thawing state at 20°C with a 40 minute continuous heating or cooling transitional state between the two.
Both dry and soaked samples were sealed within polyethylene bags throughout testing to minimize interaction with the environment and prevent the soaked samples from moisture loss. Prior to the commencement of thermal cycling, preliminary tests with thermocouples were undertaken to assess the range of internal sample temperatures within each of the defined cyclic environments. Logged temperature readings are shown in Fig. 2. From this, the duration of each thermal cycle was optimised to ensure all samples reached the pre-defined range of temperatures.

![Graphical plot of climate chamber thermal cycle and thermocouple testing of sample temperature throughout the proposed cyclic regime.](image)

With the chosen thermal cycle the upper bound temperature (20°C) falls well below the material’s glass transition temperature ($T_{g_{dry\ FRP}}$)$\approx$126°C ± 1.59– obtained by Dynamic Mechanical Thermal Analysis, see Section 6.1). Current good practice dictates that the service environment of polymer composites is to be well below this value, preventing the activation of secondary effects sourcing from chemical decomposition [16, 17]. The lower bound temperature (-10°C) is above the matrix freezing point (-30.4°C, [18]), ensuring excessive cracking and premature brittle failure of the polyester resin is avoided. The total number of cycles (300) has been chosen to reliably ascertain the material’s response throughout the entire service life of its civil applications, ranging from offshore structures with a design life of 25 years [19], to bridge decks with a service life of up to 125 years [20].

### 4.2. Testing

In order to assess the effects of thermal cycling on the behaviour of the GFRP material the tests detailed in Table 2 were completed: (i) Tensile, (ii) Iosipescu, (iii) Plate Twist, (iv) Dynamic Mechanical Thermal Analysis (DMTA) and (v) Computed Tomography imaging (CT-scan). Both dry and soaked samples were cycled and tested providing an assessment of the effects of pre-existing water molecules within the composite structure.

Batches of samples were stored in sealed polyethylene bags in a freeze condition (-10°C) to minimize any potential moisture loss. Prior to testing, the bagged samples were removed from the environmental chamber and allowed to thaw completely for 1 hour at 20°C.

<table>
<thead>
<tr>
<th>Test</th>
<th>Findings</th>
<th>Standard</th>
<th>Samples</th>
<th>Testing (Cycle N°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>Tensile Modulus &amp; Tensile Strength</td>
<td>ISO 527</td>
<td>5</td>
<td>Ref - - 300</td>
</tr>
<tr>
<td>Iosipescu</td>
<td>In-Plane Shear Strength</td>
<td>ASTM D5379</td>
<td>3</td>
<td>Ref 100 200 300</td>
</tr>
</tbody>
</table>
4.2.1. Mechanical testing

For the implementation of the tensile tests a 100kN universal testing machine by Dartec (UK) was employed. Specimens were tested at a constant displacement rate of 2mm/min. Electrical strain gauges (FLA 10-11, TML, Tokyo Sokki Kenkyujo, Ltd) were attached to one side of the tensile specimens to record strain changes during testing.

Shear tests were conducted using an Instron static testing machine equipped with a 50kN load cell. Specimens were tested at a constant rate of 1mm/min. Iosipescu tests were performed in order to define the material’s in-plane shear strength ($\tau_{12}$), whilst plate twist tests were used for the determination of the in-plane shear modulus ($G_{12}$).

4.2.2. Dynamic Mechanical Thermal Analysis testing

DMTA was conducted to assess the effects of freeze-thaw cycling on the material’s visco-elastic properties. The glass transition temperature ($T_g$) was taken by the inflection point of the tan\(\delta\) curve. In accordance with ISO 6721-11, 3 samples of dimension 50x2x6.4mm\(^3\) were prepared for both dry and soaked pre-conditioning regimes. Testing was undertaken using a TRITON T2000 (Triton Technology Ltd, UK) DMTA analyser. Specimens were tested in dual cantilever bending mode at a fixed frequency of 1Hz under a dynamic strain of 0.05%, from room temperature (25°C) up to 200°C at a heating rate of 5°C/min. Changes of the viscoelastic response of the material were recorded as a function of temperature. Samples were tested prior to and after 300 freeze-thaw thermal cycles.

4.2.3. Computed tomography scanning

Computed Tomography (CT) imaging was performed to visually assess the extent to which the aforementioned degradation mechanisms have occurred. An investigation with a view to identifying cracks, voids and moisture within the composite structure was conducted. Samples of dimension 40x40x6.4mm\(^3\) were prepared and scanned for both dry (2 reference and 2 aged, 300 cycles) and soaked (1 reference and 2 aged, 300 cycles) conditions, as shown in Fig. 3. Testing was conducted using a Nikon XT H 225 CT-scanner, equipped with a 225kV microfocus X-ray source.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Property</th>
<th>Standard</th>
<th>Ref</th>
<th>100</th>
<th>200</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate Twist</td>
<td>In-Plane Shear Modulus</td>
<td>ISO 15310</td>
<td>3</td>
<td>100</td>
<td>200</td>
<td>300</td>
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<tr>
<td>DMTA</td>
<td>Glass Transition Temperature</td>
<td>ISO 6721</td>
<td>3</td>
<td></td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>CT-scanning</td>
<td>Visual Analysis</td>
<td>ISO 15708</td>
<td>2</td>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

Figure 3. Overview of CT specimen configuration.

5. Predicting induced thermal stresses
The origin of induced thermal stresses throughout freeze-thaw cycling has been well documented in the literature [21]; they stem from the disparity between the fibre and matrix coefficients of thermal expansion, inducing cyclic compressive/tensile stresses within the resin which surrounds each fibre. These stresses result in a fatigue of the matrix structure which drives each of the physical mechanisms of degradation, and as such they are of great importance in ascertaining not only why composite materials degrade throughout thermal cycling, but also the degree to which the material may degrade in its specific service environments. Thus, they are the key to understanding GFRP’s long-term durability.

Various models have been developed to ascertain the magnitude of these internal stresses, all of which stem from the basic principle of a weighted average of the two materials’ thermal expansion under fully restrained conditions, thus inducing a calculable stress by way of an elastic analysis. One of the most widely accepted models is that presented by Kim et al. [21], given by the equation below,

$$\sigma_m = \frac{(V_fE_fE_m)(\alpha_f-\alpha_m)(T-T_0)}{(V_fE_f+V_mE_m)} \quad \text{(Eq. 1)}$$

where $\sigma_m$ is the stress induced in the longitudinal direction within the matrix, $V$ is the volume fraction, $E$ is the elastic modulus, $\alpha$ is the coefficient of thermal expansion (CTE), $T$ is the evaluation temperature, $T_0$ is the stress-free temperature (taken as room temperature $\approx 20^\circ C$), and the subscripts $m$ and $f$ denote the property of the matrix and fibre, respectively.

The material used within this study has a fibre volume fraction of approximately 45%. The quoted elastic moduli for the fibre and matrix materials from the manufacturer’s specification are 72395 N/mm$^2$ and 3586 N/mm$^2$, respectively [18, 22]. Following a review of the data presented within the current literature, a range of the coefficients of thermal expansion for the fibre ($4\times10^{-6}$ to $5.5\times10^{-6}$ m/m.$^o$C) and matrix ($1\times10^{-4}$ to $1\times10^{-5}$ m/m.$^o$C) materials were also defined.

Initially, for the dry samples it was assumed that the remaining 55% volume was occupied solely by the matrix material, from which the stresses could be calculated using Eq. 1. For the soaked samples it was assumed that the remaining 55% volume was occupied by both the matrix and a known volume of water (1.0% w/w from the initial saturation water uptake). A coefficient of thermal expansion for water ($\alpha_{\text{water}}$) between 20$^\circ$C and 0$^\circ$C was then calculated from its relative change in density and the resultant volume increase across this temperature range. From this, an area weighted average of the coefficients of thermal expansion of both the water and matrix materials was calculated, providing an estimate of the overall coefficient of thermal expansion of the wetted matrix ($\alpha_m$) of $2.79\times10^{-4}$ m/m.$^o$C. The maximum induced stresses were then calculated by substituting this modified value into Eq. 1, the results of which are summarised in Table 3 below.

Table 3. Calculated thermal stresses induced throughout freeze-thaw cycling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Induced stresses (N/mm$^2$)</th>
<th>Thaw state (20$^\circ$C)</th>
<th>Freeze State (-20$^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>-0.07 (0.05% $\sigma_{\text{m,c}}$)</td>
<td>0.53 (0.69% $\sigma_{\text{m,t}}$)</td>
<td></td>
</tr>
<tr>
<td>Soaked</td>
<td>4.65 (3.32% $\sigma_{\text{m,c}}$)</td>
<td>-32.33 (42.22% $\sigma_{\text{m,t}}$)</td>
<td></td>
</tr>
</tbody>
</table>

1 Negative thermal stress indicates a tensile stress
2 $\sigma_{\text{m,c}}$ and $\sigma_{\text{m,t}}$ = ultimate compressive (taken as 140N/mm$^2$) and tensile strength (taken as 77N/mm$^2$) of matrix.
3 For the calculations $\alpha_{\text{fibre}} = 5.5 \times 10^{-6}$ m/m.$^o$C and $\alpha_{\text{matrix}} = 1.0 \times 10^{-5}$ m/m.$^o$C were used.
It can be seen from these results that the presence of water molecules within the composite structure can generate multiple times (about 60 times) the induced thermal stresses over the defined freeze-thaw cycle, resulting from the additional expansion of the water molecules during the formation of ice crystals. These stresses are significantly below the material’s ultimate tensile strength, as provided by the manufacturer [18]. However, the work of Sauer et al. [23] suggests that true fatigue failure of a polymer usually occurs at stresses between 25-50% of the ultimate tensile strength. As such, the chosen thermal range used throughout this study is likely to induce cracking and premature failure.

Thermal fatigue of the polyester matrix may also result in significant microstructural damage throughout testing. Mechanical degradation under such thermal cyclic loading will initially involve the development of a “craze” or “damage” zone, resulting from the concentration of stresses along the fibre-matrix interface. The subsequent plastic deformation of this region (cyclic softening of polymer resin) promotes the initiation of microcracks, which propagate into the matrix material under continued cyclic loading. These mechanisms will continue until a critical crack size is reached, at which the material will experience brittle failure [23]. The freeze-thaw durability of a material is defined by its resistance to the initiation of such microstructural phenomenon, which drives the aforementioned mechanisms of degradation throughout thermal cycling. From these findings, it can be expected that the fatigue effect of the induced thermal stresses throughout freeze-thaw cycling (≈18% \( \sigma_{UTS} \) for 300 cycles) is highly possible to induce microcracking. Generated stresses may result into remarkable damage incidents, i.e. delamination within the material.

6. Results

6.1. Initial Characterisation

The original mechanical and physical properties of both the dry and soaked samples prior to freeze-thaw cycling are detailed in Table 4. These have been used as reference values in this study, from which the percentage change of specific material properties throughout thermal cycling have been calculated; they are stated in the form (percentage of reference ± standard deviation %).

<table>
<thead>
<tr>
<th>Property</th>
<th>Initial - Dry Sample</th>
<th>Initial - Soaked Sample (224 days, 25°C Water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength ( \sigma_t ) (MPa)</td>
<td>441.06 ± 9.80</td>
<td>440.16 ± 32.45</td>
</tr>
<tr>
<td>Tensile Modulus ( E_t ) (GPa)</td>
<td>26.34 ± 1.17</td>
<td>25.77 ± 2.58</td>
</tr>
<tr>
<td>In-Plane Shear Strength ( \sigma_{12} ) (MPa)</td>
<td>83.35 ± 5.30</td>
<td>87.61 ± 2.58</td>
</tr>
<tr>
<td>In-Plane Shear Modulus ( G_{12} ) (GPa)</td>
<td>3.76 ± 0.13</td>
<td>3.22 ± 0.14</td>
</tr>
<tr>
<td>Glass Transition Temperature ( T_g ) (°C)</td>
<td>126.00 ± 1.59</td>
<td>122.10 ± 2.22</td>
</tr>
</tbody>
</table>
The varying initial properties between the dry and soaked samples prior to freeze-thaw cycling highlights the potential degradation mechanisms that might have occurred as a result of water absorption into the composite structure [16]. Primarily, these stem from the following counteracting mechanisms: (i) physical changes due to swelling, accumulation of hydroscopic stresses and polymer relaxation; (ii) water induced chemical reactions, leading to an increase in molecular mobility, plasticization and/or chemical degradation of material, and (iii) additional cross-linking due to residual curing and secondary cross-linking between the water molecules and the polymer chains [15, 24].

The initial properties shown in Table 4 indicate that the soaked sample’s conditioning regime has induced the following changes: (i) a minor increase in shear strength and a negligible change in tensile strength; (ii) a significant decrease in shear stiffness and a negligible change in tensile stiffness; and (iii) a minor decrease in glass transition temperature.

6.2. Effects of thermal cycling

6.2.1. Mass Change

The presence of water molecules within the composite structure has been shown to have a significant impact on the structural integrity of composite materials [25, 26]. In this respect, particular attention was given to quantifying the moisture content of the soaked samples throughout thermal cycling. The change in mass of each sample was recorded throughout freeze-thaw cycling and is presented in Fig. 4.

As expected, the dry samples showed no mass change throughout testing. Conversely, soaked samples, which were preconditioned in 25°C distilled water for a total of 224 days prior to thermal cycling, showed significant moisture mass loss throughout testing (up to -0.6% mass loss). The degree of such mass loss strongly depends on the size of each sample; the relatively small specimens showed a faster rate of loss than the relatively larger ones. This is in accordance with findings of previous work [16] that addresses the moisture absorption size dependency.

![Figure 4. Plot of the mean percentage mass loss of each type of GFRP sample throughout 300 freeze-thaw cycles.](image-url)

As shown in Fig. 4, the amount of desorbed water was 0.24 w/w % in the plate twist samples, 0.46 w/w % in the DMTA samples and 0.61 w/w % in the Iosipescu samples. It should be noted that the mass loss shown above is a significant
percentage of their initial moisture content. As mentioned, the maximum recorded moisture uptake content of the pre-
conditioned (soaked) samples was approximately 1 w/w % after a period of 224 days at 25°C.

6.2.2. Tensile properties
To assess the potential degradation of the glass fibre structure, alongside the extent of microcracking within the matrix, the response of the material’s tensile strength (σt) and modulus (Et) was determined after 300 thermal cycles. The response of the GFRP material under longitudinal tensile testing before and after freeze-thaw cycling is presented in Figs. 5a and 5b.

The dry samples exhibited a minor increase in both tensile strength (111.8 ± 11.2%) and tensile modulus (110.1 ± 13.7%) after 300 thermal cycles. However, such increases are minimal considering the high standard deviation of test results. Conversely, the soaked samples displayed a decrease in their tensile strength (87.0 ± 3.3%) and to a lesser degree, a decrease in tensile modulus (96.0 ± 6.4%), with the latter being negligible compared to the variation of the results.

Figure 5. Degradation (%) of tensile properties of soaked and dry samples throughout 300 freeze-thaw cycles: (a) mean tensile strength; (b) mean tensile modulus.
6.2.3. In-Plane Shear

The material’s in-plane shear strength ($\tau_{12}$) and shear modulus ($G_{12}$) monitored throughout the freeze-thaw cycling through Iosipescu and plate twist tests, respectively, are shown in Figs. 6a and 6b. It can be seen that the dry samples exhibited a negligible degradation of their shear strength after 300 cycles (97.3 ± 4.5%). In addition, dry samples also showed a negligible loss in shear modulus, which shows a slight decreasing trend in the final 200 thermal cycles (97.8 ± 2.1%). Conversely, the soaked samples displayed a substantial loss in their shear strength after 300 freeze-thaw cycles (70.3 ± 1.4%). Furthermore, the soaked samples exhibited a negligible gain in shear modulus, between the 100th and 300th cycles (102.5 ± 5.4%).

![Graph showing in-plane shear properties of soaked and dry samples](image)

Figure 6. Degradation (%) of in-plane shear properties of soaked and dry samples throughout 300 freeze-thaw cycles: (a) mean in-plane shear strength (obtained from Iosipescu tests); (b) mean in-plane shear modulus (obtained from Plate Twist tests).

6.2.4. DMTA

In an attempt to assess the degradation which may occur at the molecular level during freeze-thaw cycling, the GFRP material’s Damping Factor (tan$\delta$) and Glass Transition Temperature ($T_g$) were determined after the 300 thermal cycles. These properties were obtained through DMTA, the results of which are detailed in Figs. 7a and 7b. The maximum tan$\delta$ value indicates the point at which a relaxation process is initiated; small groups and chains of molecules, which are initially fixed, begin to move relative to each other within the polymeric matrix. Typically, the higher the maximum tan$\delta$ value, the greater the degree of molecular mobility [27]. The material’s $T_g$ can then be inferred from the point of
inflection at this peak tan\(\delta\) value, marking the temperature at which sufficient energy is provided to initiate the material’s transition from a hard, glassy state to a soft, rubbery state.

Figure 7. (a) Mean \(T_g\) degradation (%) of soaked and dry samples throughout 300 freeze-thaw cycles, (b) mean tan\(\delta\) degradation (%) of soaked and dry samples throughout freeze-thaw cycles.

Deviations of \(T_g\) are related to both the degree of degradation of the material (e.g., plasticization) and any possible strengthening process (e.g., post-curing of the resin matrix). From these plots, it can be seen that following the 300\textsuperscript{th} thermal cycle, a minor loss in \(T_g\) was exhibited by both soaked (97.9 ± 1.2\%) and dry (97.2 ± 0.8\%) samples. In a similar fashion, both soaked and dry samples displayed a general decreasing trend in their maximum tan\(\delta\) values, with the dry samples showing a negligible loss in tan\(\delta\) throughout thermal cycling (98.4 ± 9.4\%), and the soaked samples exhibiting a slightly more significant loss following the 300 freeze-thaw cycles (92.6 ± 6.9\%).

Figs. 8a and 8b illustrate the thermo-mechanical dynamic scans of the reference samples, whereas Fig. 8c indicates the percentage change of storage modulus (derived by DMTA) for the aged and un-aged material both in the dry and soaked state. Comparing reference measurements, soaked samples exhibited significantly lower storage modulus values than the corresponding dry samples. This is attributed to the plasticizing effect of the water molecules in the polymeric structure. After 300 cycles of freeze-thaw fatigue, the soaked samples showed negligible change in storage modulus (98.3 ± 16.3\%), whereas dry fatigued samples exhibited a significantly lower storage modulus (73 ± 3\%), in agreement with the drop in shear modulus indicated in Fig. 6b \(G_{12}\) obtained from plate twist testing.
Figure 8. Dynamic mechanical thermal analysis for the (a) soaked and un-fatigued (reference) material, (b) dry un-fatigued (reference) material, (c) percentage retention of storage modulus between the reference and the 300 freeze-thaw cycled GFRPs for dry and soaked specimens.

6.2.5. CT-scan imaging

CT scans present a useful means of visually assessing thermally cycled material, highlighting physical changes in the composite’s microstructure. To visually assess the potential changes caused by freeze-thaw degradation, CT scans were completed on soaked and dry samples, in their unaged (reference) and aged (300 cycles) states, exhibiting a range of phenomena illustrated in Figs. 9, 10 and 11 and described next.
Fig. 9 clearly illustrates the structure of the GFRP laminates analysed in this study, highlighting the presence of water in the CSM layer. It also indicates that the distribution of such water may be non-uniform, with several cases of highly localised saturations (water pockets) being exhibited throughout the analysis, resulting in a possible localised degradation of such areas. Indeed, this may induce significantly higher thermal stresses than to those calculated earlier (Section 5, in which one assumed water to be evenly distributed throughout the composite structure), potentially
resulting in significant thermal fatigue in such regions. Furthermore, the dry sample shown in Fig. 9 exhibits what would appear to be shrinkage cracks in both the CSM and the UD layers. These likely stem from the curing of the polyester resin, which when setting from a liquid to a solid state increases in density resulting in a decrease in volume. This acts to ‘shrink’ the polymer matrix, allowing for matrix cracking directly effecting the durability of the composite. The resultant increase in ‘free-volume’ [16] of the material may lead to additional moisture absorption along the fibre-matrix interface. Throughout freeze-thaw cycling, such moisture may act to propagate/expand these cracks, potentially contributing to the more severe degradation of the material’s shear strength throughout testing.

Fig. 10 shows that a higher degree of longitudinal cracking has been induced within the UD layer in both the dry and wet aged samples. In addition, the aged samples indicate the onset of minor microcrack growth (Fig. 10); in the reference samples such cracks appear to be confined to the UD layer, whereas upon ageing cracks are shown to propagate into the CSM layer. This would appear to indicate that the chosen freeze-thaw cycling regime is inducing significant thermal stresses to initiate the growth of such pre-existing microcracks throughout the matrix structure.

Fig. 11 indicates the presence of voids and/or water (pockets) accumulating along the interface between the UD and CSM layers, which was found in multiple locations within the wet aged samples. Along this interface, localised moisture wicking may also have induced substantially greater thermal stresses, resulting in a significant localised degradation. This may have induced additional thermal stresses along this interface as the relative degree of thermal expansion/contraction of the two layers as a whole will differ. The fibres themselves have a much greater CTE, and may expand up to 25 times more than the surrounding matrix material as temperatures fluctuate. As such, the significantly higher glass fibre content of the UD layer will result in a much higher CTE.

7. Discussion
Throughout this study, all soaked samples showed a significant mass loss, which may be attributed to desorption of moisture throughout freeze-thaw cycling. Mass losses appear to be proportional to the surface area (veil surface area) vs. cross-sectional area (cut edges) ratio of each sample [16]. This has resulted in significantly lower water retentions within the smaller samples (Iosipescu and DMTA) due to their greater exposed cross-sectional areas. These samples would appear to have lost up to 50% of their initial moisture content, reducing the magnitude of the induced thermal stresses. This may be seen as an adverse effect, which could potentially be mediated through alterations to the test methodology. However, in the previously discussed applications of GFRP materials within construction, and in the service environments in which such freeze-thaw conditions may occur, a cyclic drying and wetting is highly likely. Additional control of the moisture retention within samples may produce the most severe degradation, but such humid conditions along with extremely fluctuating temperatures, are highly unlikely to be experienced by the in service material.

Generally, when a material is exposed to moisture, stresses are generated due to the state difference between the wet external and dry internal volumes. After prolonged exposure, moisture saturation is achieved. If a soaked material is dried out, stresses are generated due to the thermal difference between the wet internal and dry external volumes. This repeatable absorption and desorption may result in fatigue and cracking of the material that would negatively affect the mechanical performance [28].

Throughout freeze-thaw cycling, dry samples exhibited a minimal increasing trend in tensile strength, which was largely negligible when compared to the relatively high standard deviation of test results. Similarly, the soaked samples exhibited a slight decrease in tensile strength throughout freeze-thaw cycling. This possibly stemmed from the degradation of the matrix which acts to distribute the stresses within the glass fibres, spreading tensile loads to adjacent
fibres and enabling a full composite action of the material. The significantly higher thermal stresses induced within the soaked samples may have resulted in a more extensive microcracking of the matrix. In addition, the wicking of moisture along the glass fibres has been shown to induce degradation to the fibre/matrix interface [15, 28, 29]. It is postulated that as the soaked material dries throughout freeze-thaw cycling, any plasticization caused by the initial soaking regime might be reversed, recovering the initially depressed mechanical properties. Any fibre/matrix interface failure will likely result in isolated highly stressed fibres, which cannot distribute their stresses throughout the composite structure, inducing local failures and a reduction of the material’s tensile strength [2, 3, 14]. A negligible change in tensile modulus throughout freeze-thaw cycling was exhibited by both the soaked and dry samples. The longitudinal tensile stiffness of the GFRP material is largely dominated by the glass fibres themselves, which remain relatively unstressed throughout freeze-thaw degradation. As quantified in Section 5, the induced thermal stresses, which are largely concentrated within the weaker matrix material may have resulted in significant crack propagation or delaminations.

Of the literature reviewed, the majority of results indicate that the tensile properties of GFRP materials show a minor degradation throughout freeze-thaw cycling, which is substantially lower than that experienced by the material’s shear properties. The work of Li et al. [10] shows a similarly negligible change in the dry sample’s shear strength (105%) and stiffness (96%) throughout thermal cycling, as has been exhibited within this study. This would indicate that despite the significantly higher thermal stresses induced within Li et al.’s work (-10°C to 20°C), little degradation of the longitudinal tensile strength is exhibited whilst the material is in its dry state.

Conversely, several studies have shown that significant degradation of GFRP’s tensile properties may be induced whilst the material is cycled in its wet state. Zhang et al. [7] showed severe degradation of tensile strength (83.9%) following immersion in 2% NaCl, similar to that shown by the soaked samples within this study. The slightly higher loss exhibited in their work is attributed to the expansion of salt deposits within the composite structure, inducing additional fibre-matrix debonding. Furthermore, the work of Karbhari et al. [9] showed degradation of comparable magnitude to what was obtained herein in the tensile strength (90.4%) and modulus (95.1%) following the thermal cycling of moisture saturated samples (long-term immersion in deionised water).

The results of the Iosipescu testing indicate no significant loss in shear strength of the dry samples throughout freeze-thaw cycling. This possibly results from the minimal induced thermal stresses within the dry specimens. However, the soaked samples exhibited a substantial loss of shear strength after the 300 thermal cycles. This probably results from the significantly higher thermal stresses induced at the lower bound temperature as water molecules expand to form ice crystals, as quantified previously. In addition, possible degradation in the form of plasticization or leaching of material will likely result in additional moisture wicking along the fibres themselves, further concentrating the stresses induced throughout thermal cycling at this interface. This has probably resulted in extensive microcracking of the polyester matrix in the near fibre region throughout thermal cycling, causing the substantial loss of shear strength shown by the soaked samples.

The general consensus of the literature highlights the significant degradation of shear strength throughout thermal cycling, particularly in polyester based composites, which have been shown to develop a greater degree of matrix microcracking than other equivalent resin systems [2]. The work of Aniskevich et al. [14] indicated a similarly substantial loss of shear strength throughout thermal cycling (79.1%). This marginally lower degree of degradation may stem from a lower water content within the soaked samples, which were only submerged in water for five weeks prior to testing.
The results of plate twist testing also showed a general decreasing trend in the dry sample’s shear modulus throughout freeze-thaw cycling. This may stem from the induced freeze-thaw degradation of the fibre-matrix interface, resulting in minor microcracking of the polyester matrix. Conversely, the soaked samples showed a general increasing trend in their shear modulus. It is believed that this increase may stem from the reversible action of plasticization, which was induced during the soaked samples conditioning process, as previously discussed. Significant mass loss indicates that the soaked samples have dried considerably throughout thermal cycling, allowing water molecules to evacuate the intrinsic ‘gaps’ of the composite structure. This enables the intermolecular bonds to regain their initial strength, thus increasing the material’s stiffness under shear loading [25].

Throughout the conditioning process, the (soaked) samples exhibited a substantially larger reduction in shear modulus (85.6 ± 3.7%), compared to that gained throughout freeze-thaw thermal cycling. This would indicate that the competing mechanisms of freeze-thaw degradation have permanently reduced the shear modulus of the material to some extent, but to a lesser degree than that recovered throughout the drying process. Of the literature reviewed, only the work of Dutta and Hui [11] tested the degradation of shear modulus throughout thermal cycling, which resulted in a minimal loss (93.7%), likely stemming from the high thermal stresses inducing significant degradation of the polyester matrix, which is to be expected at the high extremes of temperature (-60°C to 50°C) used in that study.

It should be noted that the degradation of shear modulus obtained in the present study was relatively negligible in comparison with the substantial degradation of shear strength. It is suggested that this may also stem from the nature of plate twist testing, in relation to the non-uniform distribution of moisture discussed previously. Based on the fundamental dimensional difference between the plate-twist and Iosipescu samples, it is very likely that the Iosipescu samples will have more equal distribution of moisture in the area of failure and therefore higher probability to moisture-induced degradation. Plate twist tests apply a uniform and low-level in-plane shear stress which is used to obtain a ‘whole-sample’ response to loading, largely independent of local flaws. However, the confinement of water to the extremities of such large samples will probably have resulted in a localised degradation of their outer regions, hence the degradation caused by freeze-thaw cycling is unlikely to have affected the ‘whole-sample’ response of the material’s in-plane shear modulus when tested in this way.

With respect to the visco-elastic response, results indicate that both dry and soaked samples exhibit a slight decrease in $T_g$ throughout thermal cycling, which is attributed to the degradation of the matrix and fibre-matrix interface due to freeze-thaw cycling. In this regard, the $T_g$ of the soaked samples would be expected to fall significantly more than that of the dry samples, due to the more noticeable freeze-thaw degradation exhibited throughout mechanical testing. The lack of this expected trend within this study may be attributed to the hygrothermal pre-conditioning of the soaked samples (at 25°C for 224 days), which might have resulted in a recoverable loss in $T_g$ (89.2 ± 1.8%) prior to thermal cycling. This stems from the loss of organic additives through leaching and the softening of the polyester matrix (plasticization) [30]. As such, the drying exhibited by the soaked samples throughout thermal cycling might have partially reversed the effects of plasticization, resulting in an increase in $T_g$. This reversible plasticization effect is further evident in the decrease in the soaked sample’s $T_g$ value, resulting in an apparent decrease in molecular mobility throughout thermal cycling. It is hypothesised that this may also stem from the apparent drying process throughout freeze-thaw cycling. In contrast, the dry samples show negligible changes in their $T_g$ value. This indicates that in the absence of water molecules in the composite structure, the thermal cycling alone has had no significant effect on the material’s molecular mobility, which is consistent with results reported by Sousa et al. [2] (dry samples) and the quantification in Section 5. Thus, the
temperatures used throughout thermal cycling are unlikely to have induced any substantial structural degradation of the polyester matrix.

These findings match those shown within the reviewed literature, which despite minor differences in the thermal cyclic conditions and constituent materials, show a minor decreasing trend in glass transition temperature throughout freeze-thaw cycling. In the work of Aniskevich et al. [14] a similar set of results were obtained to those presented here, with both soaked and dry samples showing a minor loss in $T_g$ (97.0% and 95.8% respectively), with the slightly higher losses potentially stemming from the higher thermal stresses induced at lower freezing temperatures (-30°C). The results obtained by Zhang et al. [7] are also in close agreement with the losses shown here, with soaked samples exhibiting another minor loss in $T_g$ (95.2%); the use of 2% NaCl as the immersion media may have resulted in this slightly greater loss, generating additional stresses as salt deposits expand within the GFRP material.

8. Conclusions

This study presented a literature review and an experimental investigation into the response of pultruded GFRP materials to thermal cycling. The effects of pre-existing water molecules within the composite structure and the extent to which this compounds with the freeze-thaw process to accelerate degradation was also assessed. This was ascertained through the comparison of both dry and soaked test specimens, with the latter being pre-conditioned within a medium of distilled water for a period of 224 days. The degradation of the material was expressed as a function of its mechanical and physical properties in terms of tensile, in-plane shear, and viscoelastic responses. In addition, CT scanning was undertaken to assess the physical changes in the material’s microstructure caused by freeze-thaw cycling. In general, under the chosen environmental conditions, the GFRP material, when in its dry state, exhibited a negligible degradation throughout freeze-thaw cycling. Conversely, in its soaked state, the material exhibited a significant degradation of its mechanical properties throughout thermal cycling. The findings of this study have allowed for the following specific conclusions to be drawn:

- Calculations to estimate induced cyclic thermal stresses indicate a largely insignificant fatigue of the dry material throughout freeze-thaw cycling for the conditions used in this study. By assuming a uniform distribution of moisture throughout the FRP material, this analysis would suggest that such stresses are likely to induce significant delamination of the fibre-matrix interface and the induced microcracks are able to propagate throughout the matrix structure.

- The substantial moisture loss exhibited by the soaked samples throughout testing acts to reduce the magnitude of thermal stresses which are induced throughout thermal cycling, and may also induce significant leaching of material from the fibre-matrix interface, further degrading the composite action of the material [16].

- DMTA testing indicated a minor degradation of both the dry and soaked sample’s viscoelastic response throughout freeze-thaw cycling, showing a minor loss in $T_g$. This indicates a minor degradation of both the matrix and the fibre-matrix interface. Further analysis of the peak tan$\delta$ values revealed that the extremes of temperature used within this study are highly unlikely to have induced a significant post-curing of the matrix.

- Both tensile and in-plane shear testing exhibited a negligible degradation in the dry sample’s mechanical properties throughout thermal cycling. However, the soaked samples exhibited a significant degradation of tensile strength (87.0 ± 3.3%) and to a greater degree of in-plane shear strength (70.3 ± 1.4%). This was mainly attributed to the greater degree of induced microcracking within the matrix material, and in particular within the fibre-matrix interface, along which thermal stresses are known to be concentrated. Conversely, the soaked sample’s stiffness remained largely
unaffected, despite such a clear degradation of their mechanical strength. This was attributed to the reversible nature of plasticization, which acts to increase the GFRP’s molecular mobility when initially saturated, but is then later recovered as the soaked samples dry throughout freeze-thaw cycling.

- CT-scanning was found capable of illustrating the physical changes of the composite material under thermal cycling. Accumulation of microcracks and water pockets were effectively identified in the assessed GFRP samples.

Overall, the combined effects of freeze-thaw degradation in the presence of moisture, although complex and variable, have been shown to have a significantly detrimental impact on the long-term durability of GFRP materials under the chosen service environments. Such impact stems largely from the additionally induced thermal stresses, which result from the presence of water molecules within the composite structure.

Acknowledgements
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References
<table>
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<td>Wu et al.</td>
<td>2006</td>
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<td>Immersion in deionized water, salt water and ambient humidity</td>
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<td>Kim et al.</td>
<td>2007</td>
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<td>Li et al.</td>
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<td>Ludovico et al.</td>
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σ<sub>tu</sub> – Tensile strength / E<sub>t</sub> – tensile modulus / σ<sub>cu</sub> – compressive strength / σ<sub>f</sub> – flexural strength / E<sub>f</sub> – flexural modulus / G – shear modulus / ISS – interlaminar shear strength / T<sub>g</sub> – glass transition temperature.